Chapter 7

Periodic Properties of the Elements

I) Development of the P.T.

Generally, the electronic structure of atoms correlates w. the prop. of the elements

- reflected by the arrangement of the elements in the P.T.

A number of elements were discovered based on expected prop. of the "missing" elements.

A) Noble Gases

ns^2np^6 - very stable

B) Representative Elements

"last" e^- added to s & p orbitals

distinct & fairly regular variations in prop. w. changes in atomic #

C) d-Transition Elements

e^- added to d orbitals

$ns^2(n-1)d^x$

II) Effective Nuclear Charge

Net (+) charge attracting an e^-

$$Z_{eff} = Z - S$$

S = screening constant

- avg. number of e^-'s between nucleus & any particular e^-

- depends on specific orbitals

Subsets of e^-:

1) core e^-

2) valence e^-

Inner e^- screen or shield outer e^- from full (+) charge

Primary interaction of e^- & nucleus is due to charge:

Coulomb's Law:

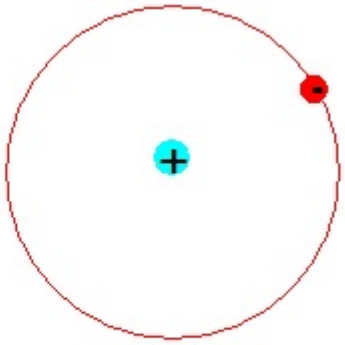
$$F = \frac{k\,(Q_e Q_n)}{r^2}$$

However, valence shell e^- do not experience full nuclear charge

- partially shielded by the core e^-

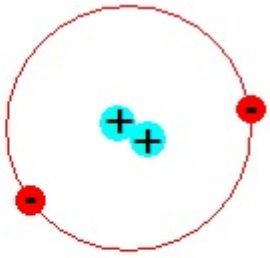
Compare H, He, Li:

H: 1 e^- in 1s orbital & 1 proton



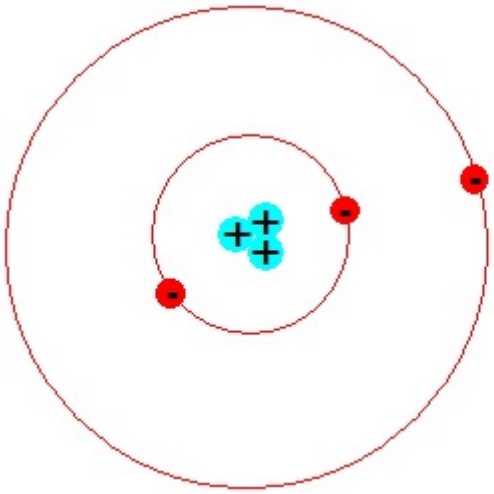
$1s^1$

He: 2 e^- in 1s orbital which dec. in size due to stronger e^- - nuc attraction, each e^- is attracted to 2 protons



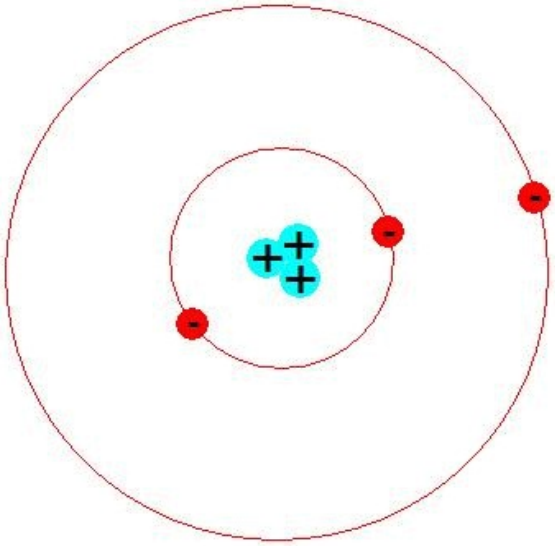
$1s^2$

Li: 1s is smaller than He but 2s is bigger than H or He 1s



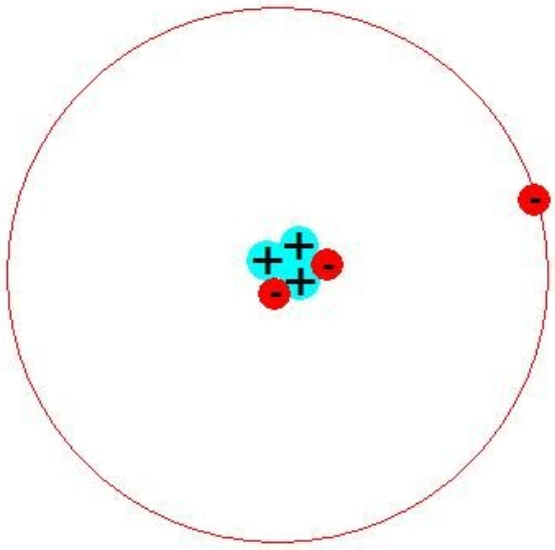
$1s^22s^1$

The effect for Li is the 2 core e^- "cancel" the chg of 2 protons in the nucleus.



