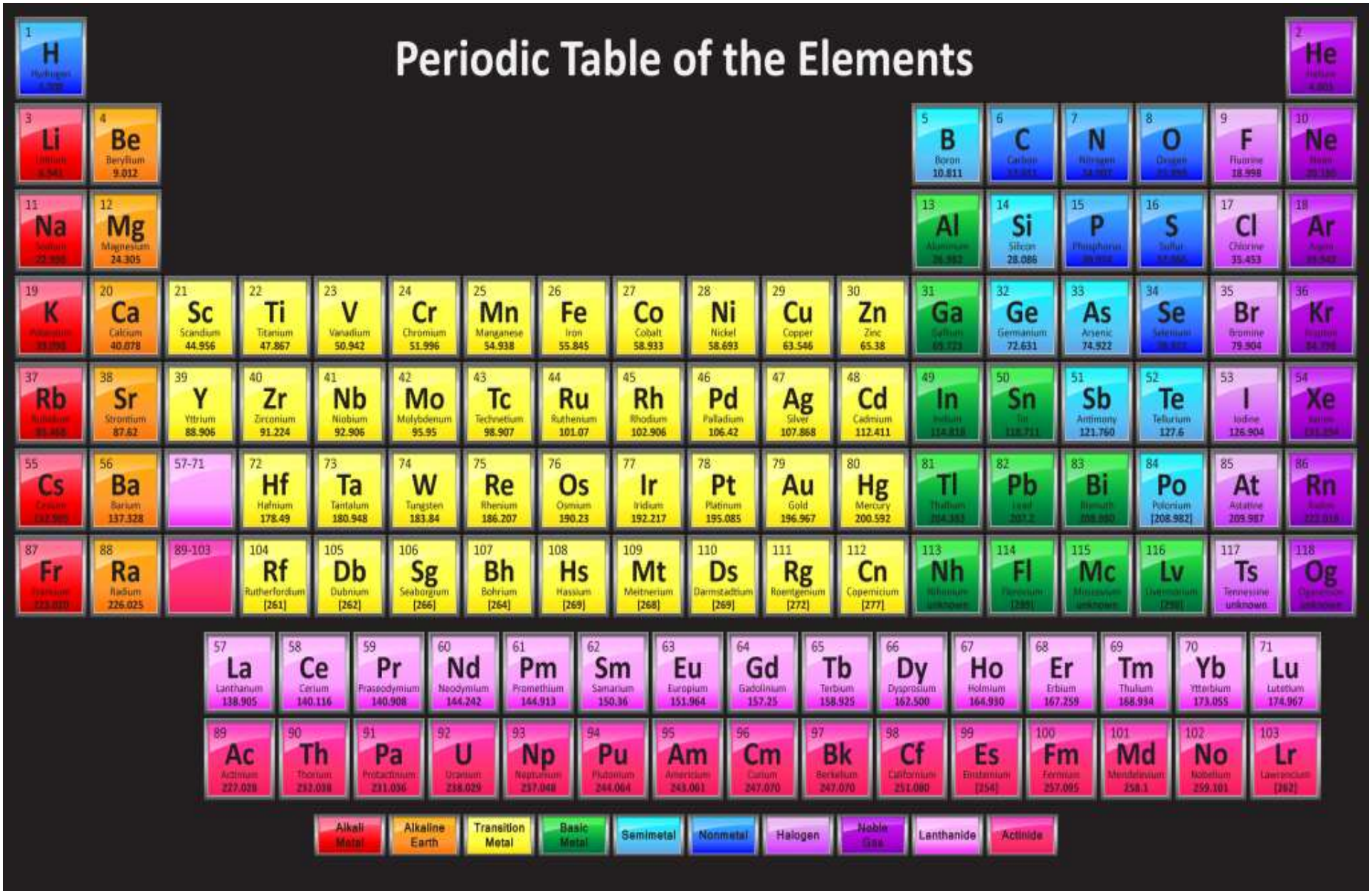

Periodic Table of the Elements
1 H
2 He
3 Li
4 Be Beryllium 9.012
5 B Boron 10.811
6 C
7 N
8 O
9 F Fluorine 18.998
10 Ne
11 Na
12 Mg Magnesium 24.305
13 Al
14 Si Silicon 28.086
15 P
16 S
17 Cl Chlorine 35.453
18 Ar
19 K
20 Ca Calcium 40.078
21 Sc Scandium 44.956
22 Ti Titanium 47.867
23 V Vanadium 50.942
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
32 Ge Germanium 72.631
33 As Arsenic 74.922
34 Se
35 Br Bromine 79.904
36 Kr
37 Rb
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 112.411
49 In
50 Sn
51 Sb Antimony 121.760
52 Te Tellurium 127.6
53 I Iodine 126.904
54 Xe
55 Cs
56 Ba Barium 137.328
57-71
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
82 Pb
83 Bi
84 Po Polonium [208.982]
85 At Astatine 209.987
86 Rn
87 Fr
88 Ra Radium 226.025
89-103
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
114 Fl
115 Mc
116 Lv
117 Ts Tennessine unknown
118 Og
57 La Lanthanum 138.905
58 Ce Cerium 140.116
59 Pr Praseodymium 140.908
60 Nd Neodymium 144.242
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

Factors Affecting Atomic Orbital Energies

- The energies of atomic orbitals are affected by
  - nuclear charge (Z) and
  - shielding by other electrons.

A **higher nuclear charge** increases nucleus-electron interactions and lowers sublevel energy.

Shielding by other electrons reduces the full nuclear charge to an *effective nuclear charge* (Z_{eff}).

Z_{eff} is the nuclear charge an electron actually experiences.

Orbital shape also affects sublevel energy.

Shielding

The energy order of orbitals for a given quantum number depends on shielding effects (σ), effective nuclear charge (Z*) & penetration of orbitals

$$Z^* = Z - \sigma$$

How to determine or estimate the Z*?

{If the electron resides in s or p orbital}

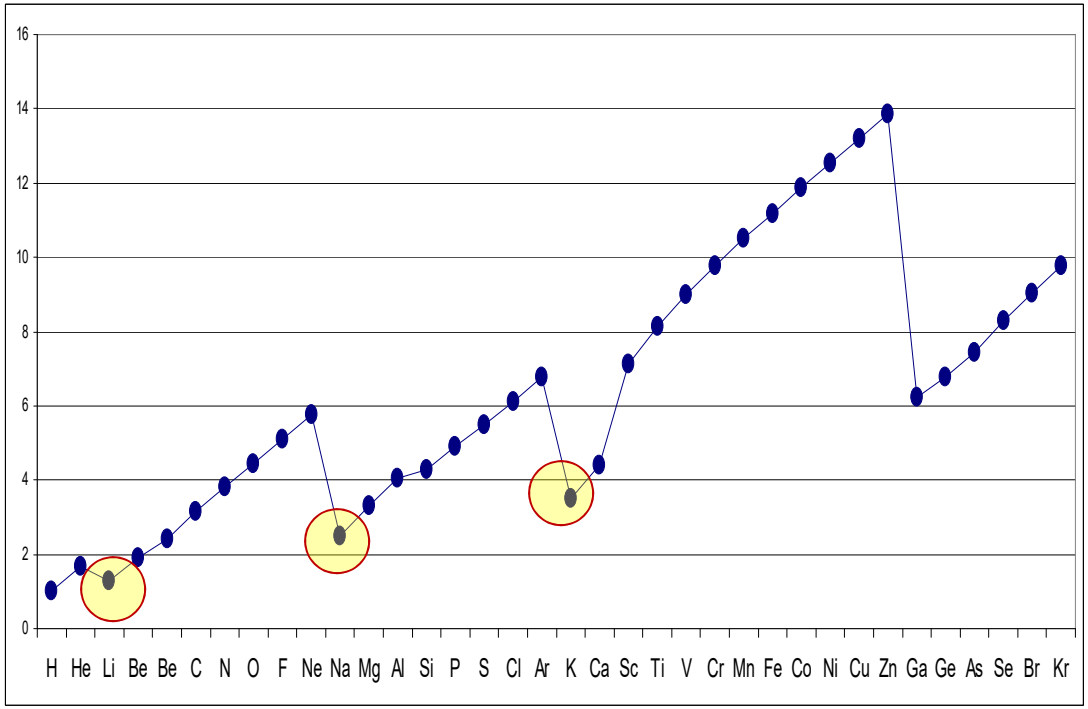
1. Electrons in principal shell higher than the e^- in question: contribute 0 to σ
2. Each e^- in the same principal shell: contribute 0.35 to σ, except 1s which is 0.3
3. Electrons in (n-1) shell: each contribute 0.85 to σ
4. Electrons in deeper shell: each contribute 1.00 to σ

How to determine or estimate the Z*? {If the e^- resides in a 'd' or 'f' orbital}

- All e^-'s in higher principal group contribute 0
- Each e^- in the same group contributes 0.35
- All inner and lower group electrons contributes 1.00

Effective nuclear charge Z* increases very slowly down a group for the "valence electron". Example of Valence configuration as 'ns^1'

