C1403 Lecture 13, Wednesday, October 19, 2005

Chapter 17 Many-Electron Atoms and Chemical Bonding

17.1 Many-Electron Atoms and the Periodic Table (Done)

17.2 Experimental Measures of Orbital Energies

17.3 Sizes of Atoms and Ions

17.4 Properties of the Chemical Bond

17.5 Ionic and Covalent Bonds

17.6 Oxidation States and Chemical Bonding

Summary: The Periodic Table built up by electron configurations: the ground state electron configurations of the valence electrons of the elements

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$																	2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 ***La** $5d^16s^2$	72 **Hf** $5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **†Ac** $6d^17s^2$	104 **Rf** $6d^27s^2$	105 **Db** $6d^37s^2$	106 **Sg** $6d^47s^2$	107 **Bh**	108 **Hs**	109 **Mt**	110	111	112	Unknown	114	Unknown	††116	Unknown	††118

*	58 **Ce** $4f^26s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$	71 **Lu** $4f^{14}5d^16s^2$
†	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$	103 **Lr** $5f^{14}6d^17s^2$

17.2 Experimental Measures of Orbital Energies

Photoelectron spectroscopy

Effective nuclear charge and screening by inner electrons

Periodic trends in ionization energies

Periodic trends in electron affinities

The Bohr one electron atom as a starting point for the electron configurations of multielectron atoms.

$E_n = -(Z_{eff}^2/n^2)Ry$ = energy of electron in orbit

$r_n = (n^2/Z_{eff})a_0$ = radius of a Bohr orbit

Replace Z (actual charge) with Z_{eff} (effective charge)

Structure of multielectron atoms:

Quantum numbers of electrons: n, l, m_l, m_s

Electron configurations: $1s^x2s^x2p^x3s^x3p^x$, etc (^{x} = number of electrons)

Core electrons and valence electrons (Highest value of n)

Some periodic properties of atoms we shall study:

Energy required to remove and add an electron (E_n)

Size of atoms (r_n)

Effective nuclear charge

Effective nuclear charge, Z_{eff}: the net positive charge attracting an electron.

An approximation to this net charge is

Z_{eff}(effective nuclear charge) = Z(actual nuclear charge) - Z_{core}(core electrons)

The core electrons are in subshell between the electron in question and the nucleus. The core electrons are said to "shield" the outer electrons from the full force of the nucleus.

Example: A 3s electron is in an orbital that is closer to the nucleus than a 3 p orbital. Therefore, an electron in a 3s orbital is less shielded from the nucleus than the 3 p orbital.

Rule: In many electron atoms, for a given value of n, Z_{eff} decreases with increasing *l*, because screening decreases with increasing *l*

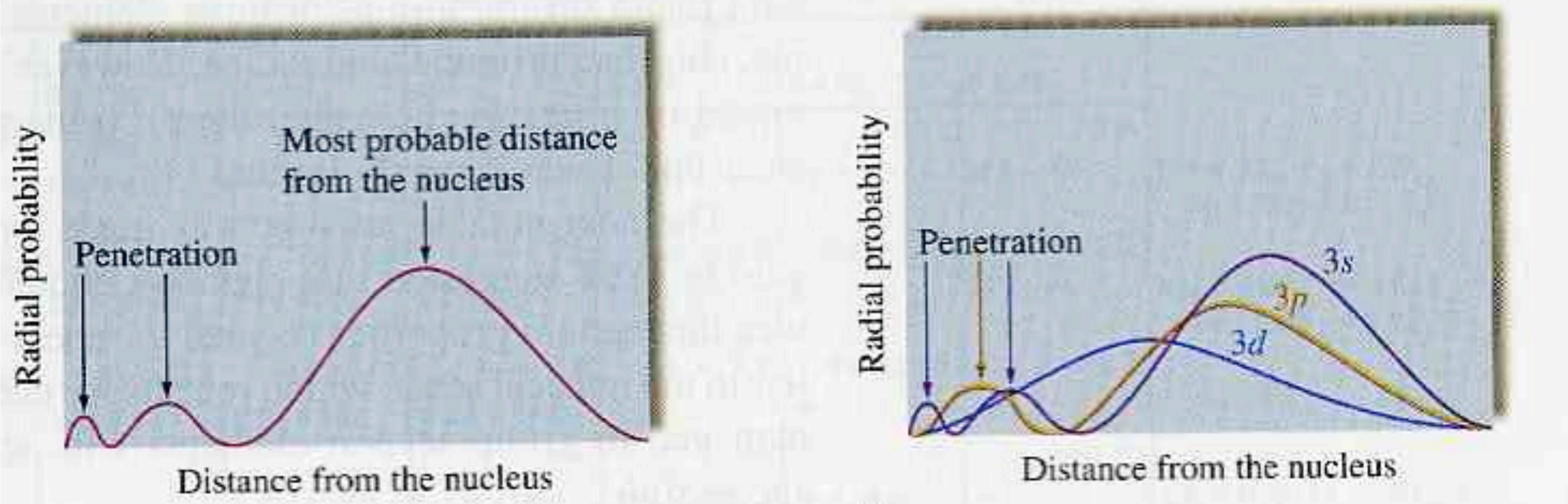
For a given n: s < p < d < f

Since the energy of an orbital depends on Z_{eff}, in a many electron atom, for a given value of n, the energy of a orbital increases with increasing value of *l*.

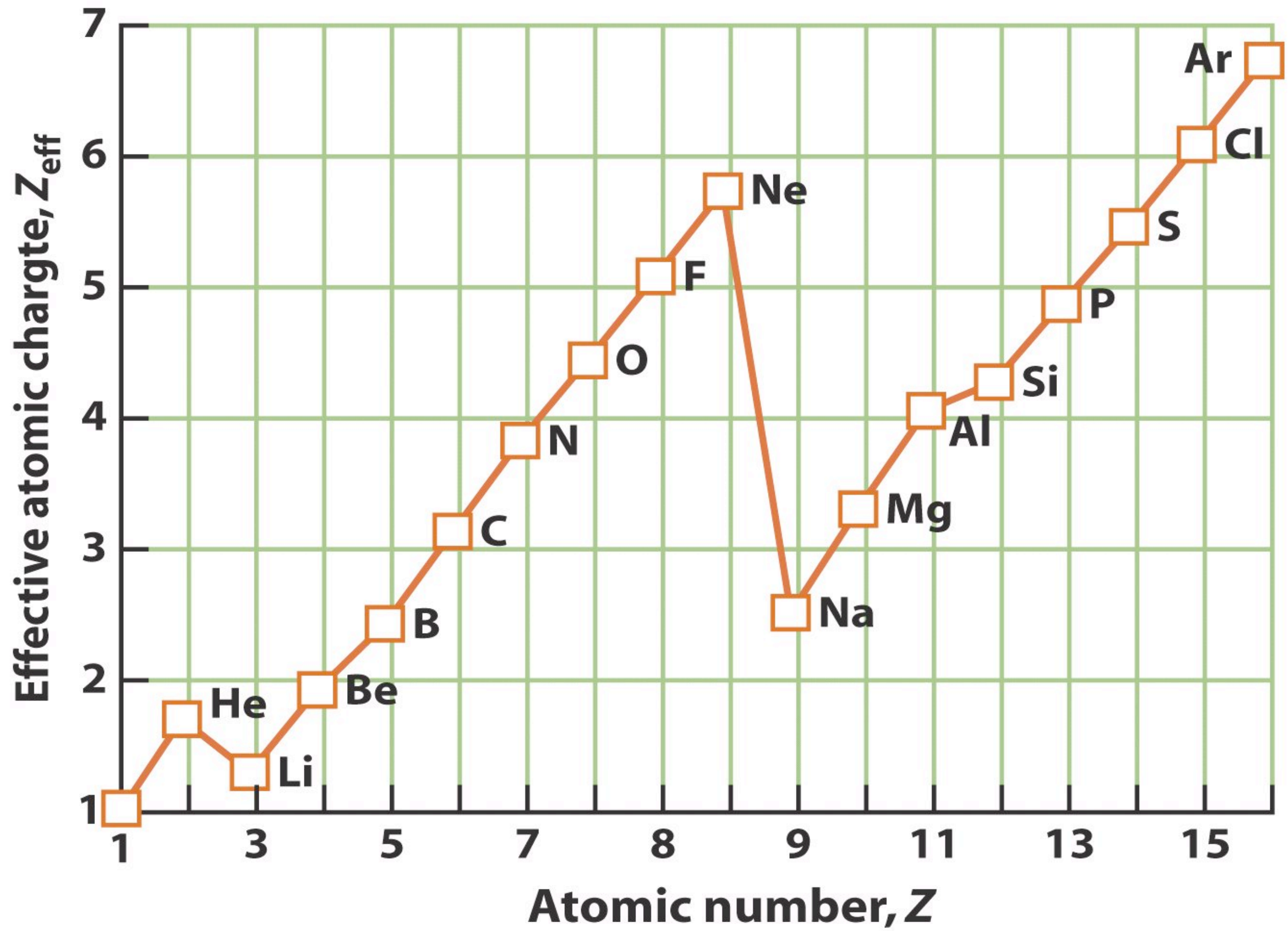
Electron shielding (screening) of the nuclear charge by other electrons

Why is the energy of a 3s orbital lower than than of a 3p orbital? Why is the energy of a 3p orbital lower than the energy of a 3d orbital?

A qualitative explanation is found in the concept of effective nuclear charge "seen" by an electron



Effective charge, Z_{eff}, seen by valence electrons*



*Note x-axis is incorrect. What should it be?