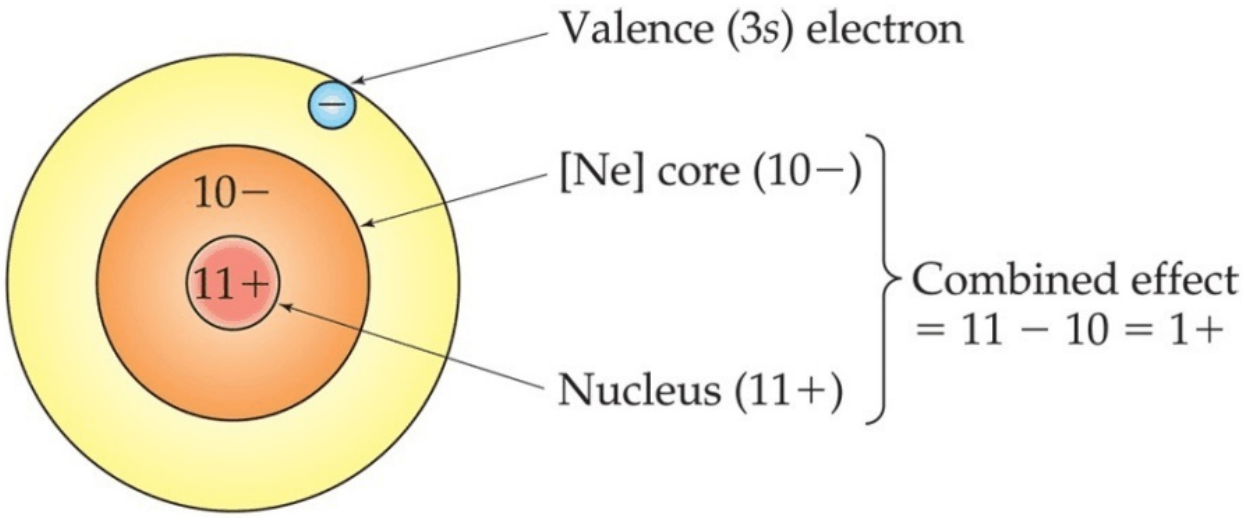
$1s^2 2s^1$

The "effective nuclear chg" the 2s e^- interacts with is only +1

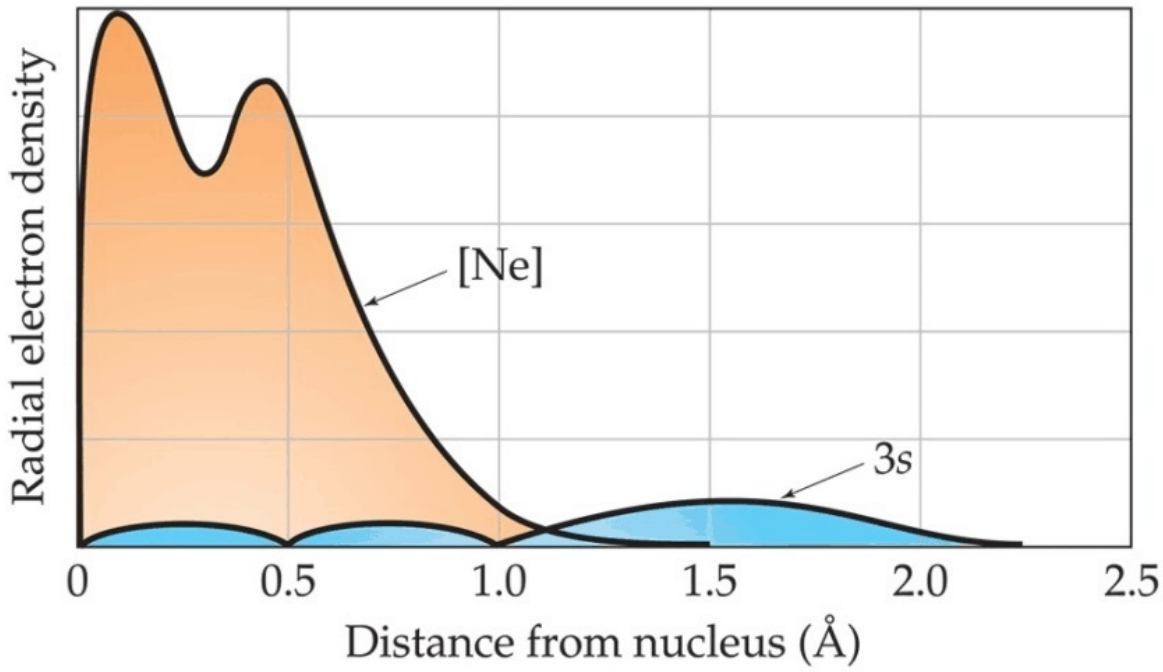


$1s^2 2s^1$

Core e^- shield the valence e^-
- dec. the nuclear chg.