	n	Z	Z*
H	1	1	1.0
Li	2	3	1.3
Na	3	11	2.2
K	4	19	2.2
Rb	5	37	2.2
Cs	6	55	2.2

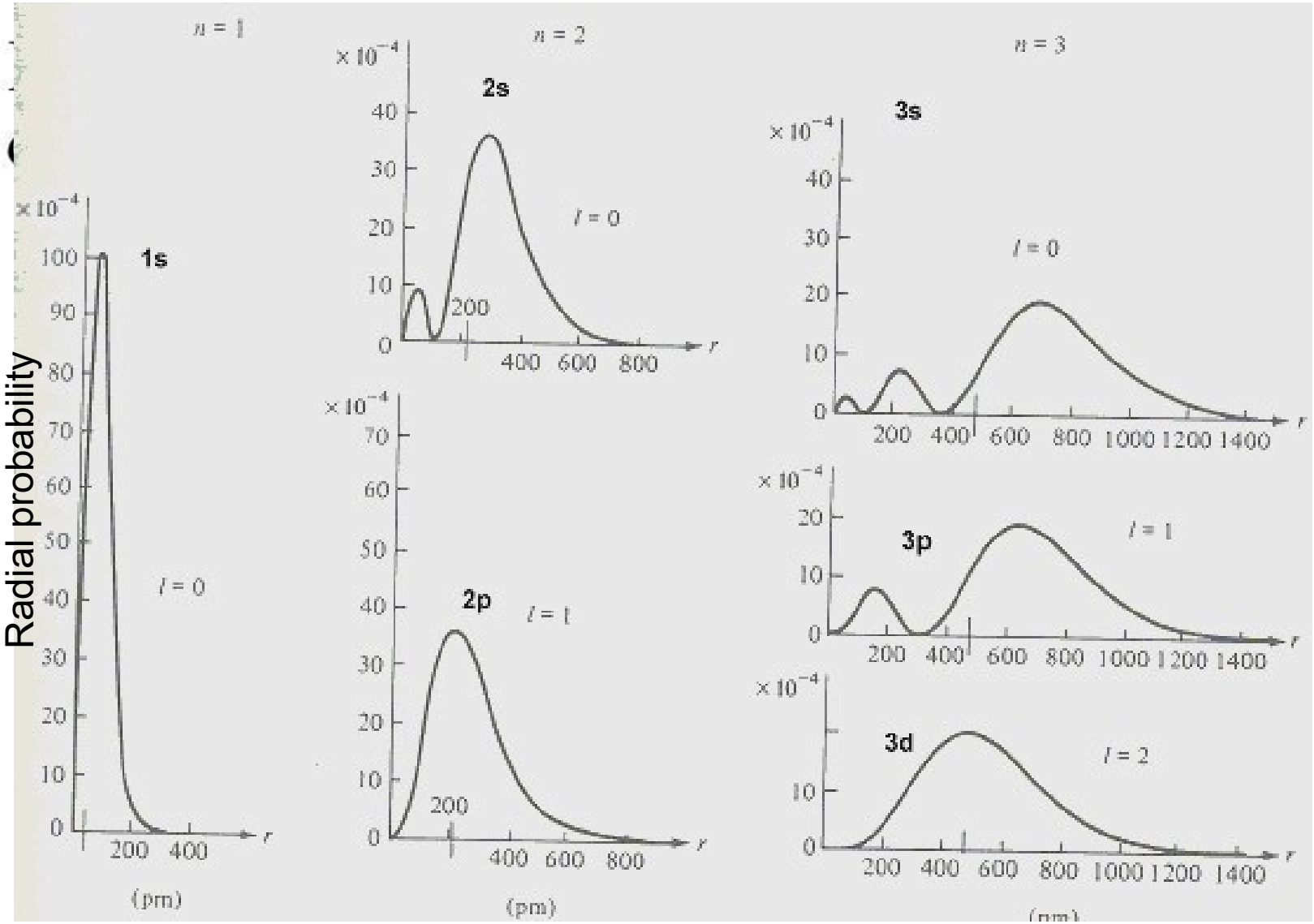


Effective nuclear charge Z* increases rapidly along a period. For example, take period two

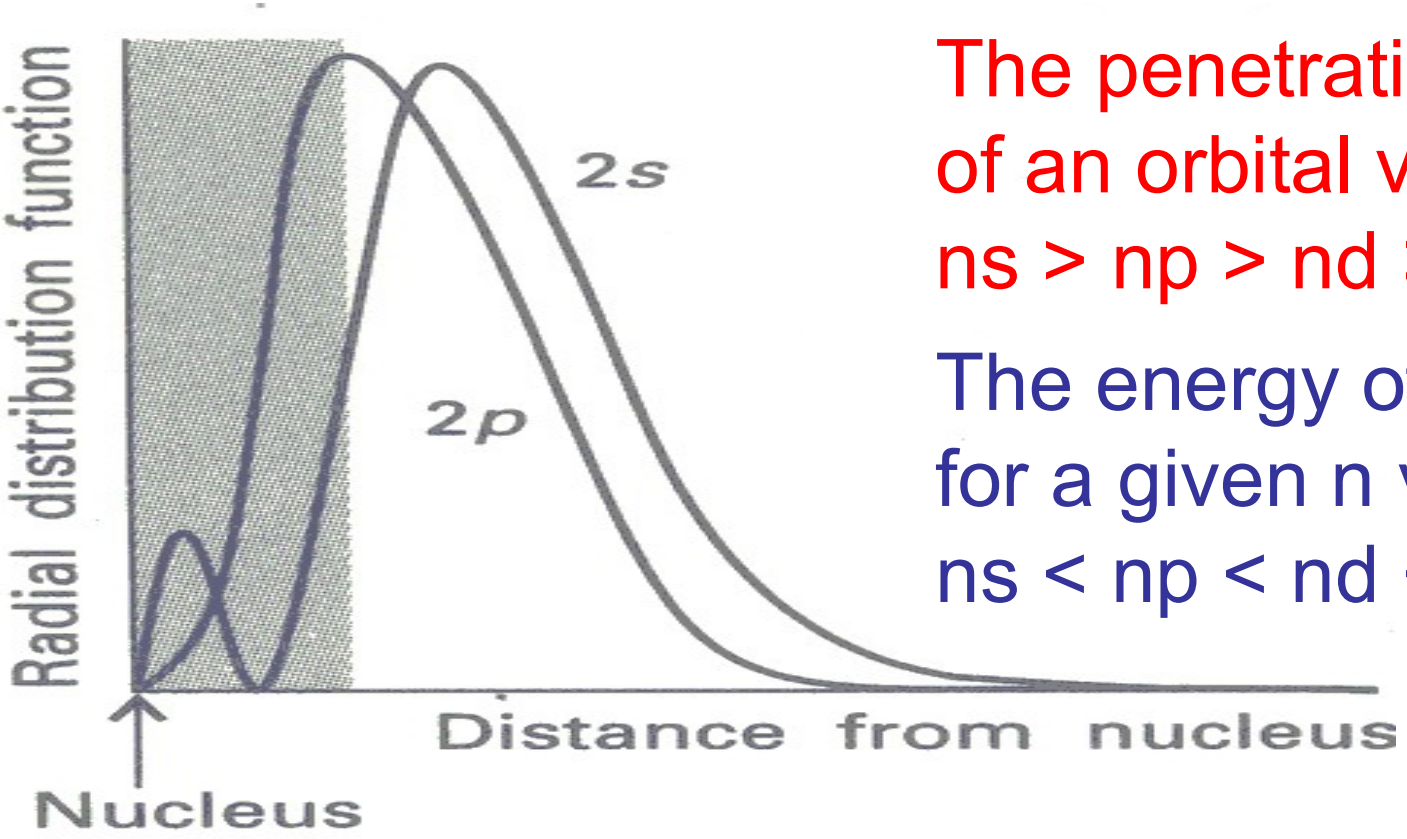
Li	Be	B	C	N	O	F	Ne
3	4	5	6	7	8	9	10
1.3	1.95	2.4	3.1	3.8	4.5	5.1	5.8
$2s^1$	$2s^2$	$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$

Penetration of Orbitals

Orbital shape causes electrons in some orbitals to “penetrate” close to the nucleus. Penetration increases nuclear attraction and decreases shielding.



Penetration of Orbitals



The penetration potential of an orbital varies as:
ns > np > nd > nf

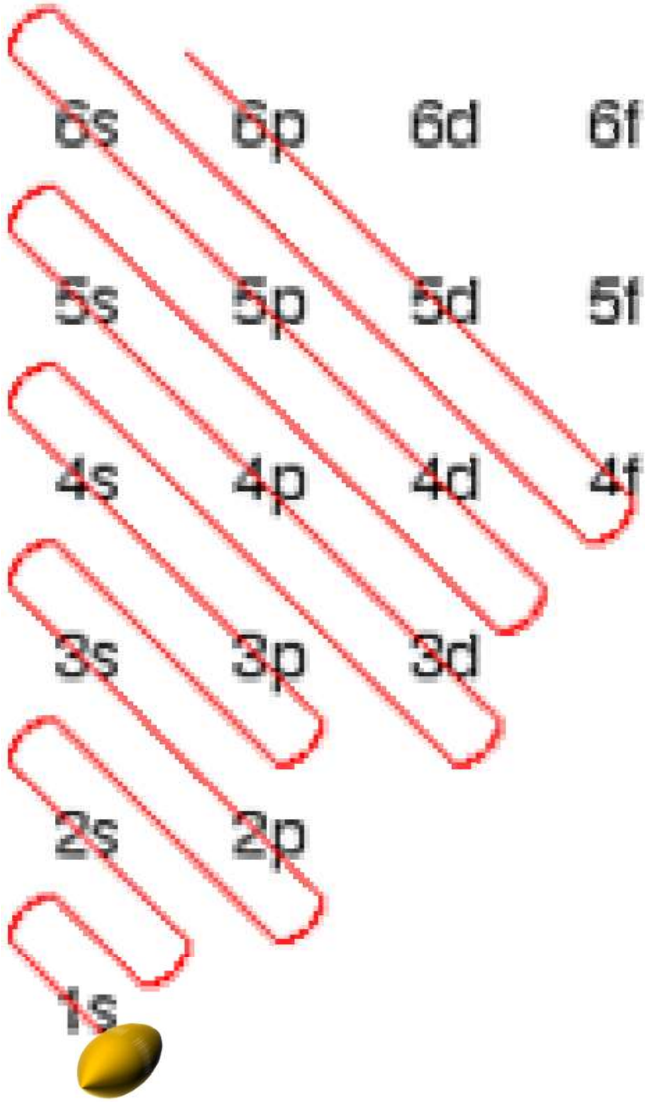
The energy of the orbitals for a given n varies as:
ns < np < nd < nf

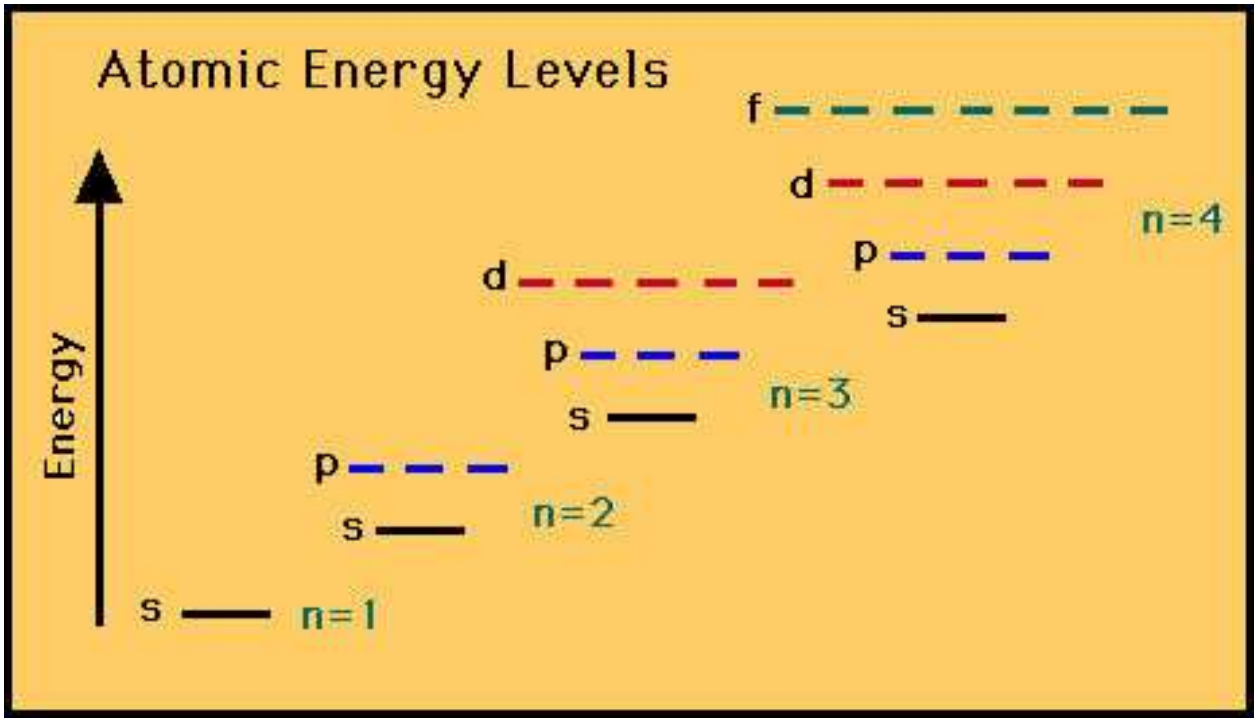
The penetration of 2s electron through the inner core is greater than that of a 2p electron because the latter vanishes at the nucleus. Therefore, the 2s electrons are less shielded than the 2p electrons.