Ionization energies (ionization potentials):

The ionization energy (IE) of an atom is the minimun energy required to remove an electron from a gaseous atom.

$$X(g) \longrightarrow X^+(g) + e^-$$

The first ionization energy IE_1 is the energy required to remove the first electron from the atom, the second ionization energy IE_2, is the energy required to remove the second electron from the +1 positive ion of the atom and so on.

Conclusions from experimental IE values:
An abrupt change in IE in going along a row or column of the periodic table indicates a change in the valence electron shell or subshell. Let's take a look:

The ionization energy (IE) of an atom is the minimun energy required to remove an electron from an atom.

$$X(g) \longrightarrow X^{+}(g) + e^{-}$$

Periodic trends ionization energies of the representative elements: What are the correlations across and down?

H 1310

Period	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
								He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

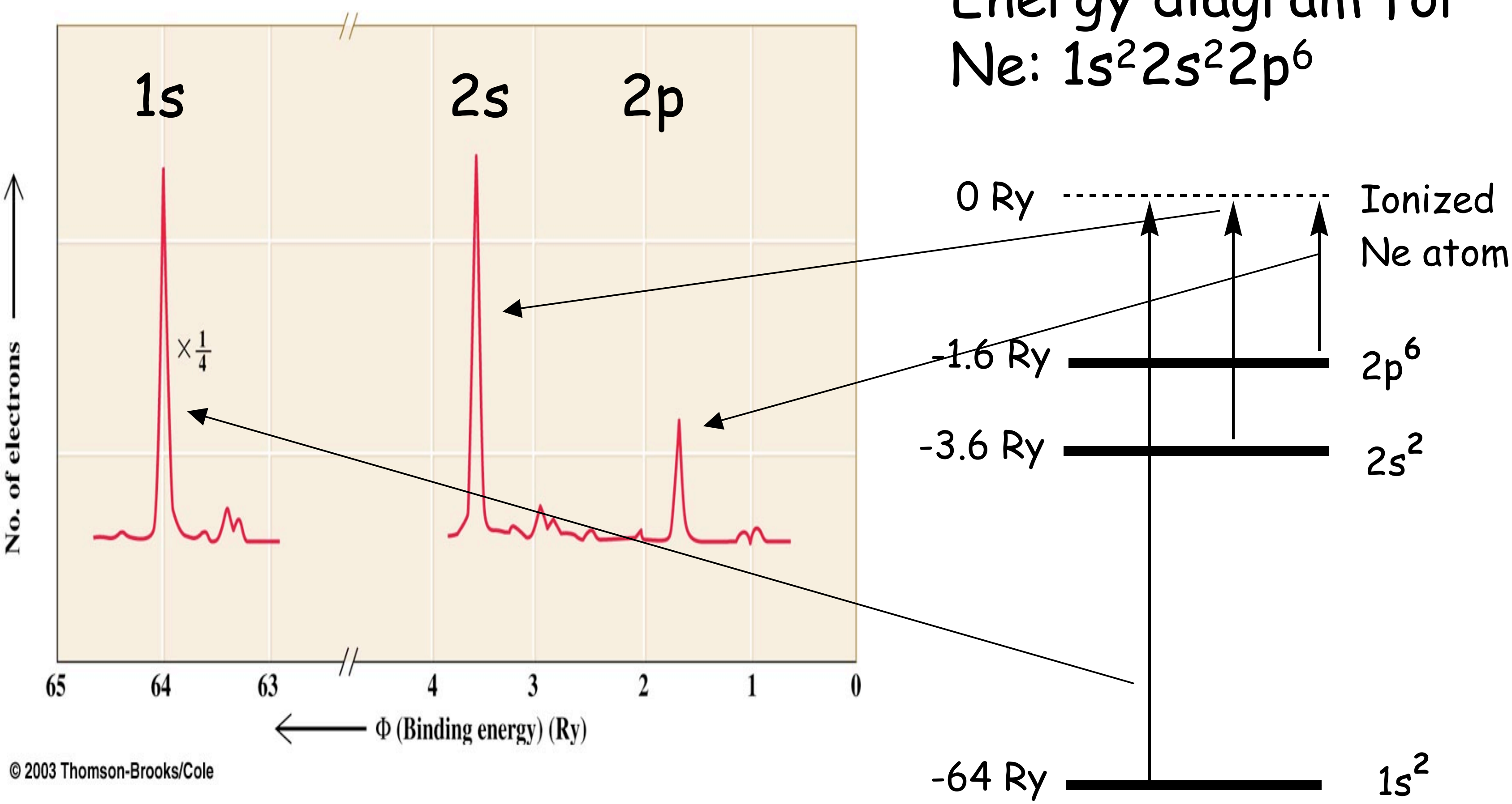
Ionization energy ($kJ \cdot mol^{-1}$)

- 2001–2500
- 1501–2000
- 1001–1500
- 501–1000
- 1–500

Photoelectron spectroscopy: the photoelectric effect for ejecting electrons from gaseous atoms.

Φ (ionization energy, IE) = $h\nu - 1/2(mv^2)$

Energy diagram for Ne: $1s^2 2s^2 2p^6$



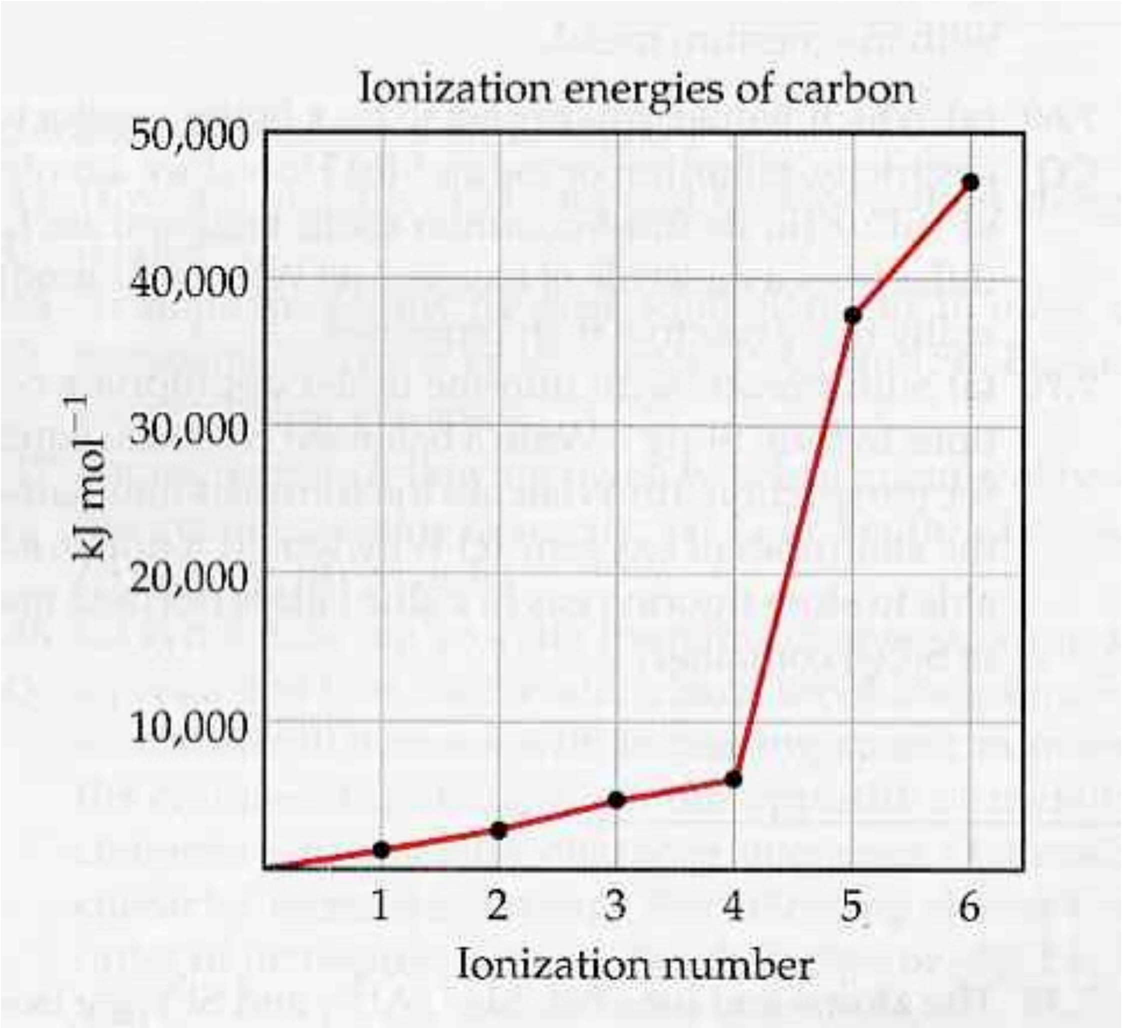
Ionization Energy, IE:
The Alkali Metal (IA) Family of Elements

Reactivity increases with the number of shells shielding the electrons in the outer (valence) shell.

IA Family	IE, Volts	Valence Shell
Li	5.39	$2s^1$
Na	5.14	$3s^1$
K	4.34	$4s^1$
Rb	4.18	$5s^1$
Cs	3.89	$6s^1$

Experimental data and theoretical ideas

Explain the “two slopes” for the ionization energies of carbon.



It gets more and more energy to remove an electron from an increasingly positively charged atom.

The first smaller slope is due to removal of n = 2 electrons, the second larger slope is due to removal of n = 1 electrons.