(a)

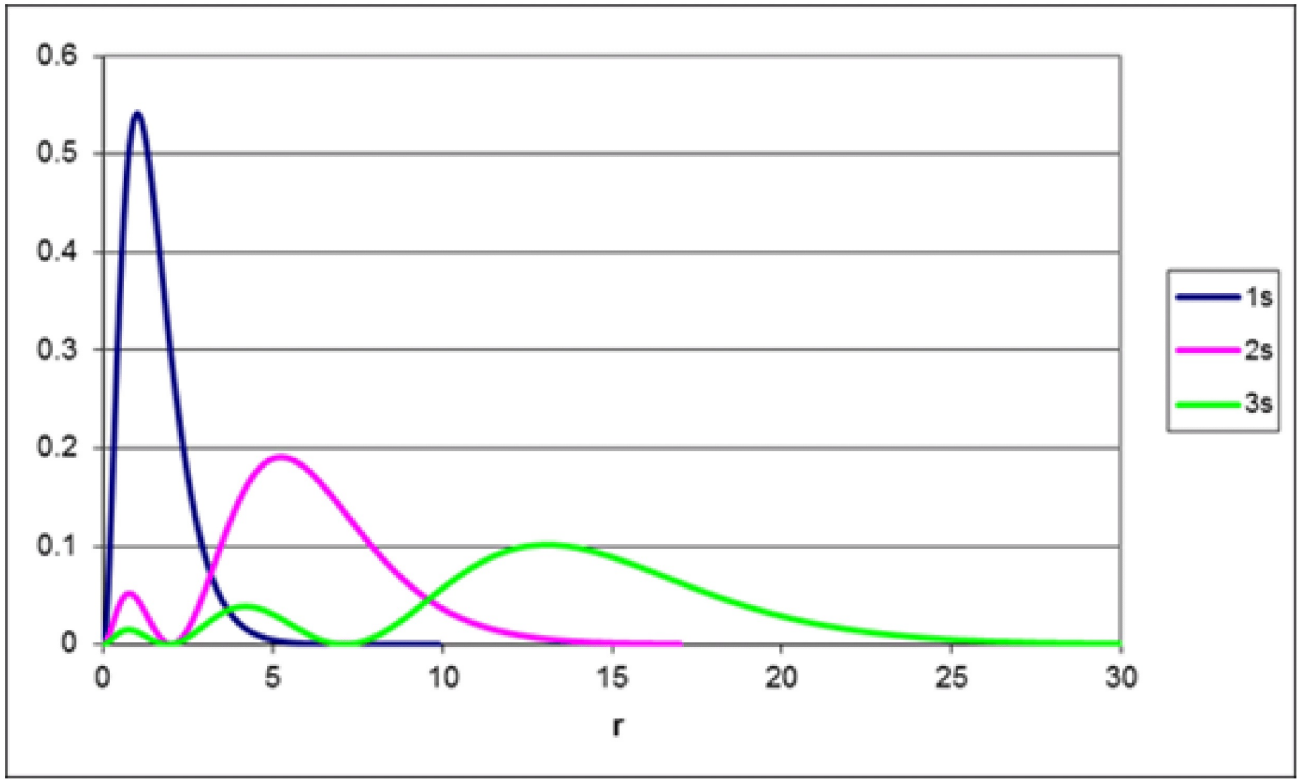


(b)

Assumes core e^- shield valence e^- completely. However, not true.

valence e^- can penetrate closer to the nucleus than core e^- for some types of orbitals

For Li the 2s orbital has a small area closer to the nucleus than the 1s orbital. Allows 2s e^- to be closer to nucleus than 1s e^- for small portion of time. When this happens the 1s e^- are not shielding 2s e^-