Influence of nucleus on electrons

- Two electrons present in the same d-orbital repel each other more strongly than do two electrons in the same s-orbital.
- The electrons present in f are much less influenced by the nucleus as compared to d, those present in d much less influenced as compared to p, than s, etc.
- It is essential to consider all contributions to the energy of a configuration, and just not one-electron orbital energies.

Considerations of principles such as penetration and shielding have enabled atomic orbitals to be arranged in rough order of increasing energy (order of filling of orbitals).





How do you fill electrons ?

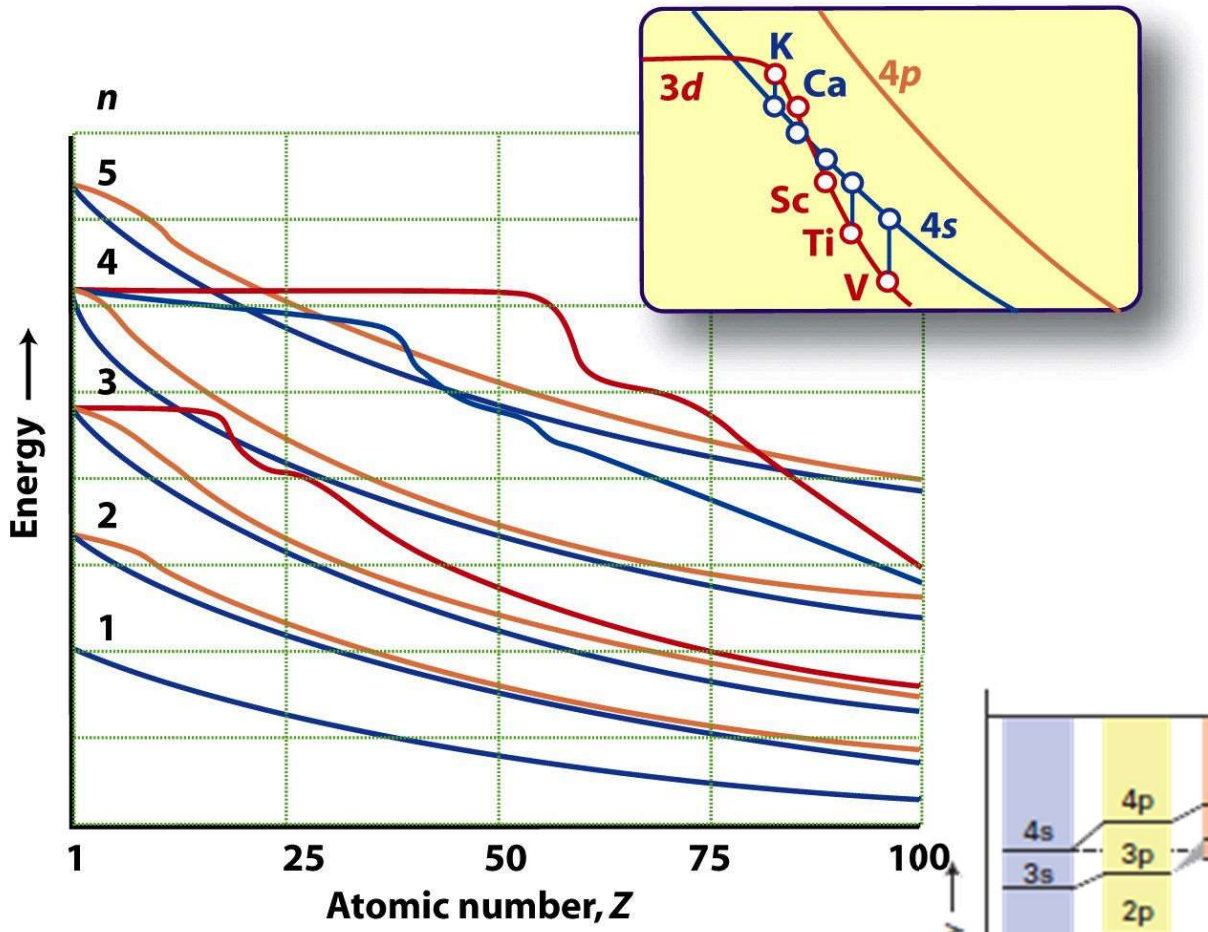
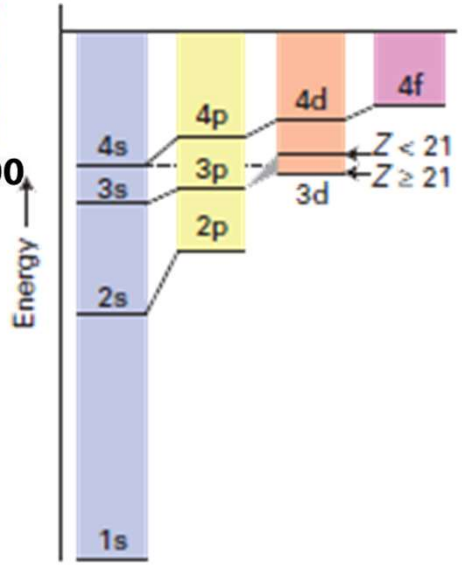


Figure 1-22
Shriver & Atkins Inorganic Chemistry, Fourth Edition



H $1s^1$
He $1s^2$
Li $1s^22s^1$
.....
F $1s^22s^22p^5$
Ne $1s^22s^22p^6$

Na $[Ne]3s^1$
Al $[Ne]3s^23P^1$
....
Ar $[Ne]3s^23p^6$

Now what next
?

19 K $[Ar]4s^1$
20 Ca $[Ar]4s^2$

then? Sc

Two electrons present in the same d-orbital repel each other more strongly than do two electrons in the same s-orbital.

Therefore, occupation of orbitals of higher energy can result in a reduction in the repulsion between electrons (for eg., 4s), otherwise the repulsion will be more if the lower-energy 3d orbitals were occupied.

It is essential to consider all contributions to the energy of a configuration, and just not one-electron orbital energies

Experimental data show that Ground State configurations of d-block elements are of the form $3d^n4s^2$, with 4s orbital fully occupied.

Sc (at. No. 21) is $[Ar]3d^14s^2$

This order is followed in most cases - but not always! (some exceptions)

Two atomic configurations do not follow the sequence of filling of orbitals

Z = 24 Cr $[Ar]\ 3d^54s^1$; not $[Ar]\ 3d^44s^2$

Z = 29 Cu $[Ar]\ 3d^{10}4s^1$; not $[Ar]\ 3d^94s^2$

As atomic number increases, energy of 3d orbitals decrease relative to both 4s and 4p
At z = 29, energy of 3d becomes much lower than 4s
Hence order of filling 3d < 4s < 4p

Filling & removal in Transition elements

- Transition series: filling order: 4s, 3d
- removal order (cation formation): 4s, 3d

(not 3d, 4s)

e.g. Ti [Ar] $3d^2$ $4s^2$

- Ti^{2+} [Ar] $3d^2$ (not [Ar] $4s^2$) Why?

The following properties are important to address the compounds formed

- Atomic size (radius)
- Ionic size (radius)
- Atomic volume
- Ionization energy
- Electron affinity
- Electronegativity
- Hard soft acid base (HSAB)
- Polarizability
- Oxidation states
- Coordination number & geometry

Size (Radius)

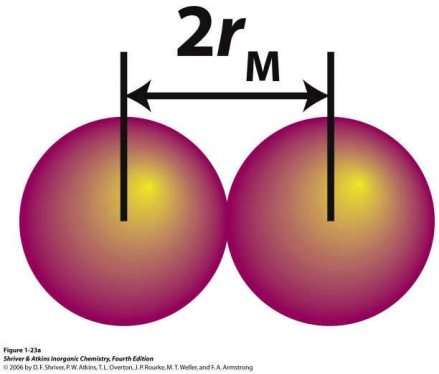


Figure 1-23a
Shriver & Atkins Inorganic Chemistry, Fourth Edition

The METALLIC RADIUS is half of the experimentally determined distance between the nuclei of nearest neighbors in the solid

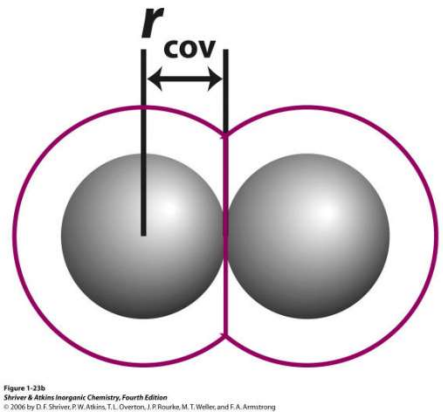


Figure 1-23b
Shriver & Atkins Inorganic Chemistry, Fourth Edition

The COVALENT RADIUS of a non-metallic element is half of the experimentally determined distance between the nuclei of nearest neighbors in the solid

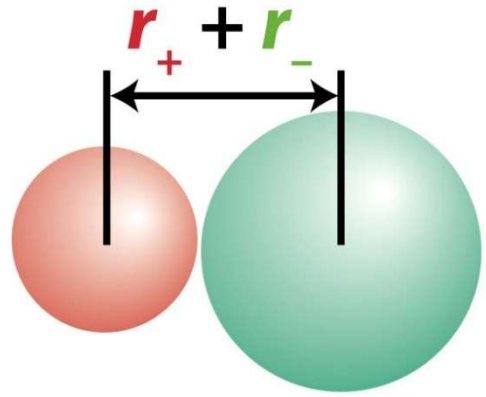


Figure 1-23c
Shriver & Atkins Inorganic Chemistry, Fourth Edition

The IONIC RADIUS of an element is related to the distance between the nuclei of neighboring cations and anions

Ionic radius of O^{2-} is 1.40 Å;

What is the ionic radius for Mg^{2+}?