$^{6}C^{+5}$ $1s^{1}2s^{0}2p^{0}$

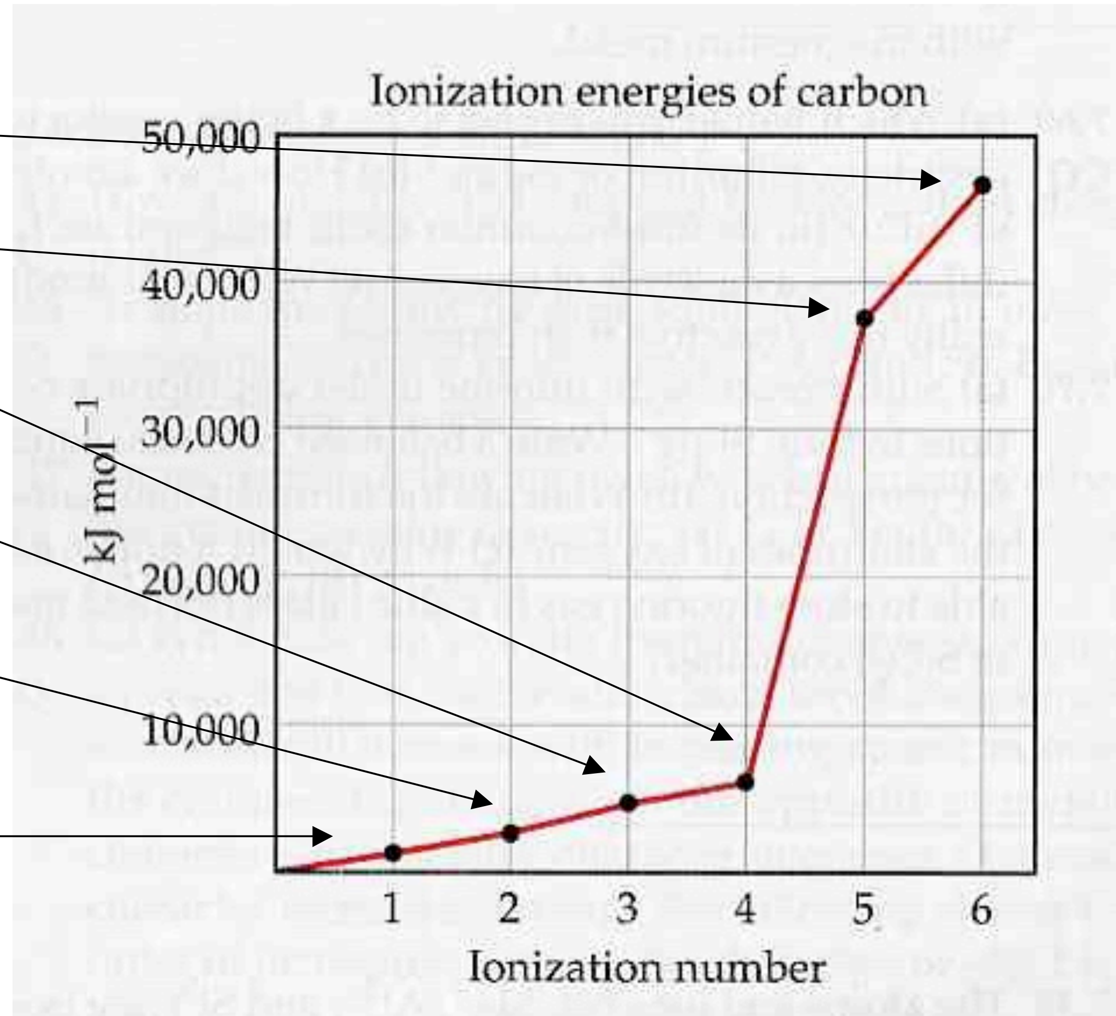
$^{6}C^{+4}$ $1s^{2}2s^{0}2p^{0}$

$^{6}C^{+3}$ $1s^{2}2s^{1}2p^{0}$

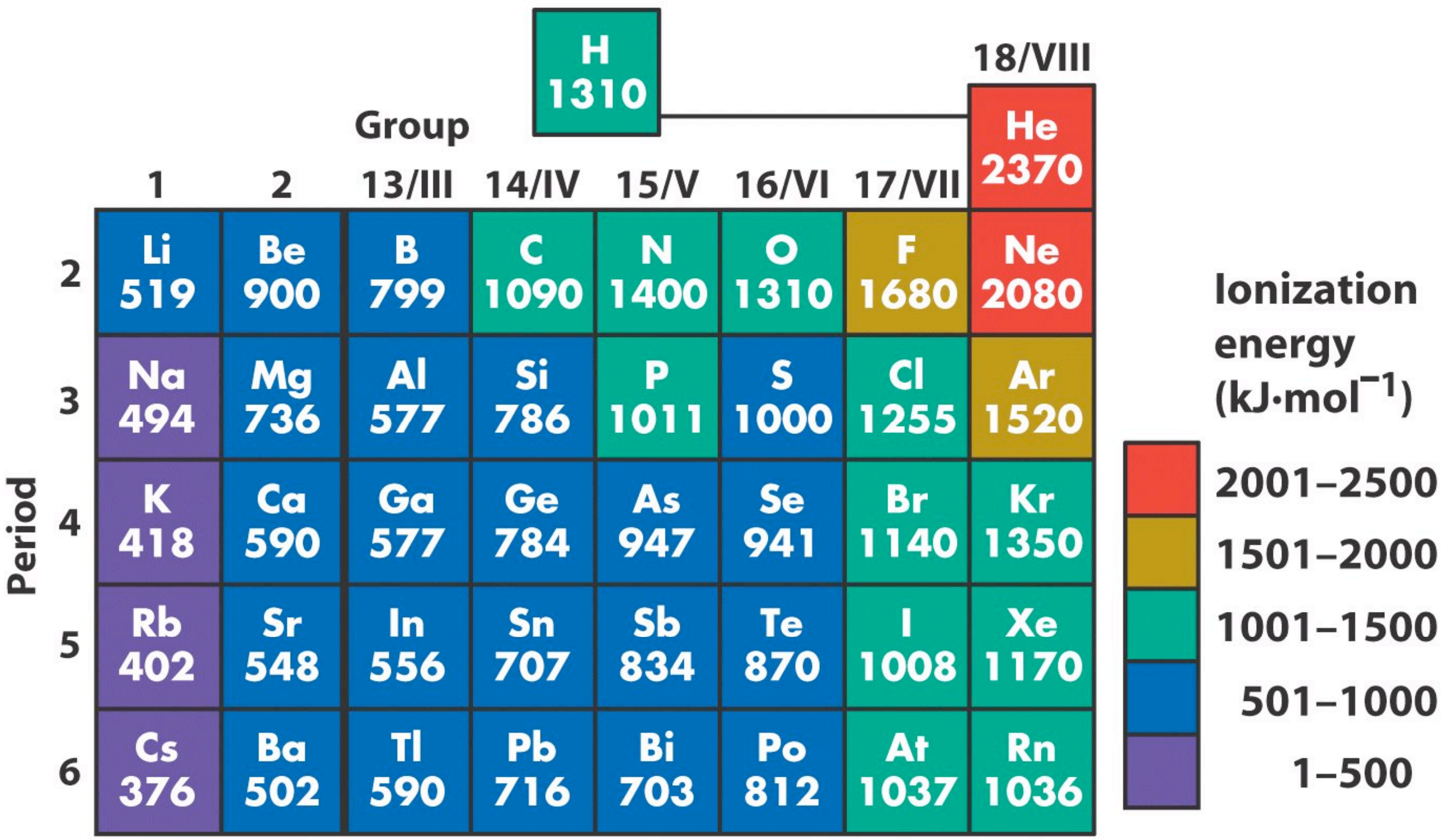
$^{6}C^{+2}$ $1s^{2}2s^{2}2p^{0}$

$^{6}C^{+1}$ $1s^{2}2s^{2}2p^{1}$

^{6}C $1s^{2}2s^{2}2p^{2}$



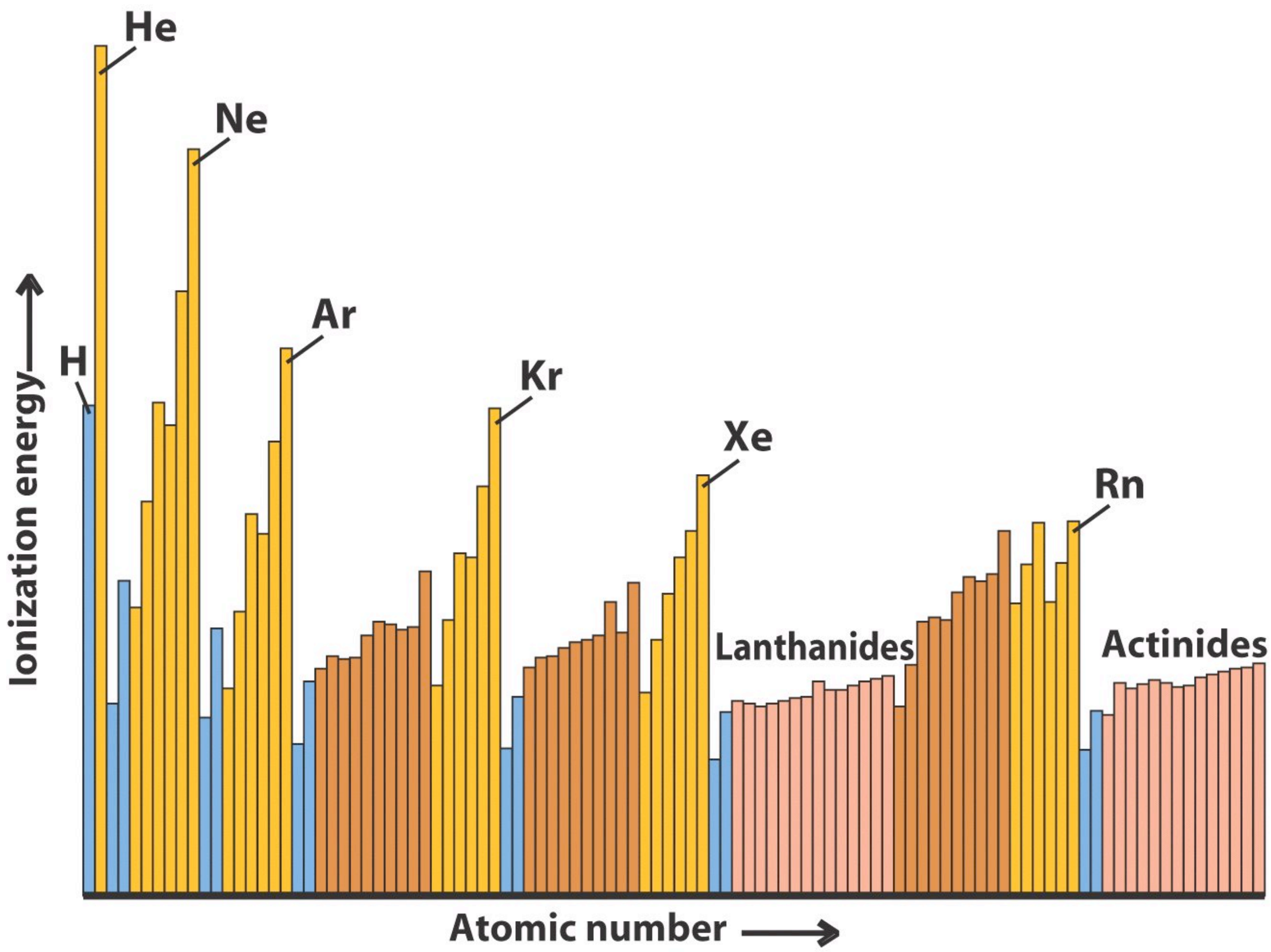
Periodic trends of the first ionization energies of the representative elements: What are the correlations across and down?



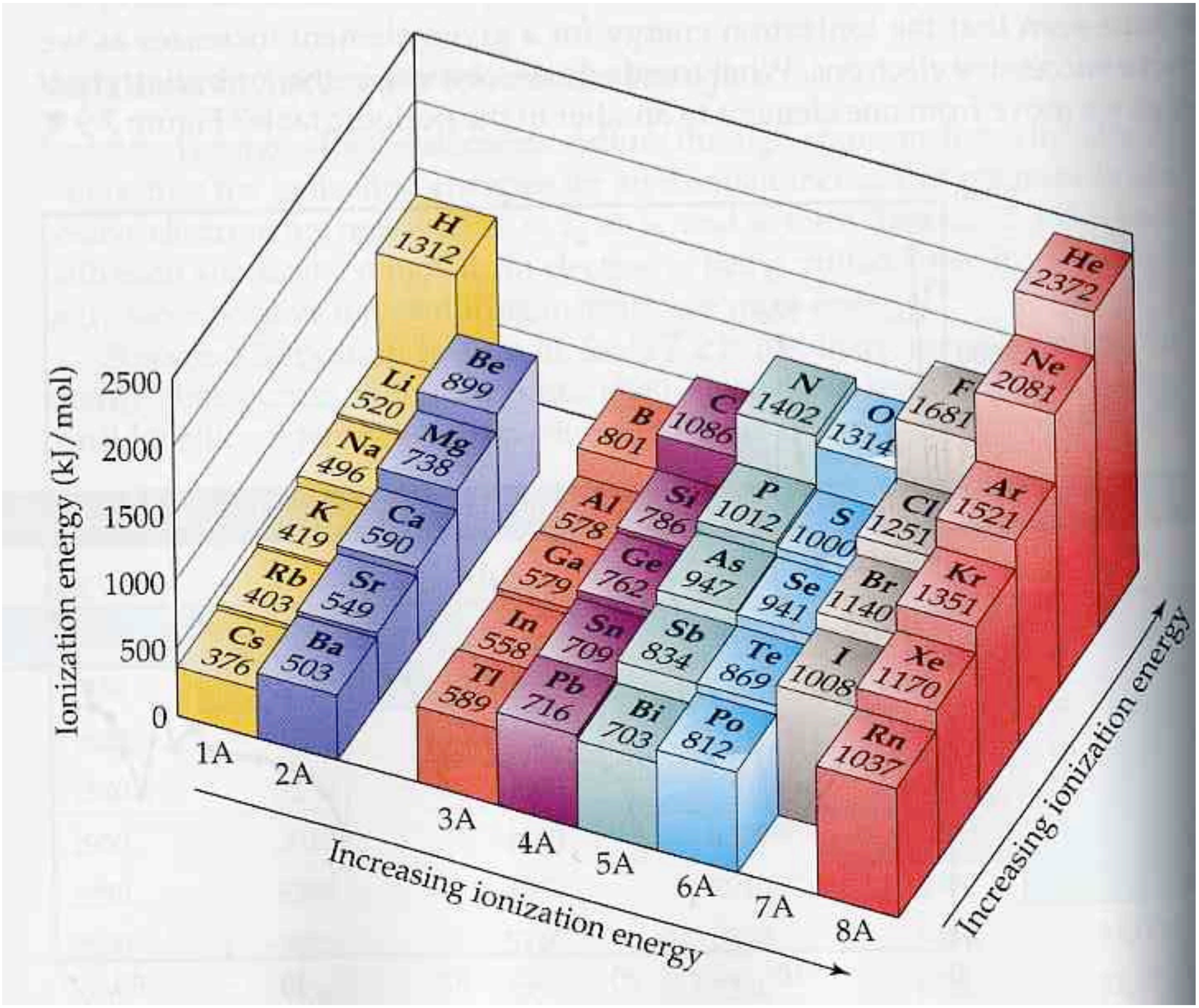
Ionization energies in tabular form

Z	Element	1st	2nd	3rd	4th	5th	6th	7th	8th
1	H	13.6	(13.6×2^2)						
2	He	24.6	54.4	(13.6×3^2)					
3	Li	5.4	75.6	122	(13.6×4^2)				