Measure the Mg-O distance in MgO and subtract 1.40 Å

Size (Radius)

In a period, left to right

1. n (number of shells) remain constant.
2. Z increases (by one unit)
3. Z* increases (by 0.65 unit)
4. Electrons are pulled close to the nucleus by the increased Z*

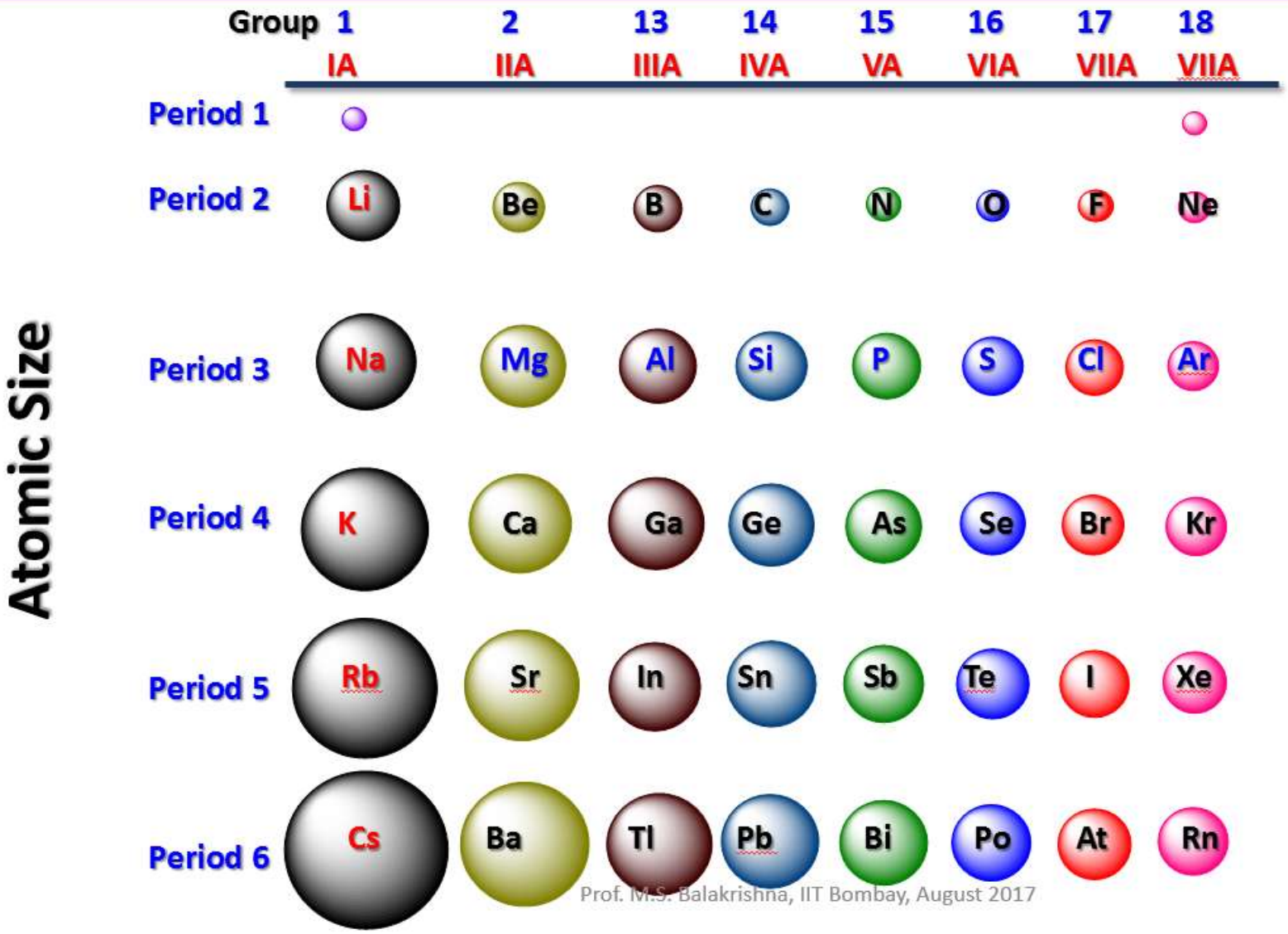
So atomic radius decreases with increase in atomic number (in a period left to right)

In a group, top to bottom

1. n increases
2. Z increases
3. No dramatic increase in Z* - almost remains constant

So atomic radius increases moving down the group

How periodic properties guide us to know chemical bonding



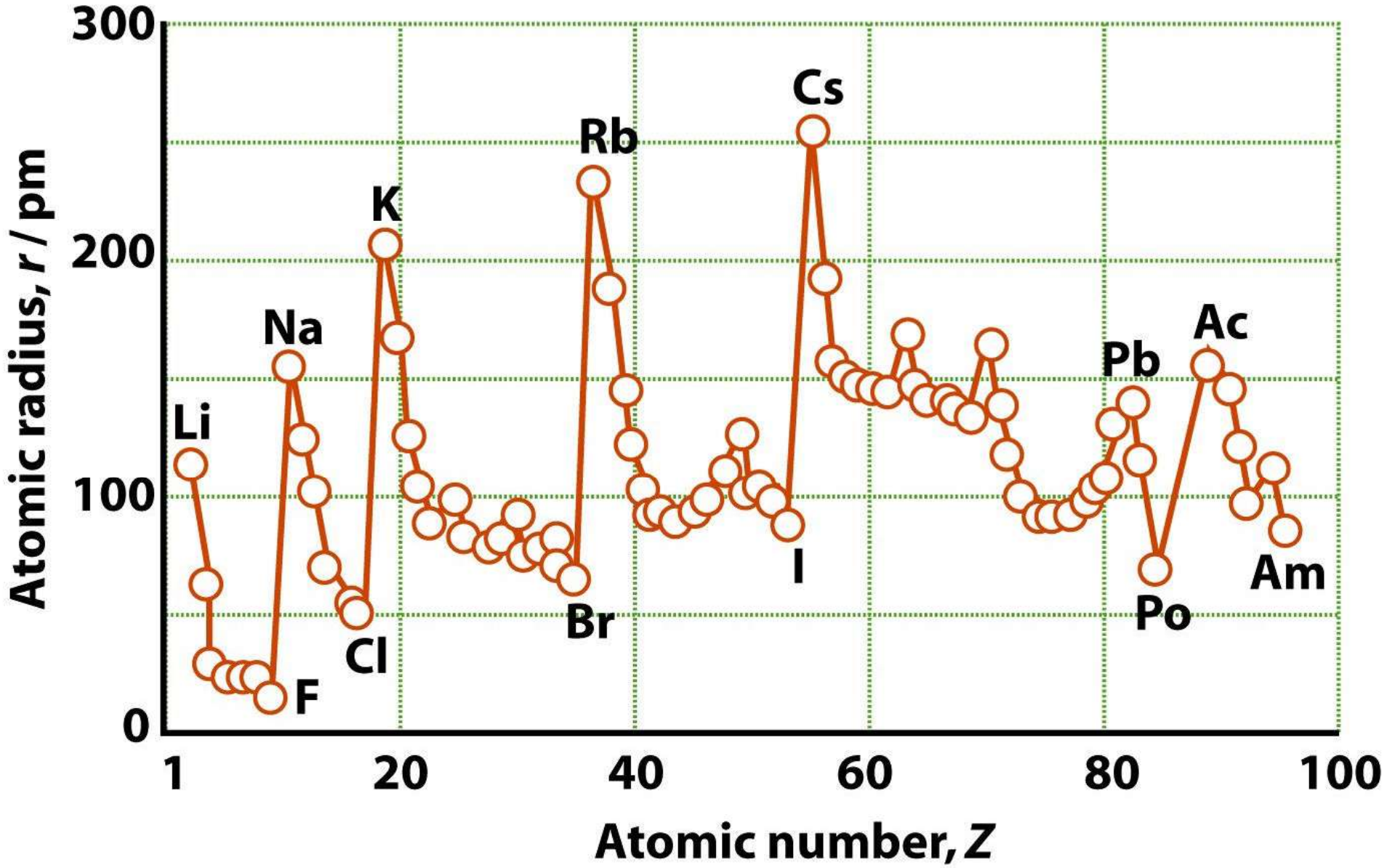


Figure 1-24
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Table 1.4 Atomic radii, *r*/pm*

Li	Be											B	C	N	O	F
157	112											88	77	74	66	64
Na	Mg											Al	Si	P	S	Cl
191	160											143	118	110	104	99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
235	197	164	147	135	129	137	126	125	125	128	137	153	122	121	117	114
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
250	215	182	160	147	140	135	134	134	137	144	152	167	158	141	137	133
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
272	224	172	159	147	141	137	135	136	139	144	155	171	175	182		

*The values refer to coordination number 12 (see Section 3.2).

Decreases with increase in atomic number in a period left to right

Increases moving down a group

Metallic Radius

Metallic radii of 5d- block elements are expected to be larger than that of the 4d- elements, but found that these are not larger. Of course these are larger than 3d- block elements.

Lanthanide Contraction

f-orbitals have poor shielding properties; low penetrating power.

So Z_{eff} increases from left to right across the period leading to more compact atoms.

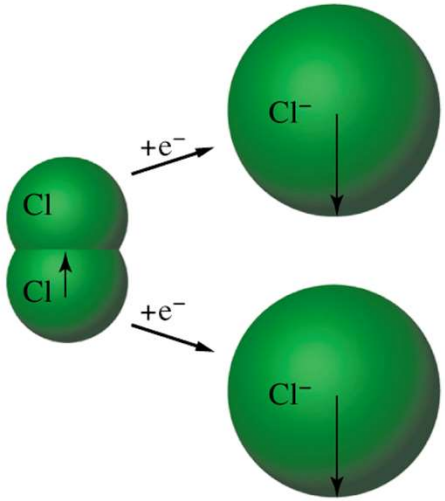
Table 1.5 Ionic radii, *r*/pm*

Li^+	Be^{2+}	B^{3+}			N^{3-}	O^{2-}	F^-
59(4)	27(4)	11(4)			146	135(2)	128(2)
76(6)						138(4)	131(4)
						140(6)	133(6)
						142(8)	
Na^+	Mg^{2+}	Al^{3+}			P^{3-}	S^{2-}	Cl^-
99(4)	49(4)	39(4)			212	184(6)	181(6)
102(6)	72(6)	53(6)					
118(8)	89(8)						
K^+	Ca^{2+}	Ga^{3+}			As^{3-}	Se^{2-}	Br^-
138(6)	100(6)	62(6)			222	198(6)	196(6)
151(8)	112(8)						
159(10)	123(10)						
160(12)	134(12)						
Rb^+	Sr^{2+}	In^{3+}	Sn^{2+}	Sn^{4+}		Te^{2-}	I^-
152(6)	118(6)	79(6)	83(6)	69(6)		221(6)	220(6)
160(8)	125(8)	92(8)	93(8)				
173(12)	144(12)						
Cs^+	Ba^{2+}	Tl^{3+}					
167(6)	149(6)	88(6)					
174(8)	156(8)	Tl^+					
188(12)	175(12)	164(6)					