4	Be	9.3	18.2	154	218	(13.6×5^2)			
5	B	8.3	25.1	38	259	340	(13.6×6^2)		
6	C	11.3	24.4	48	64	392	490	(13.6×7^2)	
7	N	14.5	29.6	47	77	98	552	667	(13.6×8^2)
8	O	13.6	35.1	55	77	114	138	739	871
9	F	17.4	35.0	63	87	114	157	185	954
10	Ne	21.6	41.1	64	97	126	158	207	238
11	Na	5.1	47.3	72	99	138	172	208	264
12	Mg	7.6	15.0	80	109	141	186	225	266
13	Al	6.0	18.8	28	120	154	190	241	285
14	Si	8.1	16.3	33	45	167	205	246	303
15	P	10.5	19.7	30	51	65	220	263	309
16	S	10.4	23.4	35	47	72	88	281	329
17	Cl	13.0	23.8	40	54	68	97	114	348
18	Ar	15.8	27.6	41	60	75	91	124	143

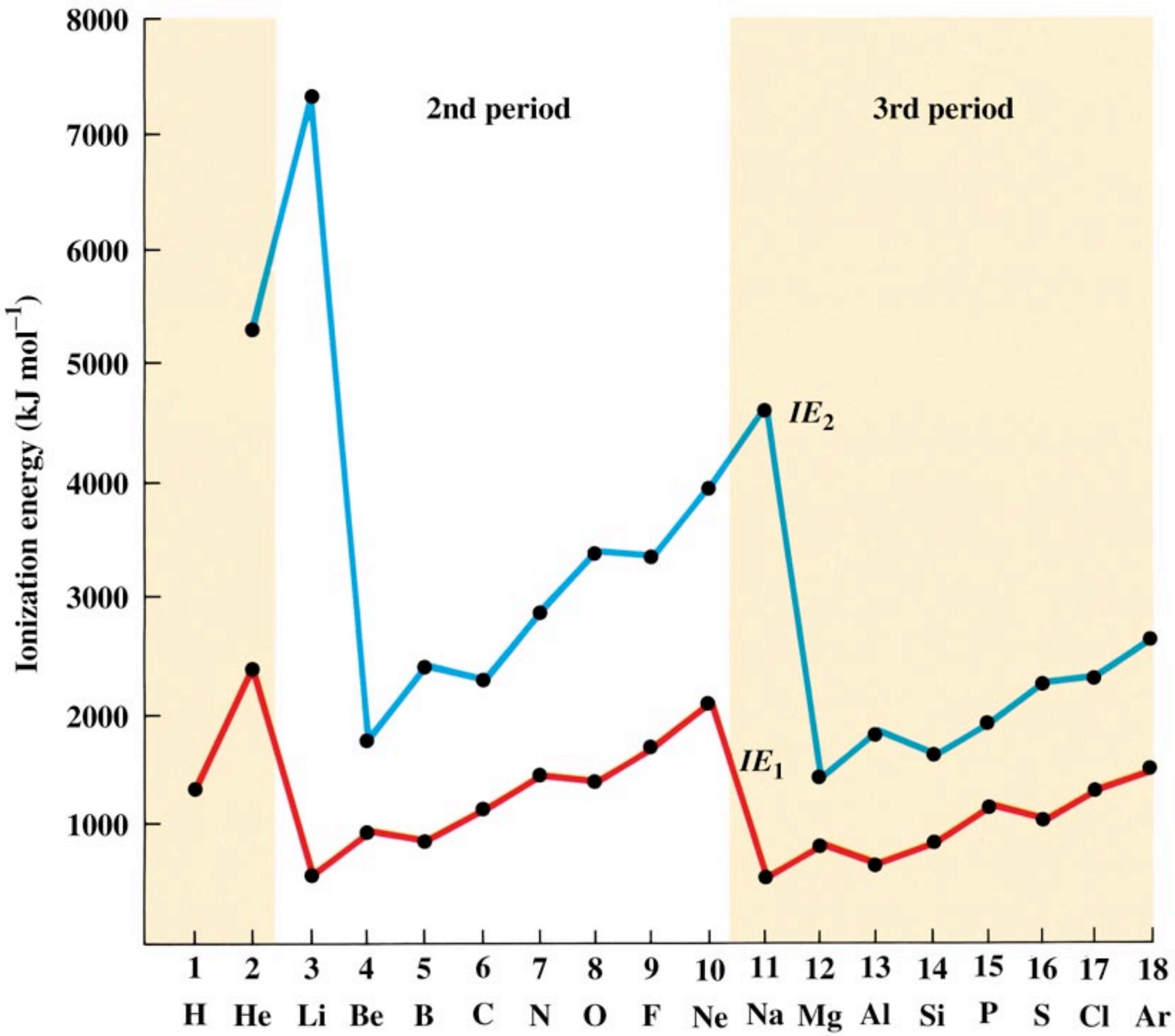
Ionization energies as a function of atomic number