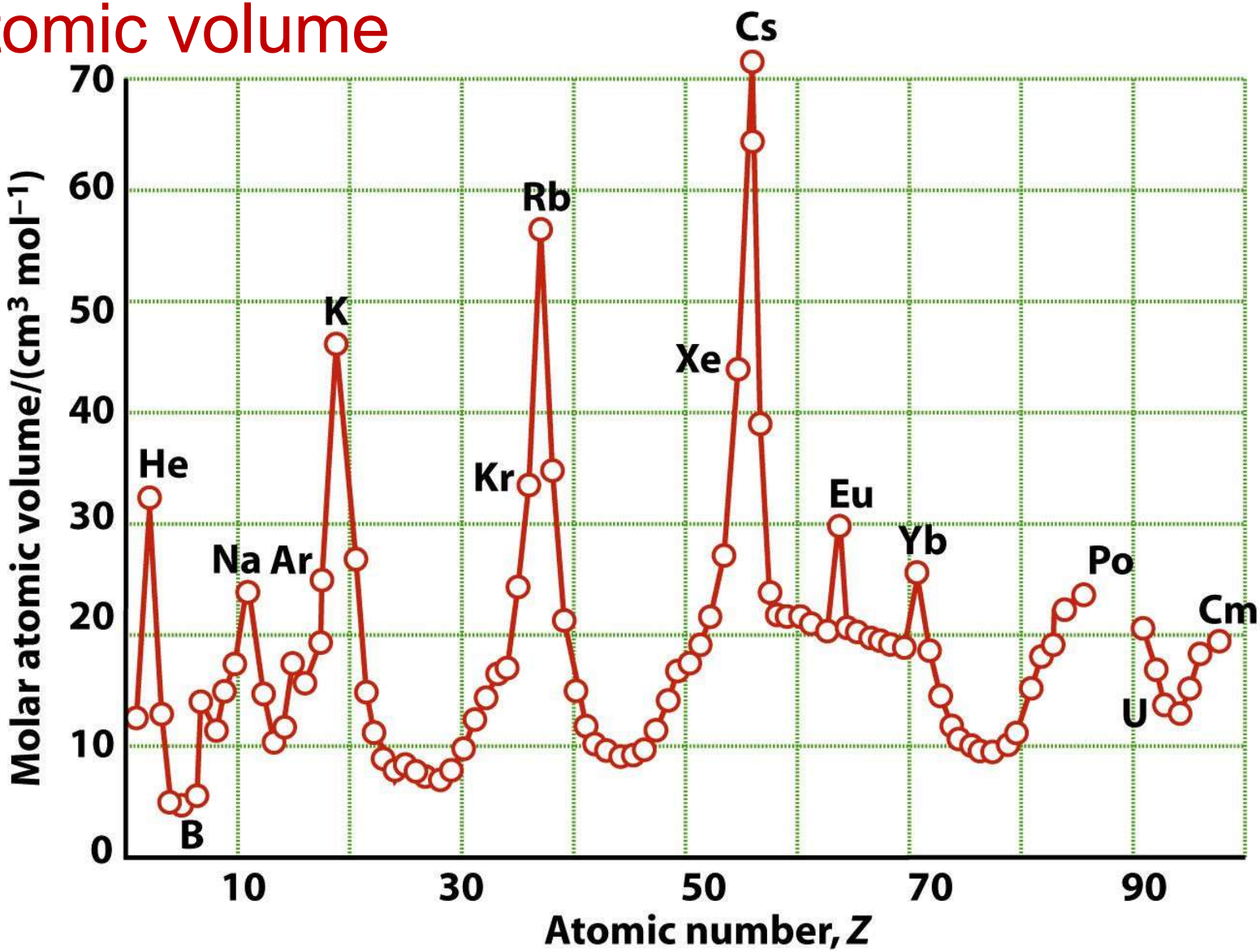
*Numbers in parentheses are the coordination number of the ion. For more values, see *Resource section* 1.

All anions are larger than their parent atoms

The cations are smaller



Atomic volume



Density, melting point, etc. depend on atomic volume; related to compactness or the lack of it

Ionisation Energy (IE)

The minimum energy needed to remove an electron from a gas phase atom

Depends on: (a) Size of the atom - IE decreases as the size of the atom increases; (b) Nuclear Charge - IE increases with increase in nuclear charge; (c) The type of electron - Shielding effect

1st IE: H = 1312 KJ mol^{-1} Li = 520 KJ mol^{-1}

Reasons: 1. Average distance of 2s electron is greater than that of 1s; 2. Penetration effect; 3. Electronic configuration

Ionisation Energy (IE)

On moving down a group

1. nuclear charge increases
2. Z* due to screening is almost constant
3. number of shells increases, hence atomic size increases.
4. there is an increase in the number of inner electrons which shield the valence electrons from the nucleus

Thus IE decreases down the group

Ionisation Energy (IE)

On moving across a period
1. the atomic size decreases
2. nuclear charge increases
Thus IE increases along a period

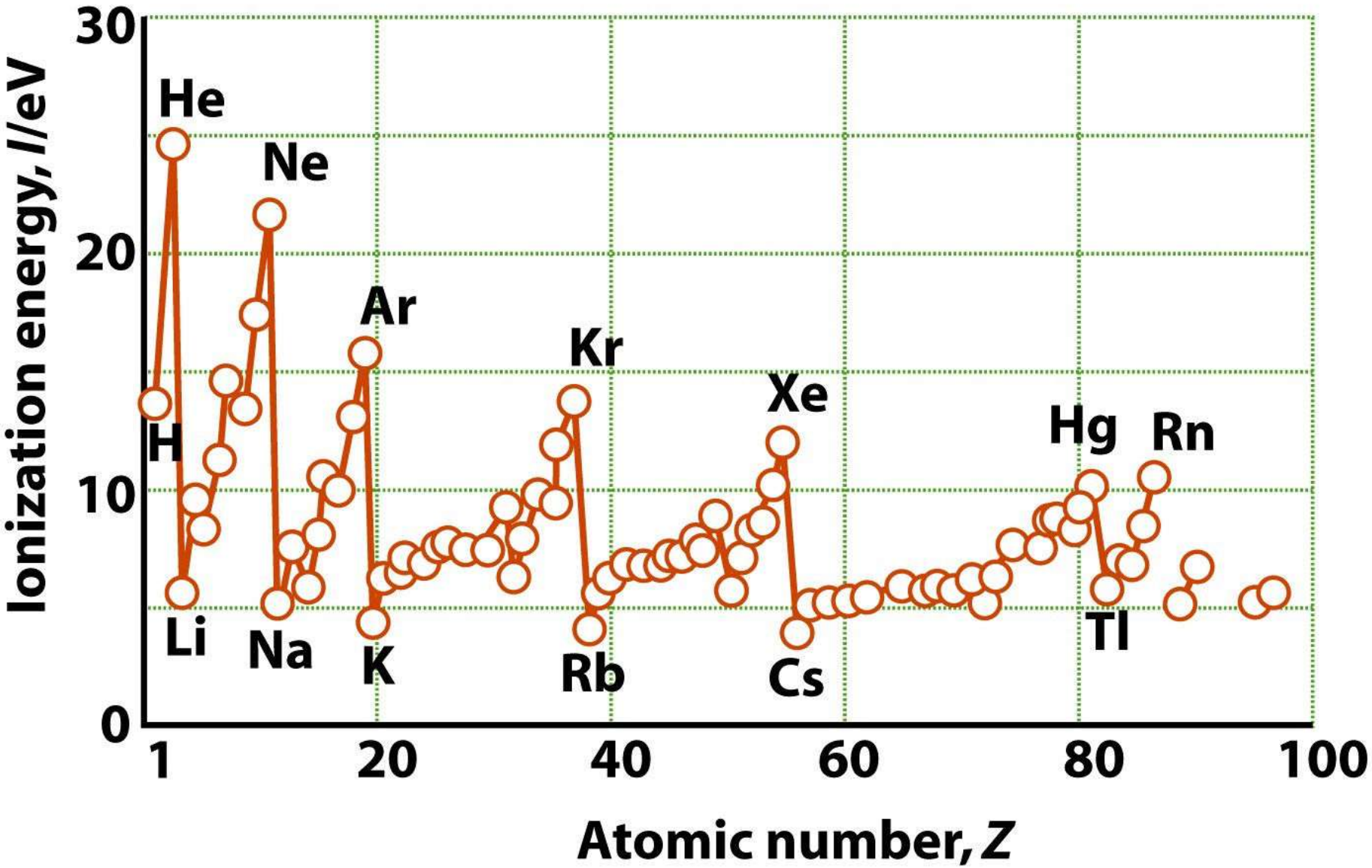


Figure 1-25
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Table 1.6 First and second (and some higher) ionization energies of the elements, I/(kJ mol^{-1})

H							**He**
1312							2373
							5259
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
513	899	801	1086	1402	1314	1681	2080
7297	1757	2426	2352	2855	3386	3375	3952
11809	14844	3660	4619	4577	5300	6050	6122
		25018					
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
495	737	577	786	1011	1000	1251	1520
4562	1476	1816	1577	1903	2251	2296	2665
6911	7732	2744	3231	2911	3361	3826	3928
		11574					
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
419	589	579	762	947	941	1139	1351
3051	1145	1979	1537	1798	2044	2103	3314
4410	4910	2963	3302	2734	2974	3500	3565
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
403	549	558	708	834	869	1008	1170
2632	1064	1821	1412	1794	1795	1846	2045
3900	4210	2704	2943	2443	2698	3197	3097
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
375	502	590	716	704	812	926	1036
2420	965	1971	1450	1610	1800	1600	
3400	3619	2878	3080	2466	2700	2900	

Electron affinity (EA)

- the amount of energy associated with the gain of electrons

The greater the energy released in the process of taking up the extra electron, greater is the EA

The EA of an atom measures the tightness with which it binds an additional electron to itself.

Electron affinity (EA)

On moving across a period,

-As the size decreases, the force of attraction by the nucleus increases. Consequently, the atom has a greater tendency to attract added electron, i.e., EA electron affinity increases

-Generally the EA's of metals are low while those of non-metals are high

-Halogens have high EA. This is due to their strong tendency to change their configuration to ns^2np^6

On moving down a group,

- the atomic size increases and therefore, the effective nuclear attraction decreases and thus electron affinity decreases

Table 1.7 Electron affinities of the main-group elements, E_a/(kJ mol^{-1})*

H							**He**
72							−48
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
60	≤0	27	122	−8	141 −780	328	−116
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
53	≤0	43	134	72	200 −492	349	−96
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
48	2	29	116	78	195	325	−96
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
47	5	29	116	103	190	295	−77

* The first values refer to the formation of the ion X^- from the neutral atom; the second value to the formation of X^{2-} from X^-.

The process can be Exo or endothermic

Electronegativity

measure of the tendency of an element to attract electrons to itself (from its neighbour)

On moving down the group,

-Z increases but Z* almost remains constant

-number of shells (n) increases

-atomic radius increases

-force of attraction between added electron and nucleus decreases

Therefore EN decreases down the group

Electronegativity

On moving across a period left to right

-Z and Z* increases
-number of shells remains constant
-atomic radius decreases
-force of attraction between added electron and nucleus increases