Ionization energies of the main group elements in topographical relief form

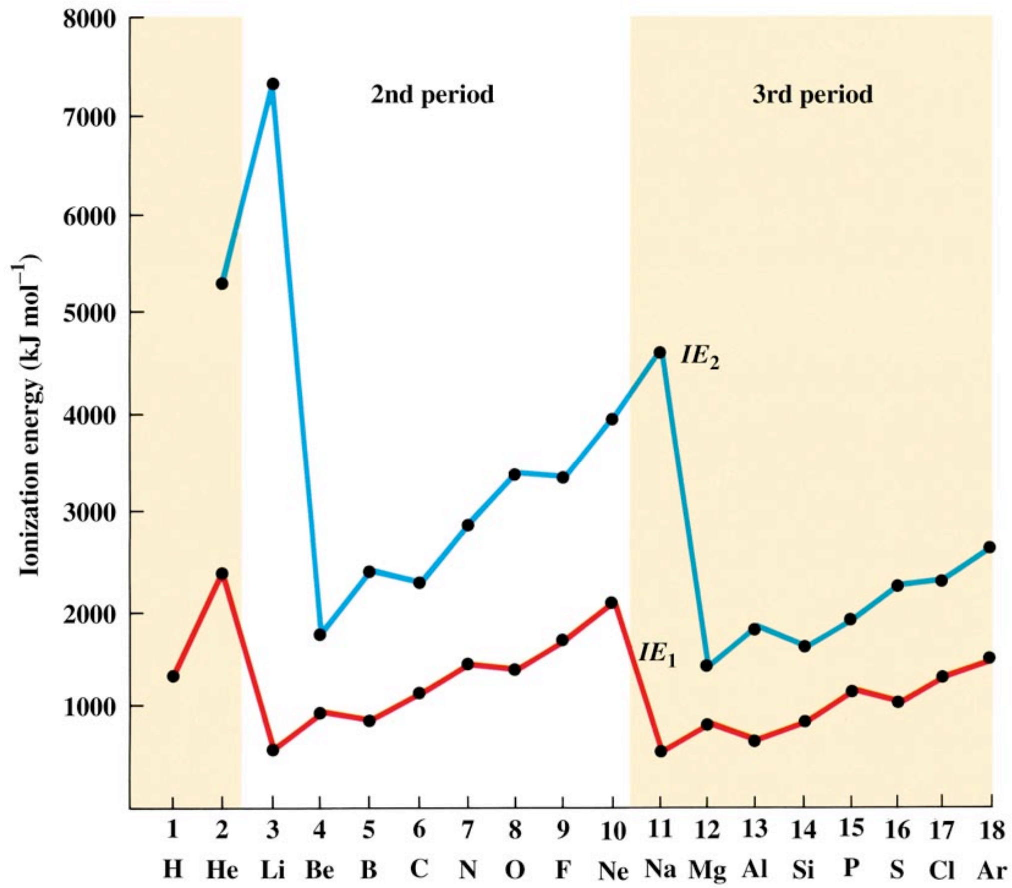


Ionization energies in graphical form



Using electron configurations to explain Ionization Energies

Removal of an electron from a neutral atom: IE_1



Z_{eff} increases →

$E_n = -(Z_{eff}^2/n^2)$

$E_n = -(Z_{eff}^2)$ if n is fixed

(across a row)

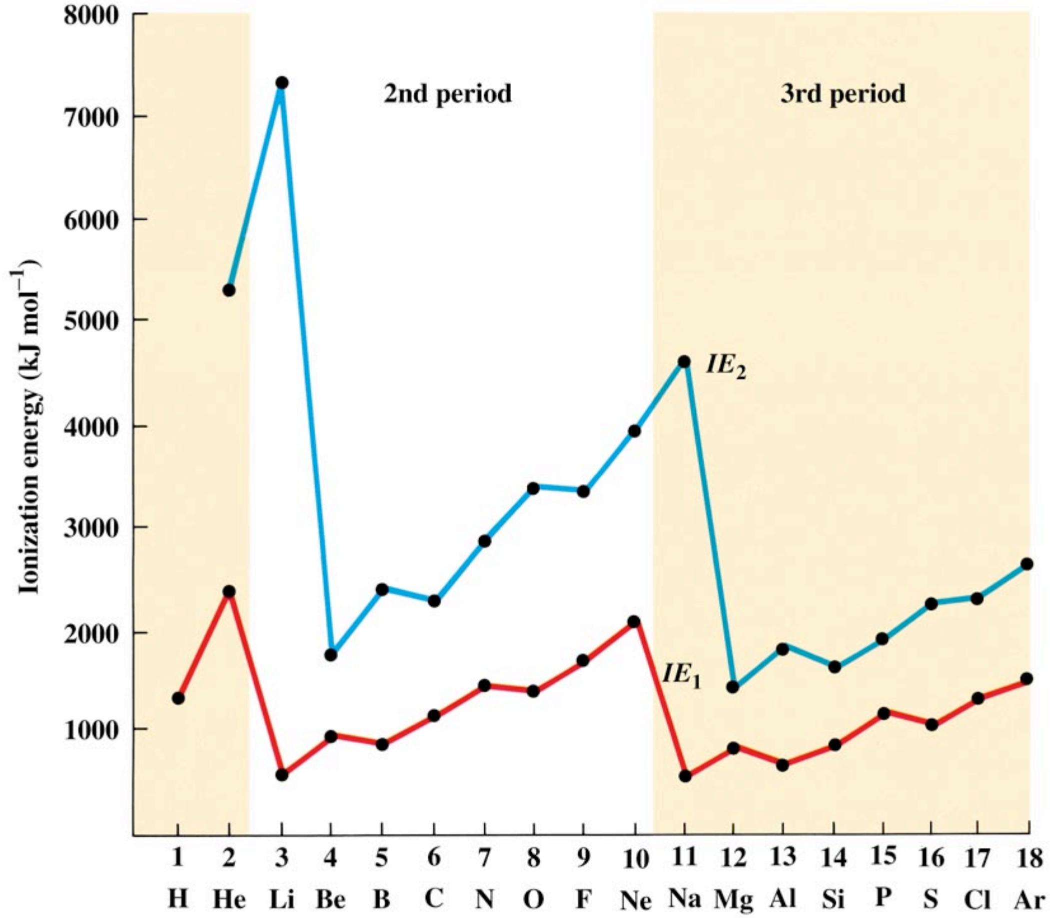
$E_n = -(n^2)$ if Z_{eff} is fixed

(down a row)

IE_1

^{3}Li	[Ne]2s (↑)
^{4}Be	[Ne] $2s^2$ (↑↓)
^{5}B	[Ne] $2s^22p^1$ (↑)
^{6}C	[Ne] $2s^22p^2$ (↑↑)
^{7}N	[Ne] $2s^22p^3$ (↑↑↑)
^{8}O	[Ne] $2s^22p^4$ (↑↓↑↑)
^{9}F	[Ne] $2s^22p^5$ (↑↓↑↓↑)
^{10}Ne	[Ne] $2s^22p^6$ (↑↓↑↓↑↓)

Using electron configurations to explain Ionization Energies
Removal of the second electron from the cation: IE_2



IE_2 (removal from E^+)

^{3}Li	[Ne]
^{4}Be	[Ne] $2s^2$ (↑)
^{5}B	[Ne] $2s^22p^1$
^{6}C	[Ne] $2s^22p^2$ (↑)
^{7}N	[Ne] $2s^22p^3$ (↑↑)
^{8}O	[Ne] $2s^22p^4$ (↑↑↑)
^{9}F	[Ne] $2s^22p^5$ (↑↓↑↑)
^{10}Ne	[Ne] $2s^22p^6$ (↑↓↑↓↑)

The electron affinity (EA) of an atom is the energy change which occurs when an atom gains an electron.

$$X(g) \ + \ e^- \longrightarrow Xe^- \ (g)$$

Electron affinities of the representative elements:
What are the correlations across and down?

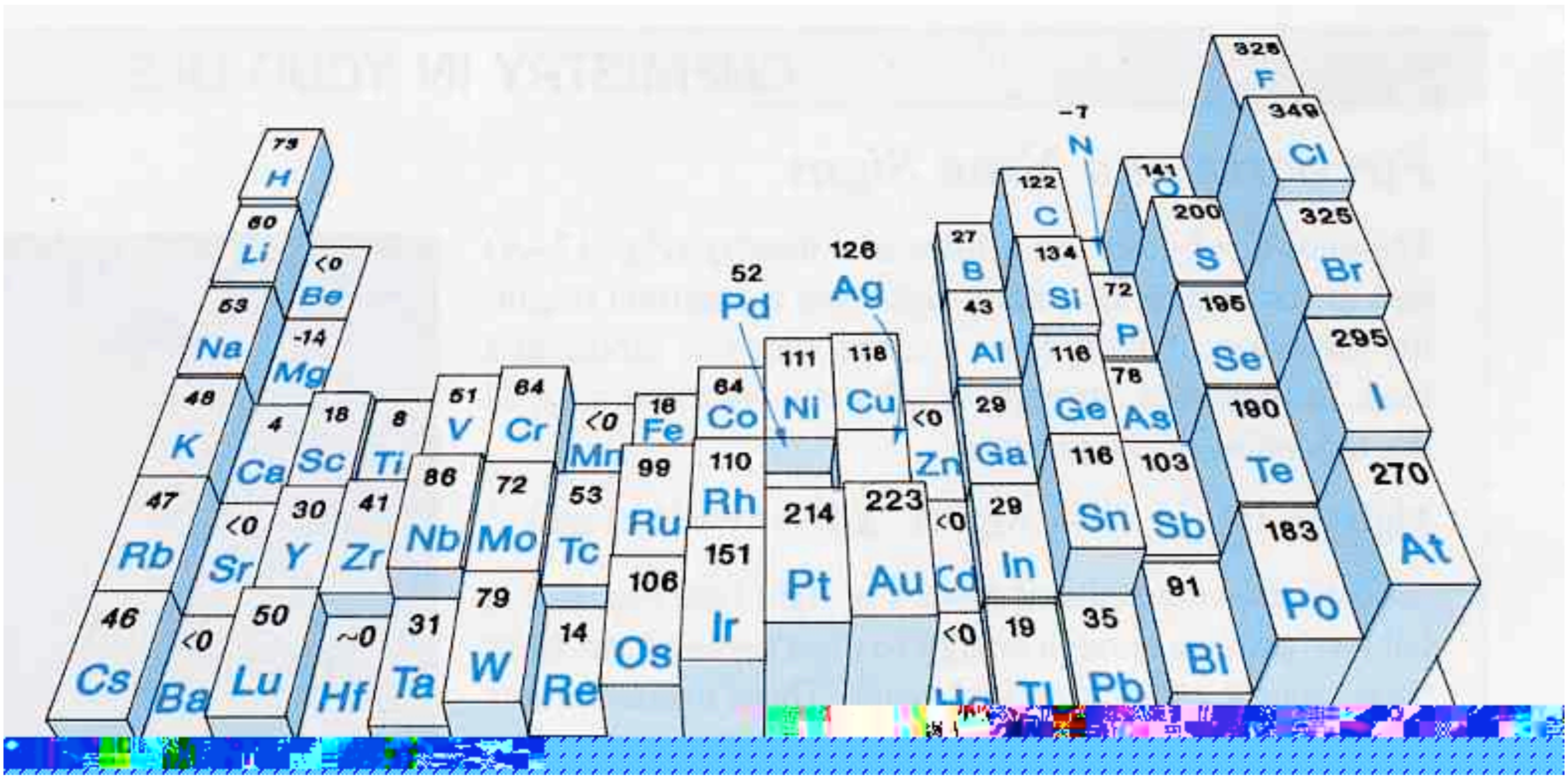
Group

	H +73							18/VIII
								He <0
Period	1	2	13/III	14/IV	15/V	16/VI	17/VII	
2	Li +60	Be ≤0	B +27	C +122	N −7	O +141 −844	F +328	Ne <0
3	Na +53	Mg ≤0	Al +43	Si +134	P +72	S +200 −532	Cl +349	Ar <0
4	K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0
5	Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0
6	Cs +46	Ba +14	Tl +19	Pb +35	Bi +91	Po +174	At +270	Rn <0

Electron affinity ($kJ \cdot mol^{-1}$)

- >300
- 200–300
- 100–200
- 0–100
- <0

Electron affinities of the elements



17.3 Sizes of Atoms and Ions

The radii of atoms and ions

Covalent radius, atomic radius and ionic radius

Periodic trends in the radius of atoms and ions

Radii generally increase down a group (n of outer shell increases) and decrease (Z_{eff} decreases for same shell) from left to right across a period. Cations are generally smaller than their parent atoms and anions are larger.

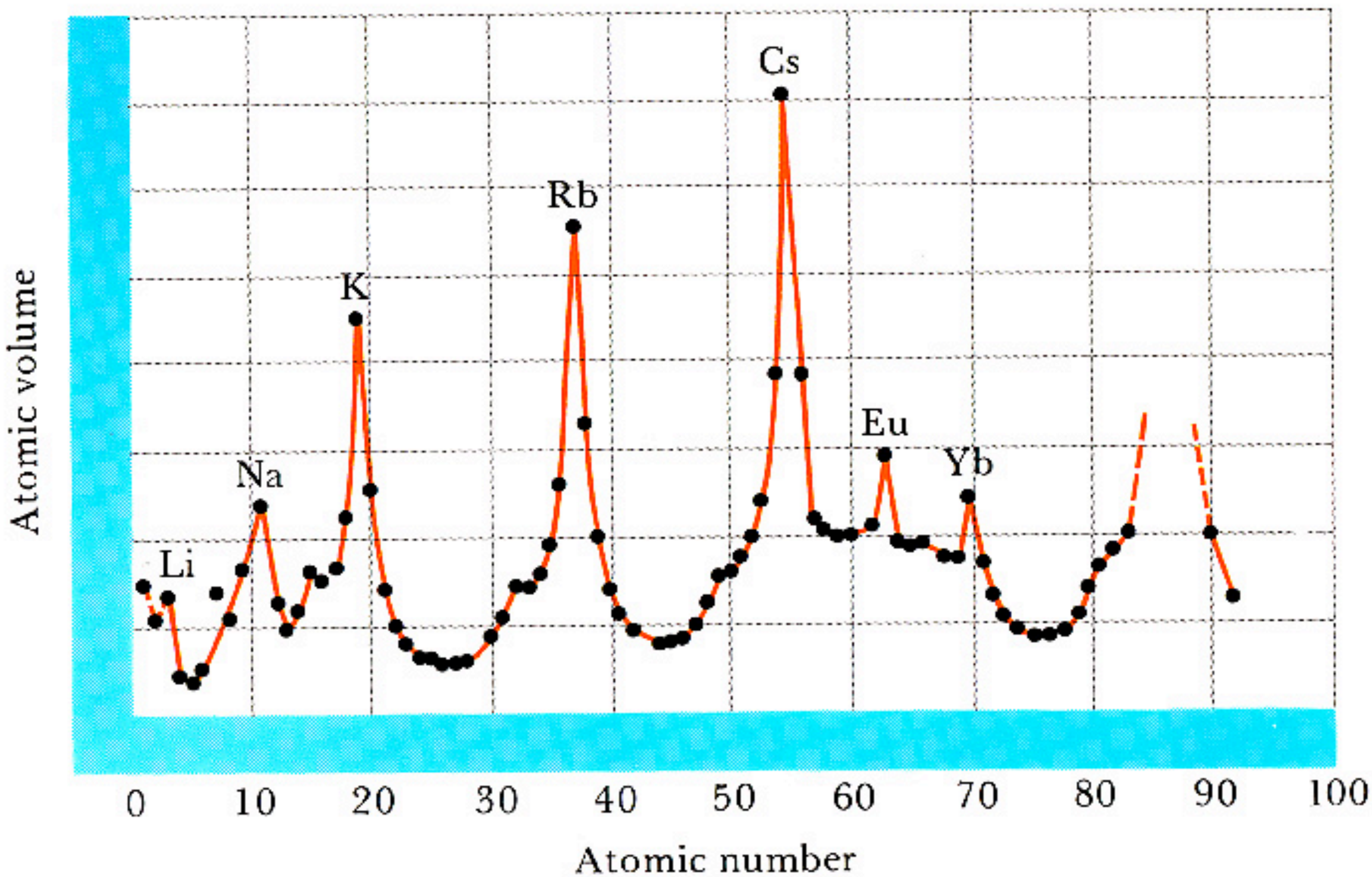
From the Bohr atom to all atoms: a model for the size of atoms.

$r = a_0(n^2/Z)$ so that for the same value of n for a multielectron atom
$r \propto a_0(1/Z_{eff})$

When electrons are added to the same shell (same value of n) they are about the same distance from the nucleus as the other electrons in the shell. The electrons in a shell with the same n are spread out and do not shield each other from the positive charge of the nucleus very well. Thus, the effective nuclear charge, Z_{eff}, increases as Z increases across the periodic table. The increasing value of Z_{eff} draws the electrons in closer to the nucleus, and the atom becomes more compact.