Hence EN increases along a period

The variation of Electronegativity through Periodic Table

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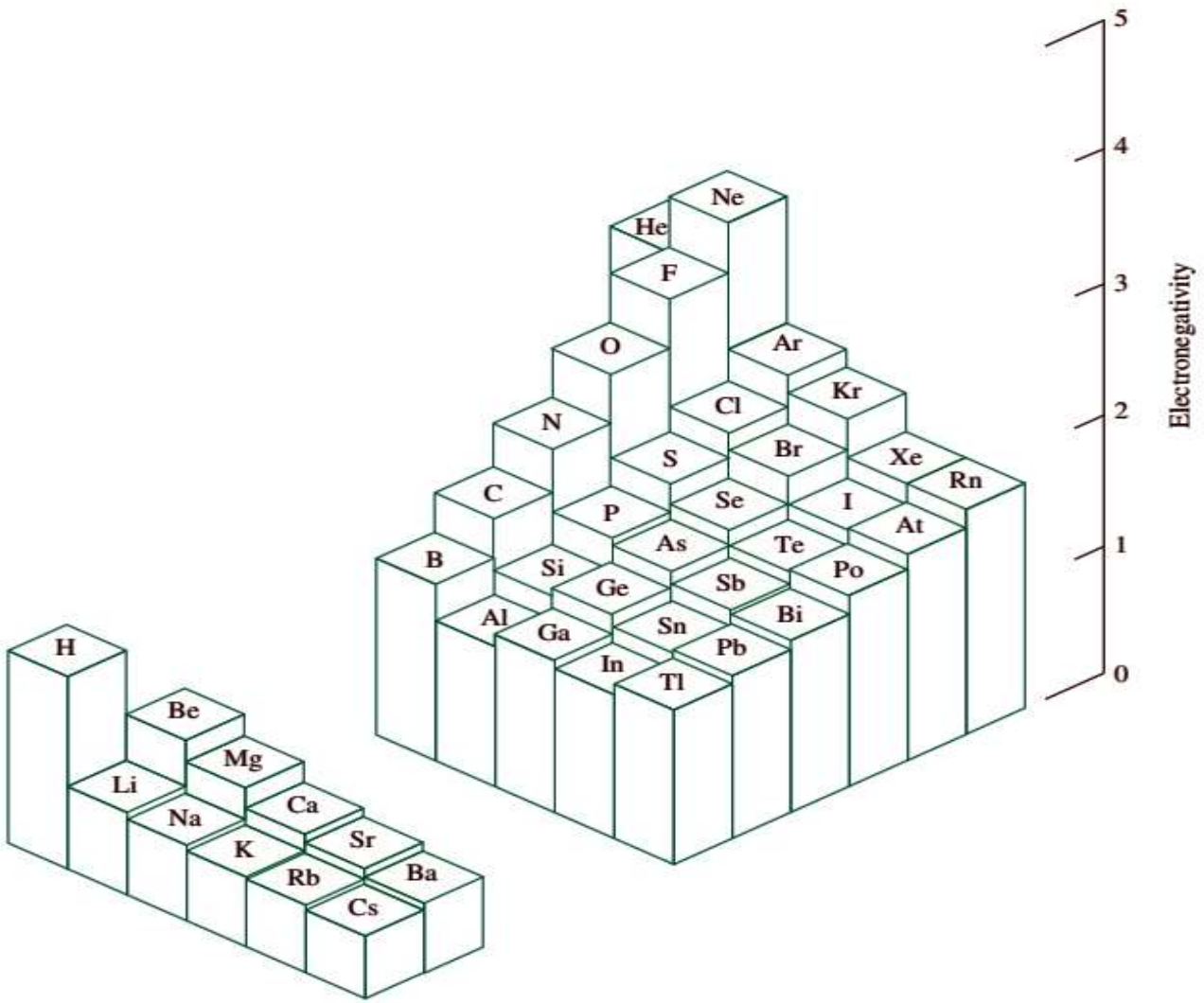
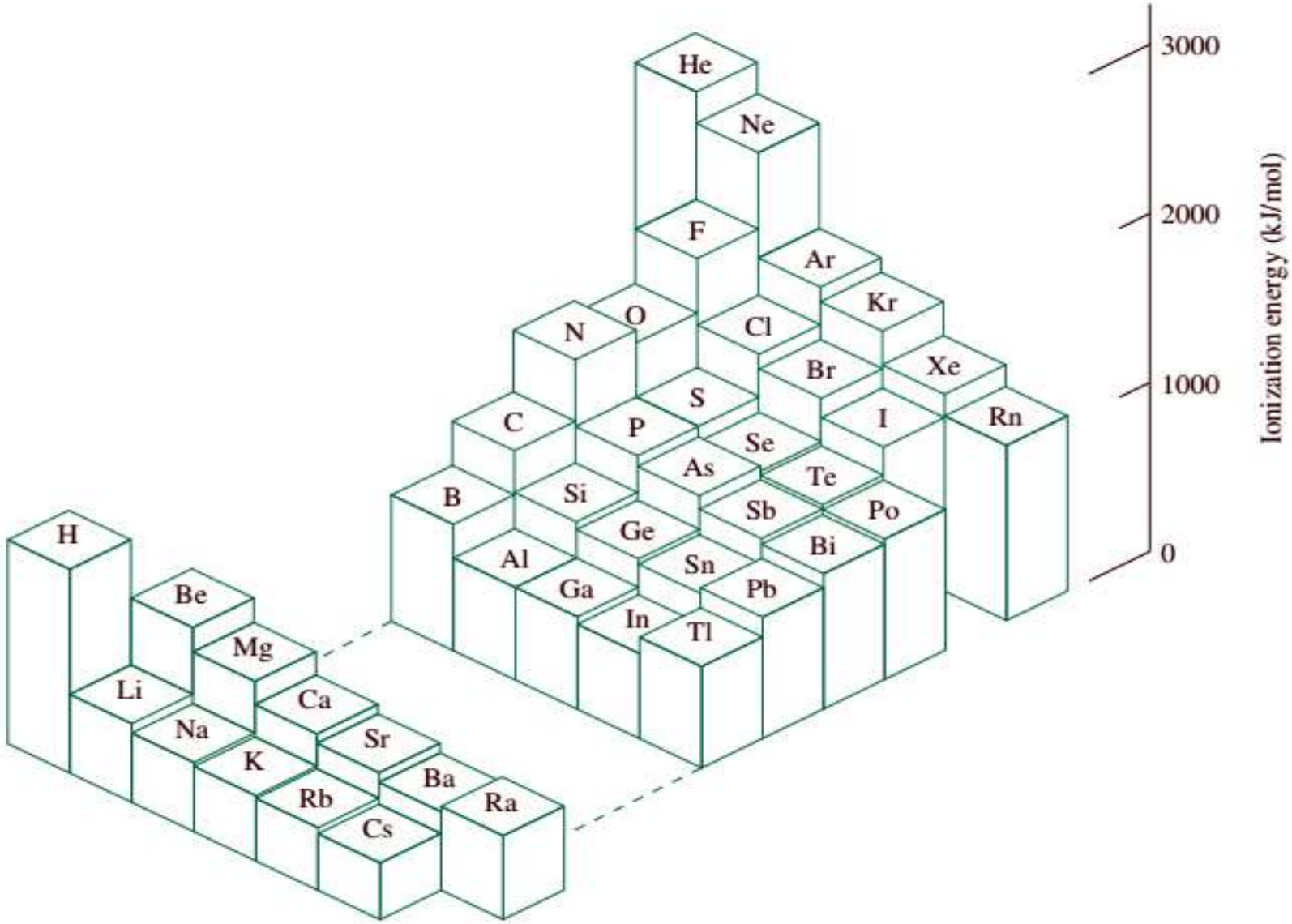


The variation of Ionization Energy through Periodic Table



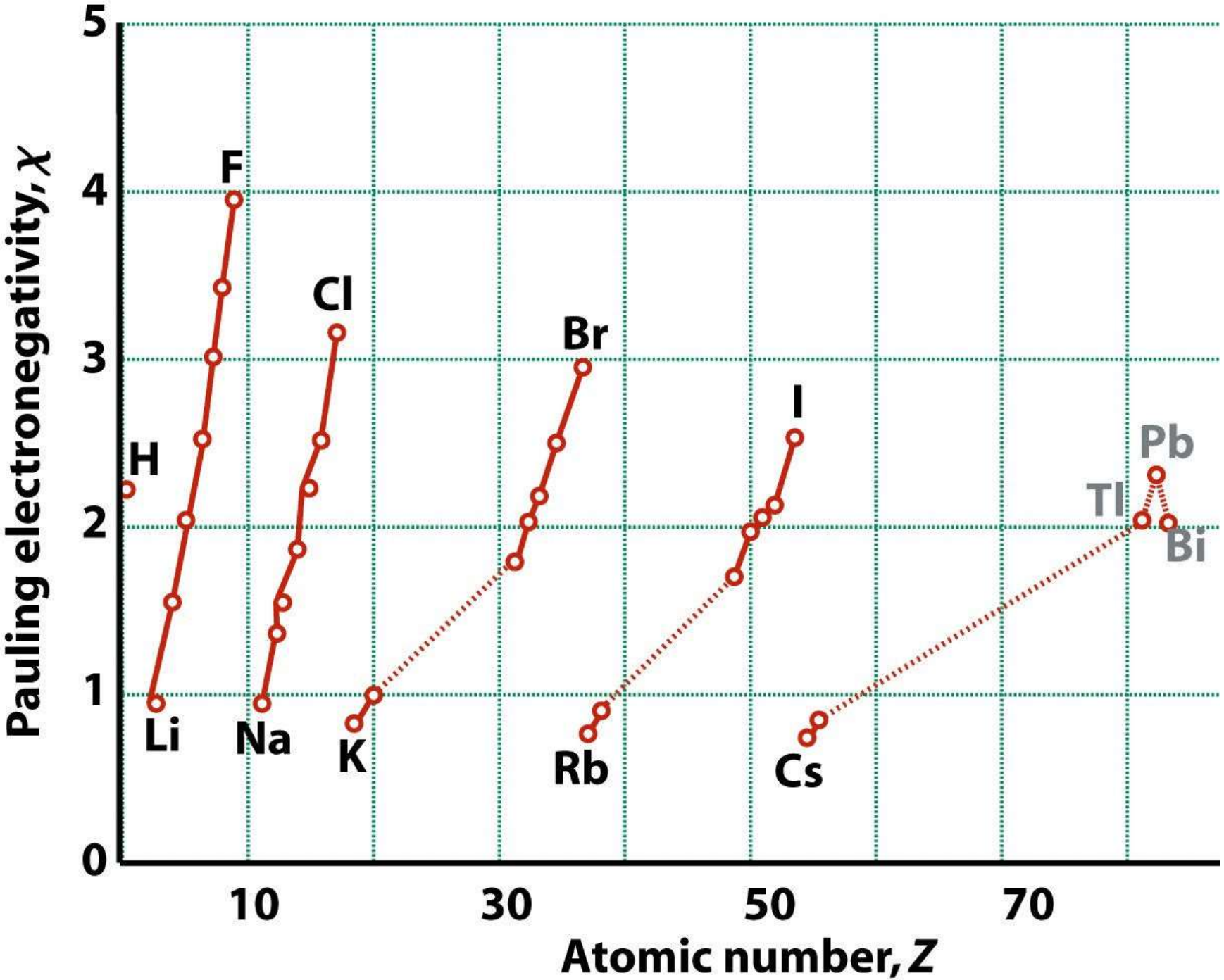

Pauling electronegativity, χ
5
4
3
2
1
0
F
Cl
Br
I
H
Li
Na
K
Rb
Cs
Pb
Tl
Bi
10
30
50
70
Atomic number, Z

Table 1.8 Pauling χ_P, Mulliken, χ_M, and Allred–Rochow, χ_{AR}, electronegativities

H							**He**
2.20							5.5
3.06							
2.20							
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
0.98	1.57	2.04	2.55	3.04	3.44	3.98	
1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
0.97	1.47	2.01	2.50	3.07	3.50	4.10	5.10
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
0.93	1.31	1.61	1.90	2.19	2.58	3.16	
1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
1.01	1.23	1.47	1.74	2.06	2.44	2.83	3.30
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
0.82	1.00	1.81	2.01	2.18	2.55	2.96	3.0
1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
0.91	1.04	1.82	2.02	2.20	2.48	2.74	3.10
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
0.82	0.95	1.78	1.96	2.05	2.10	2.66	2.6
0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
0.89	0.99	1.49	1.72	1.82	2.01	2.21	2.40
Cs	**Ba**	**Tl**	**Pb**	**Bi**			
0.79	0.89	2.04	2.33	2.02			
0.70	0.90	1.80	1.90	1.90			
0.86	0.97	1.44	1.55	1.67			

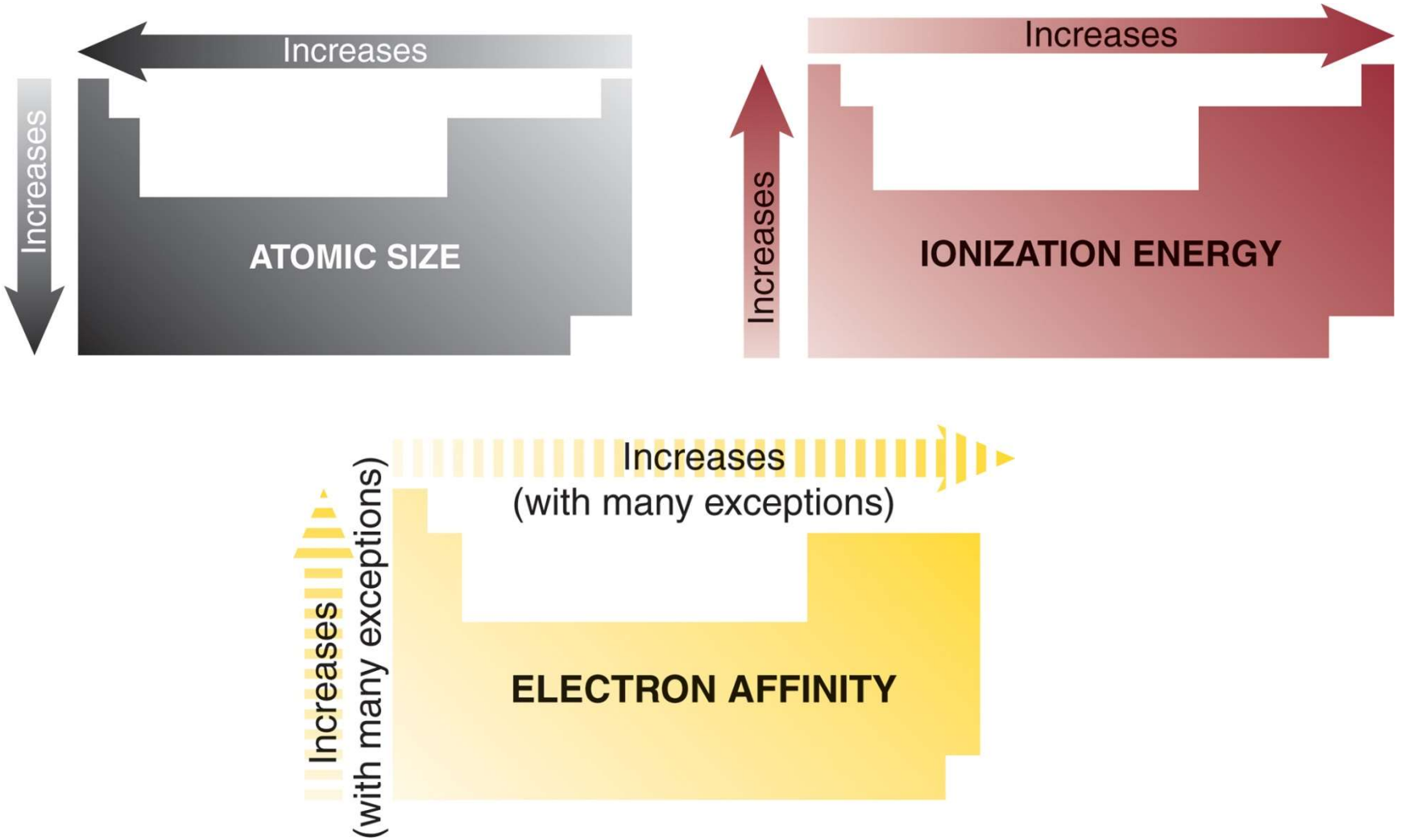
Also

$\Delta\chi > 2$: ionic

$2 > \Delta\chi > 0.5$: polar

$\Delta\chi < 0.5$: covalent

Trends in three atomic properties.



Hardness and Softness
[Chemical but not mechanical]
An important concept of compounds formed

Chemical Hardness or Softness of an atom can be correlated with ionization energy (IE), electron affinity (EA), size and polarizability. If the IE > EA, the EA can be ignored.

High IE, smaller size, low polarizability -- makes Harder

Low IE, larger size, high polarizability -- makes softer

The lighter atoms of a group are chemically harder

The heavier atoms of a group are chemically softer

Hardness and Softness

The difference between the IE of a neutral atom and its anion: If it is more, the hardness is more & if it is less, the hardness is less or it will be softer.

Pearson's Absolute Hardness $\eta = \frac{I - A}{2}$

Same as saying that the separation between the two frontier orbitals is large it is hard and if small it is soft. .ie. I= HOMO energy and A=LUMO energy

So….
Hard acids tend to bind to hard bases.
Soft acids tend to bind to soft bases.

SCN^- can bind through either S or N depending upon the HSAB nature of the metal ion.

For eg., Si or Pt

N will prefer Si due to Hard … Hard type interactions, since 'N' is hard Lewis base, & 'Si' is hard Lewis Acid.

S will prefer Pt due to Soft … Soft type interactions, since 'S' is soft Lewis base & 'Pt' is soft Lewis Acid

Trends are exhibited,

By keeping the metal same and changing the anion/ligand

By keeping the anion/ligand same and changing the metal

Oxidation States

[In atomic state they are all zero]

Tendency of an atom to form ions with different oxidation states (negative or positive) would depend on solvation or hydration or ligation and lattice formation energies of the corresponding ions. Compare this with the IE.

More electronegative atoms tend to form anions and lesser electronegative atoms tend to form cations when combined with others

Alkali atoms show +1 & alkaline earth shows +2

Oxidation States

Oxidation states vary as a fn. of valence e's
In d-block, the highest Ox. St. is more favoured down the group
In p-block, a lower Ox. St. is favoured down the group, generally by -2 due to inert pair effect

Formal charge or formal oxidations state of the central atom or ion

CH_4, CH_3OH, HCHO, HCOOH, CO_2 HCO_3^-, CO_3^{2-} CO_2^-, $C_2O_4^{2-}$

NH_3, N_2H_4, NH_2OH, NO, HNO_2, NO_2, HNO_3, N_2O_3, N_2O_4, N_2O_5

Similarly for S, P, etc.

Coordination numbers

Number of neighbours in interaction with the central ion

-- Can be primary (closely interacting and/or bonding)

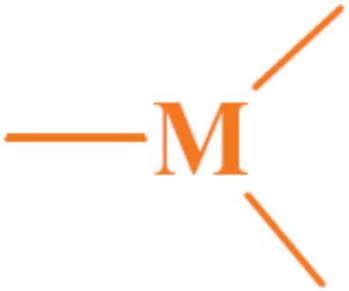
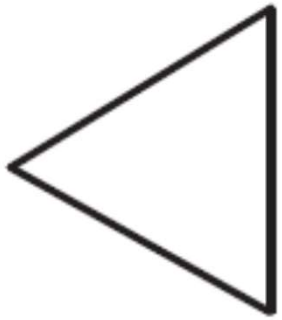
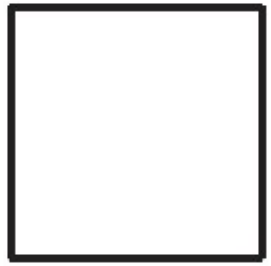
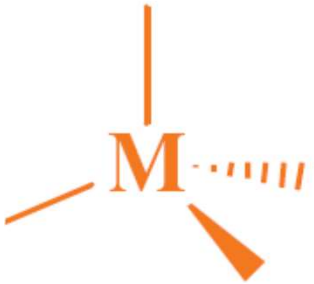
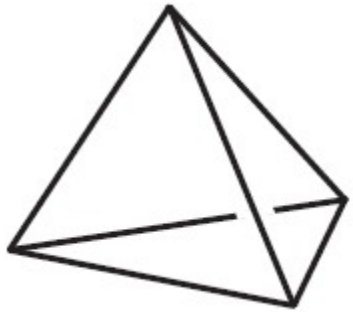
-- Can be secondary (distant than the primary but interacting – mostly no bonding)

-- All this affects the reactivity, conductivity, electronic and magnetic properties

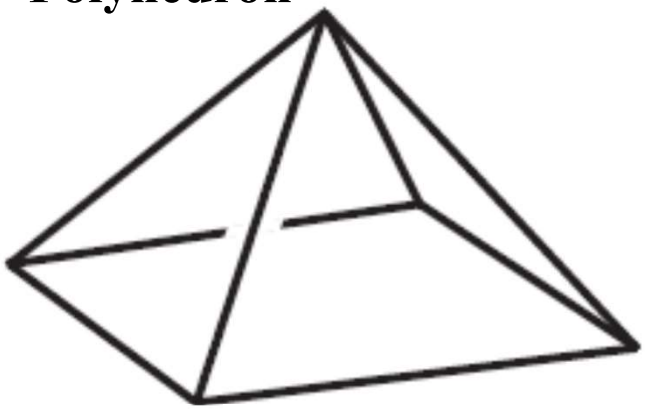
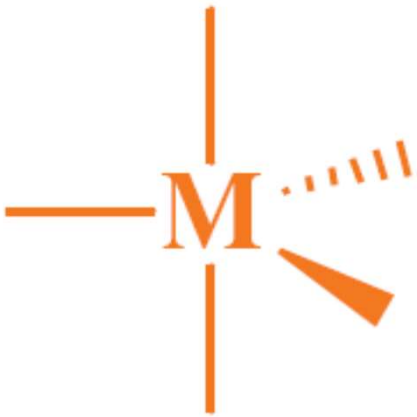
Coordination Geometry

The way the nearest neighbours are arranged in space, a variety of geometries emerge: (Main group, Transition and Lanthanides)

Linear (2),
Trigonal (3)
Tetrahedral (4),
Square planar (4)
Trigonal bipyramidal (5)
Square pyramid (5),
Octahedral (6)
Pentagonal bipyramid (7)
Singly capped octahedron (7),
Doubly capped octahedron (8),
Capped pentagonal bipyramid (9),
Decahedron (10),
Dodecahedron (12)

Number	Geometry	Polyhedron
Linear (2)		
Trigonal plane (3)		
Square planar (4)		
Tetrahedral (4)		

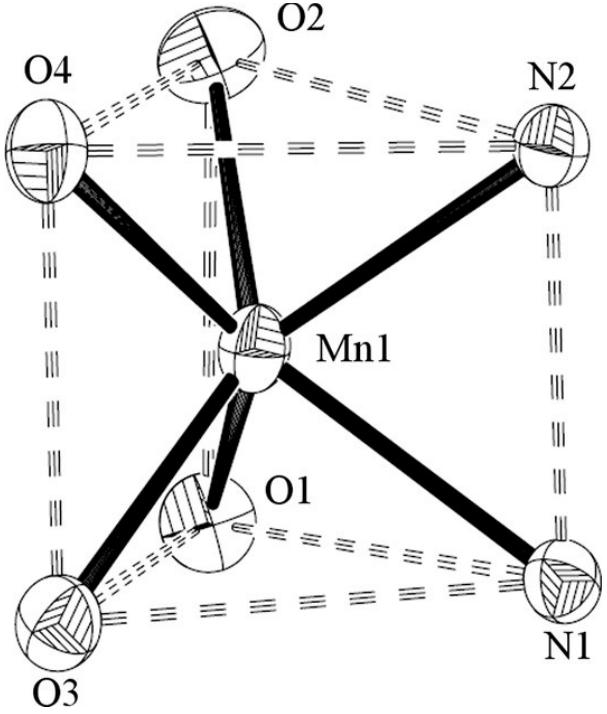
Coordination No. 5

Number	Geometry	Polyhedron
Square pyramid (5)		
Trigonal bipyramid (5)		