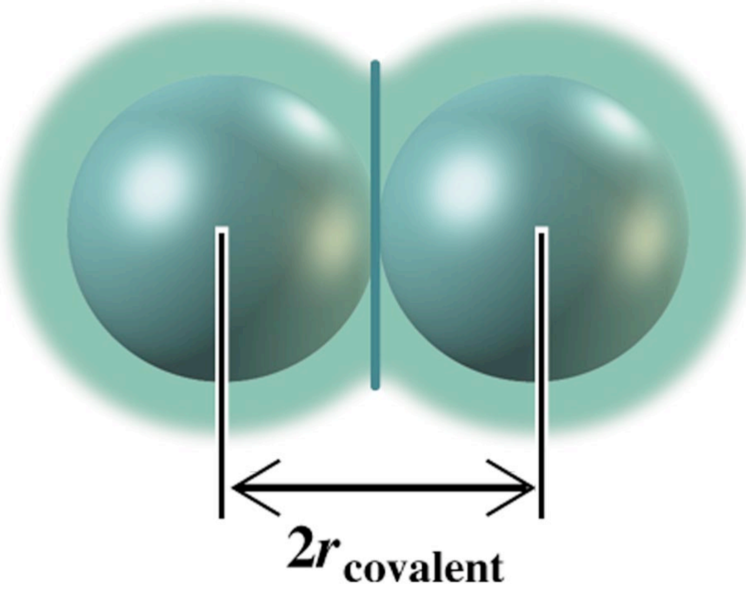
Conclusion: The atomic radius of an atom decreases as one goes across a period for atoms of the same value of n.

Atomic Volumes



Covalent Radii from Experiment

- The covalent radius is defined as half the distance between two atoms bound by a single bond in a molecule.

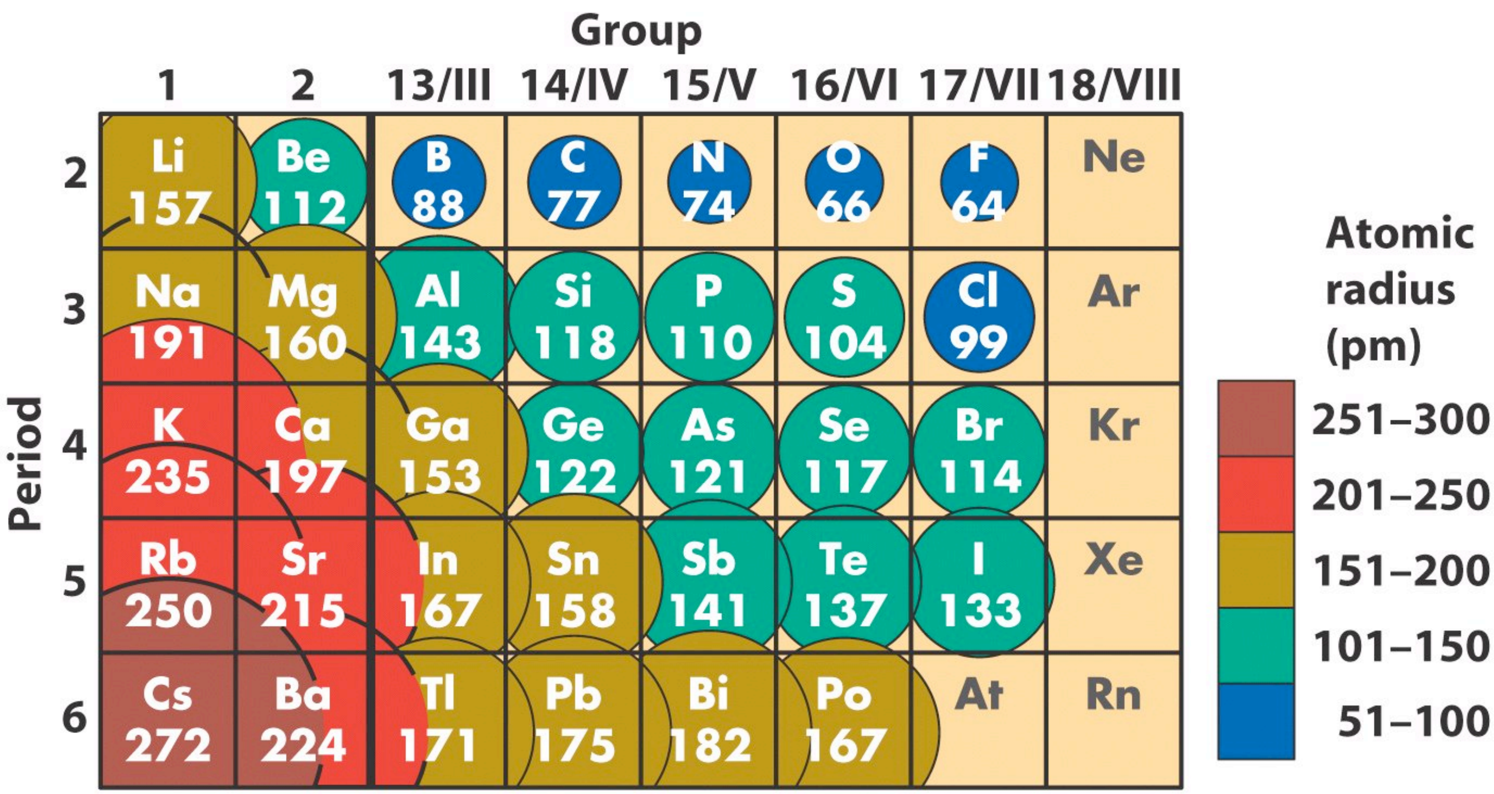


Atomic radius: $r = (n^2/Z_{eff})a_0$

$r = kn^2$ (r increases)if Z_{eff} is fixed (going down a column)

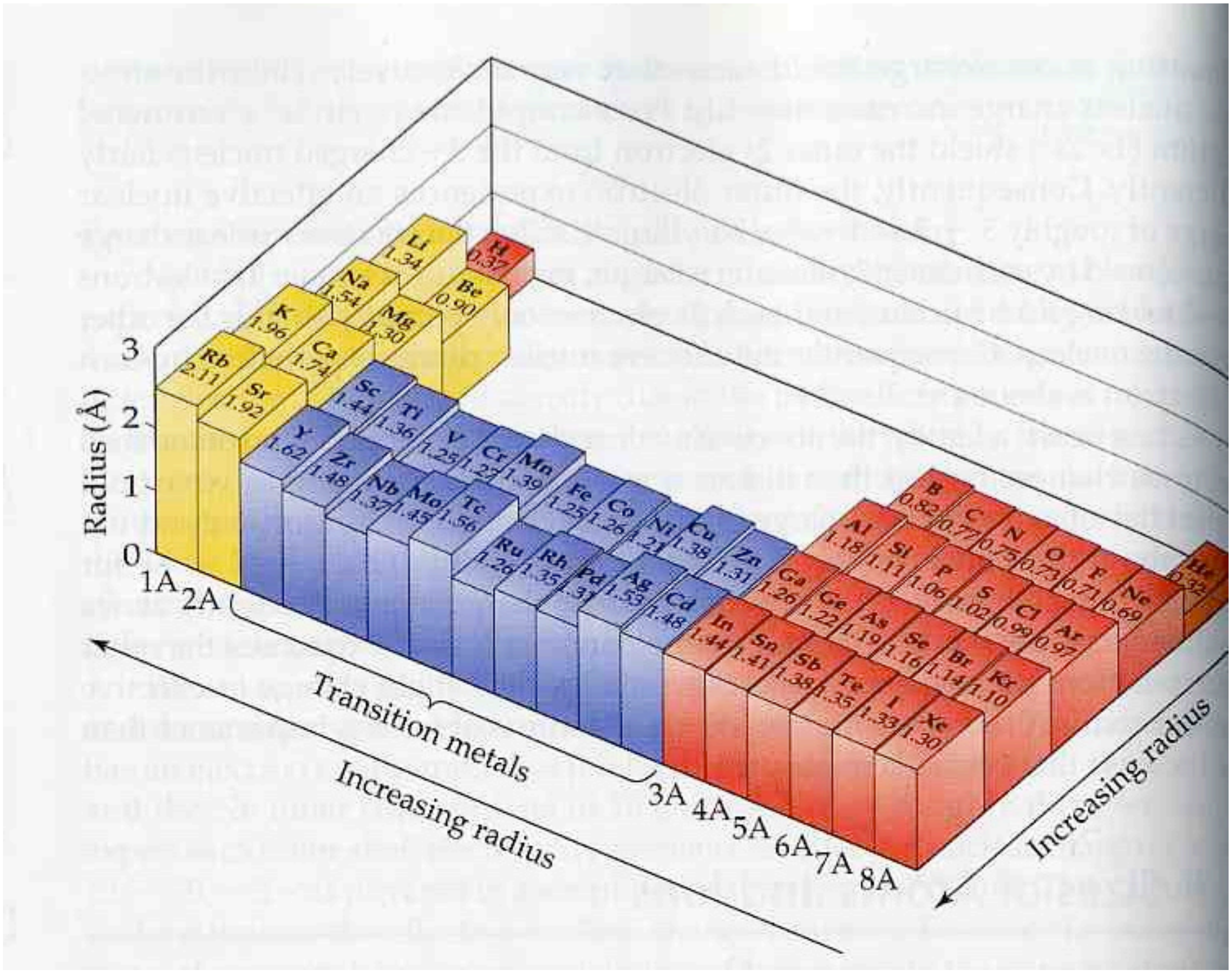
$r = k'/Z_{eff}$ (r decreases) if n is fixed (going across a row)

Periodic properties of atomic radius: What are the correlations?