Coordination No. 6

Octahedral (6)

Triagonal prism

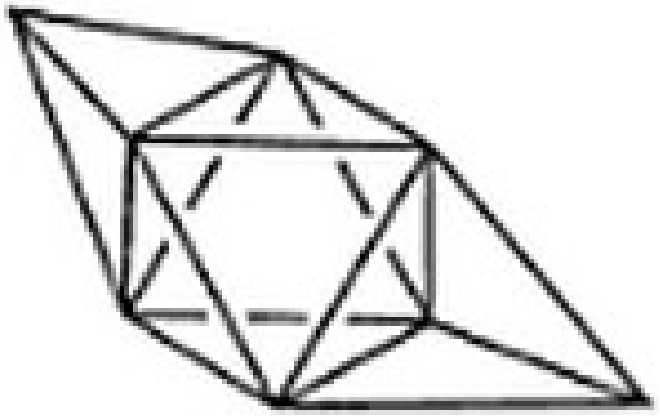


Coordination No. 7

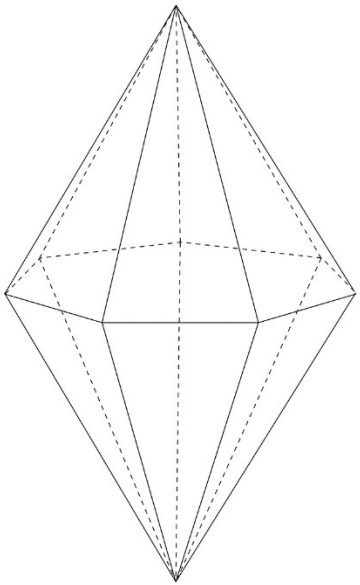
Number	Geometry	Polyhedron
Singly capped octahedron (7)		
Pentagonal bipyramidal (7)		

Coordn. No. 8

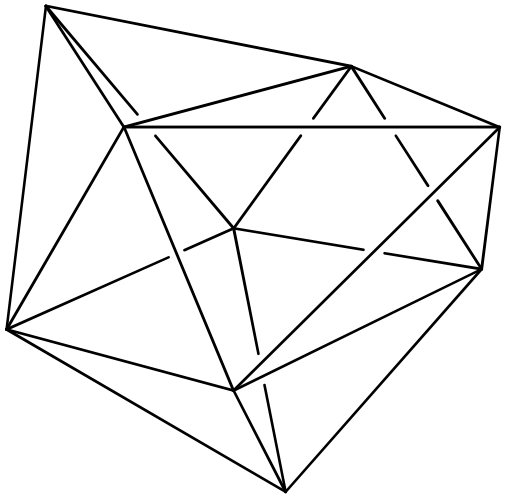
Doubly capped octahedral (8)

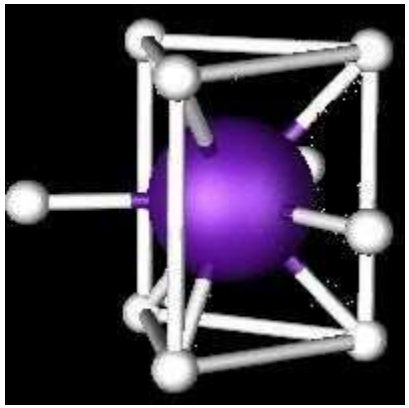


Coordn. No. 9



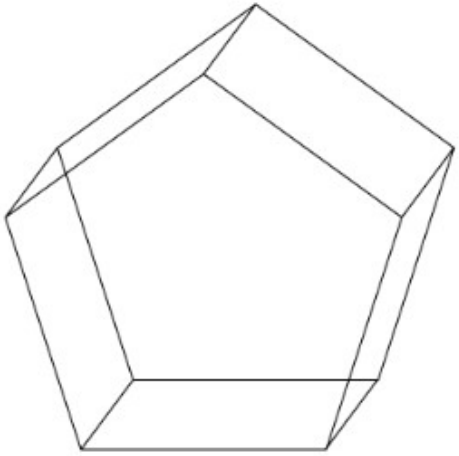
Heptagonal dipyramid



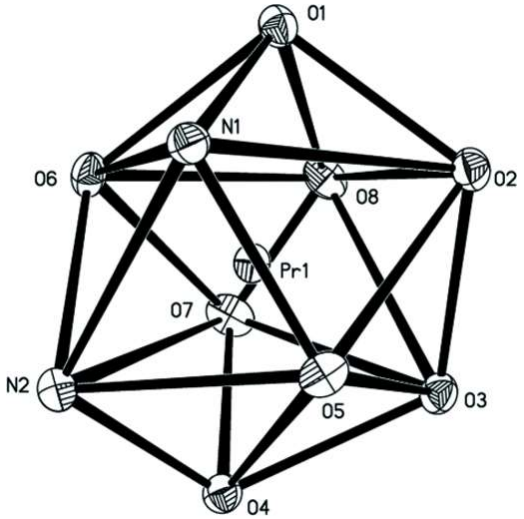


Tricapped triagonal prism

Coordn. No. 10

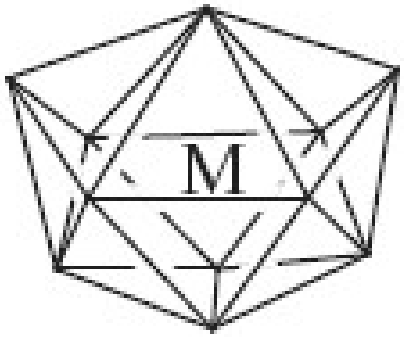


Pentagonal Prism

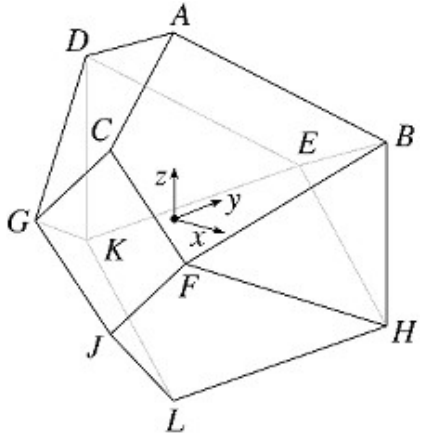


Bicapped square Prism

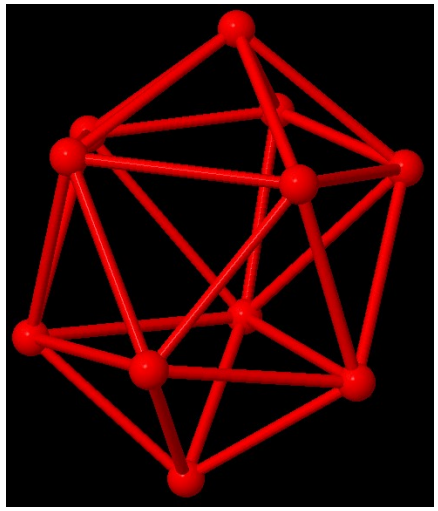
Coordn. No. 11



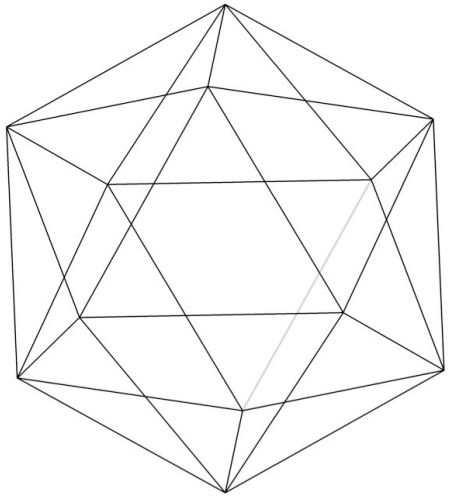
Octadecahedron



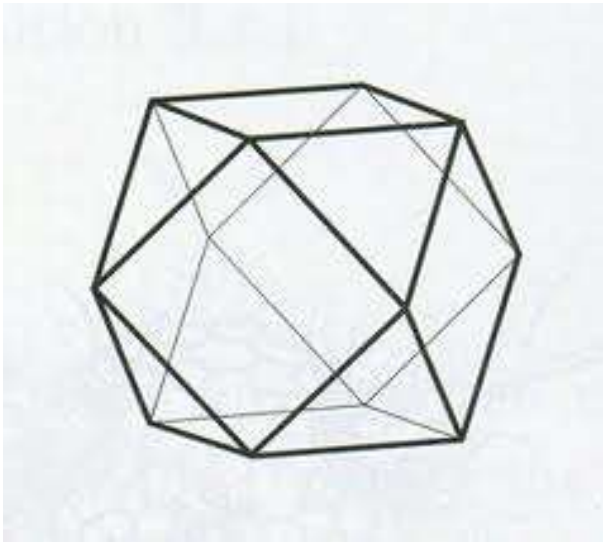
Hendecahedron



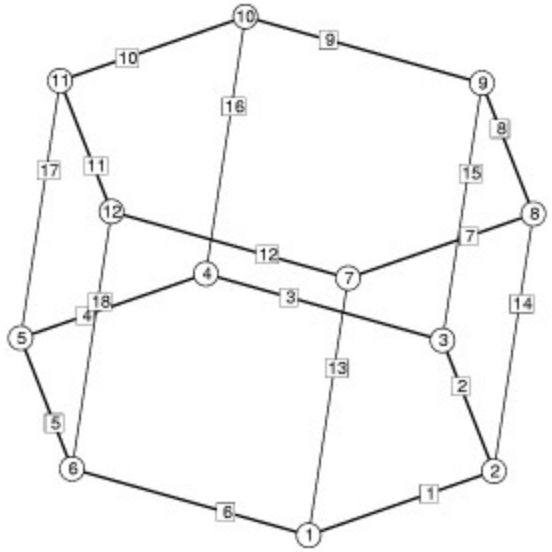
Coordn. No. 12



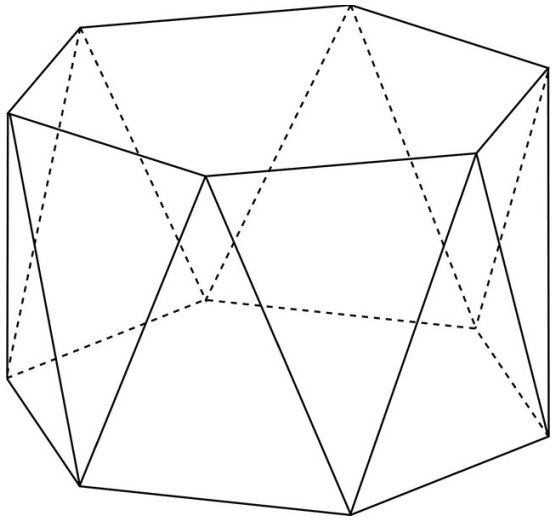
Icosahedrons



Cuboctahedrons



Hexagonal prism



Hexagonal antiprism