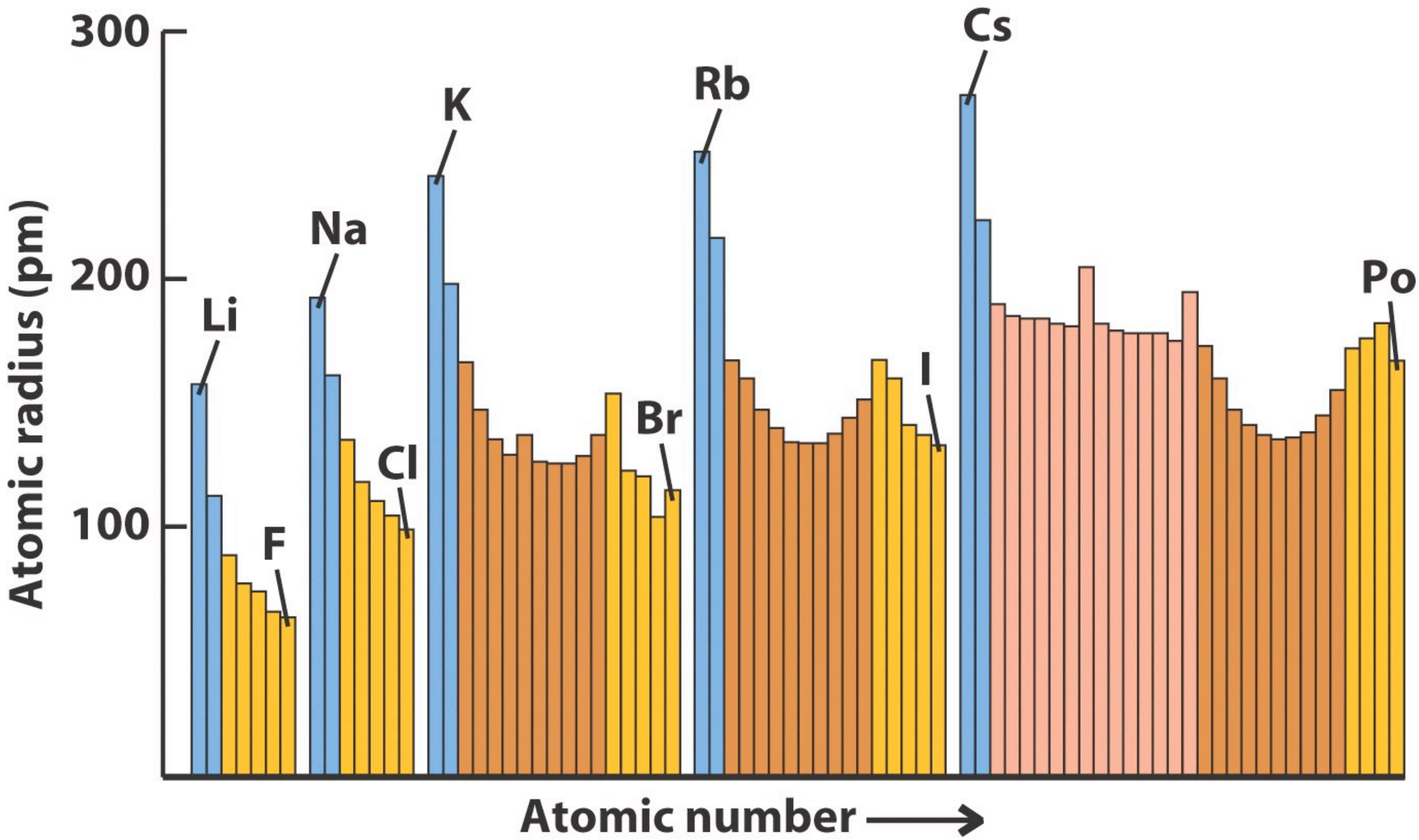


General Rule: The size of an atom decreases in a row as the nuclear charge increases and the size of an atom increases in a column as the nuclear charge increases

Radii of the elements



The radii of atoms as a function of atomic number



17.4 Properties of the Chemical Bond

Bond length: The distance between the nuclei of two bonded atoms.

Bond enthalpy: The energy required to break a bond between two atoms.

Bond order: The number of shared electron pairs (not electrons) in a covalent bond.

Bond Lengths
H_2 = 0.74Å

- F_2 1.42
- Cl_2 1.99
- Br_2 2.28
- I_2 2.67
- ClF 1.09
- BrCl 2.14
- BrF 1.76
- ICl 2.32

- HF 0.92
- HCl 1.27
- HBr 1.41
- HI 1.61
- N_2 1.09
- O_2 1.21
- NO 1.15
- CO 1.13

The Nature of the Chemical Bond

- Pose the question:“Why do atoms sometimes form stable molecules and compounds…. and sometimes not?”

- Or perhaps reducing the general question to more limited questions for which there is a higher probability of getting answers:
  - “What is the energy in bonds?”
  - “What is the distance between atoms?”
  - “What is the shape and geometry that results?”

Bond Energies
H_2 = 400 kJ/mol

Li_2	105
Na_2	71
K_2	50
Rb_2	46
Cs_2	44

F_2	154
Cl_2	247
Br_2	192
I_2	151
N_2	946
O_2	498

Bond Energy (Enthalpy): the energy required to break a bond between 2 atoms

Bond	kJ/mol	Bond	kJ/mol	Bond	kJ/mol
H—H	431	Sn—Sn	163	N—Cl	201
C—C	345	Sb—Sb	121	O—Cl	218
C=C	610	C—H	416	Si—Cl	381
C≡C	835	N—H	391	P—Cl	326
N—N	163	O—H	464	S—Cl	339
N≡N	945	F—H	565	As—Cl	293
O—O	146	Si—H	318	Se—Cl	243
O=O	494	P—H	322	Sn—Cl	318
F—F	155	S—H	347	Sb—Cl	310
Cl—Cl	242	Cl—H	431	C—N	305
Br—Br	193	As—H	247	C≡N	890
I—I	151	Se—H	276	C—O	358
Si—Si	222	Br—H	366	C=O	745
P—P	201	Te—H	239	C—S	272
S—S	226	I—H	299	C=S	536
Se—Se	209	C—Cl	339	S=O	498

17.5 Ionic and Covalent Bonds

Ionic bonds: Electron density is mainly transferred from one atom to another atom to create a bond between two atoms.

Covalent bonds: Electron density is shared by two bonded atoms.

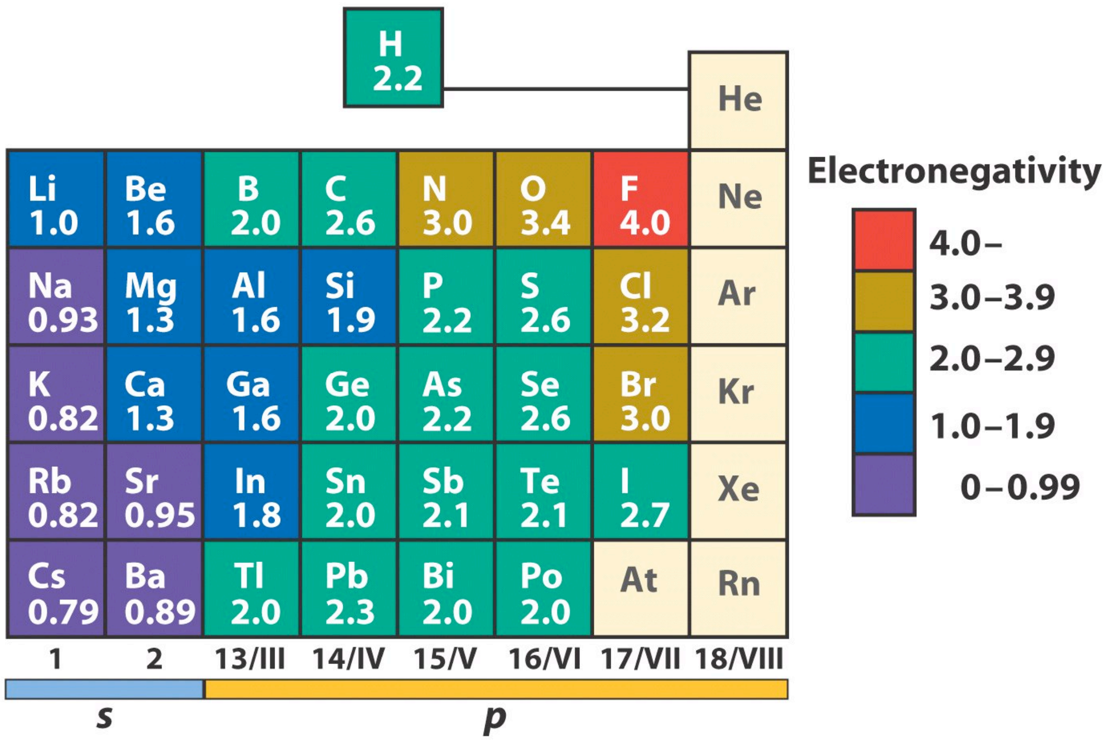
Electronegativity: A measure of the ability of an atom in a bond to attract electrons from other atoms.

Percent covalent (ionic) character: A measure of the polarity of a bond between two atoms.

% Ionic character from dipole moments: Compare the measured dipole moment to the dipole moment for complete transfer of one electron (=1).

TABLE 17–4	Ionic Character of Diatomic Molecules		
Molecule	**Percent Ionic Character (100 δ)**	**Molecule**	**Percent Ionic Character (100 δ)**
H_2	0	CsF	70
CO	2	LiCl	73
NO	3	LiH	76
HI	6	KBr	78
ClF	11	NaCl	79
HBr	12	KCl	82
HCl	18	KF	82
HF	41	LiF	84
		NaF	88

Electronegativity: a measure of the power of an atom to attract electrons to itself in a bond. Most electronegative atoms: F > O > Cl >N ~ Br > I



$E_n = -(Z^2/n^2)$

Across row Z increases for similar n (valence electrons see more + as Z increases)

Down column Z_{eff} is similar for increasing n and r (valence electrons further away with same Z_{eff})

% Ionic character as a function of electronegativity difference: % IC = $(EN_L - EN_{S)})/ EN_L x100\%$