Value of S is usually close to # core e^-

$$Z_{eff} = Z - S$$

$$\#\text{protons} - \text{core } e^-$$

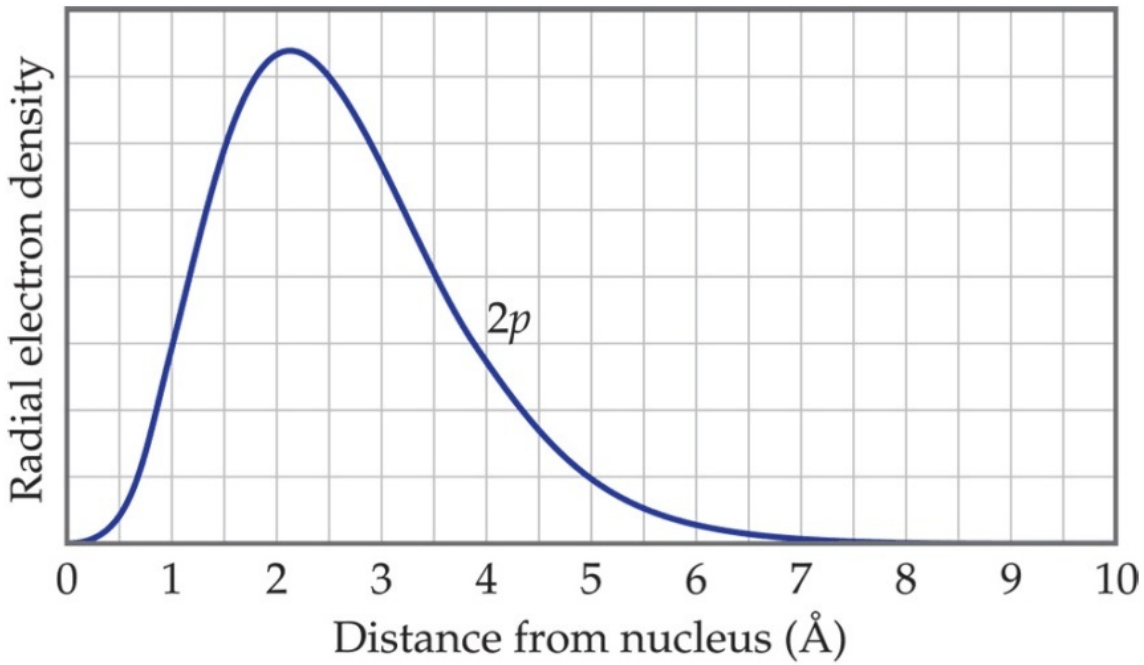
Valence shell e^- do not screen each other effectively.

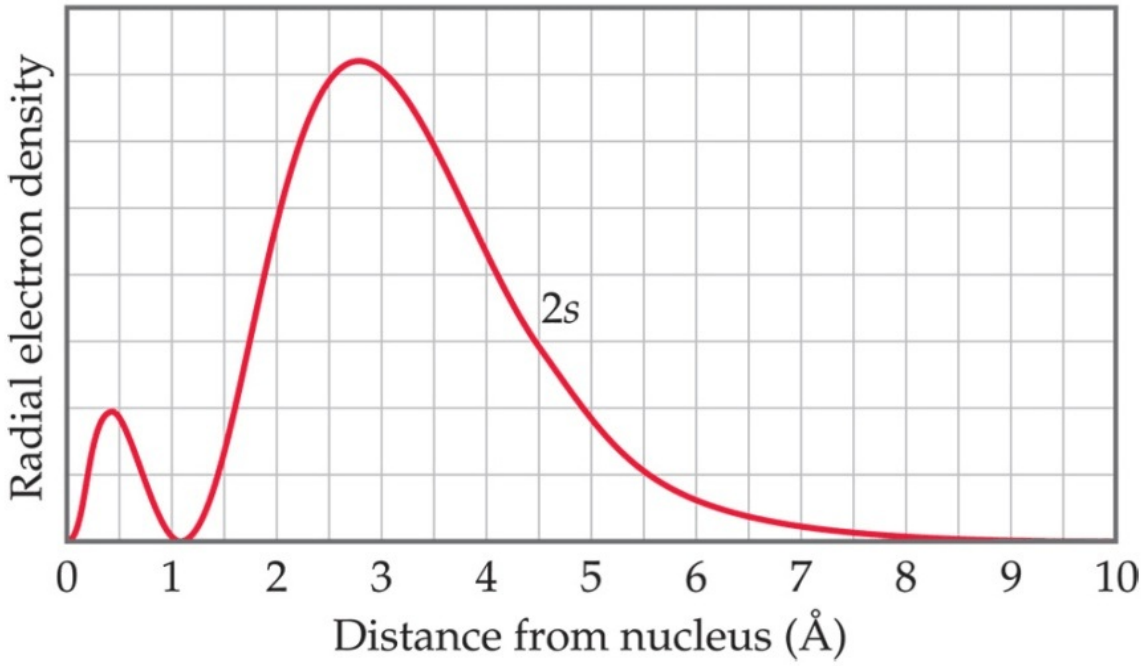
- same distance from nucleus

The "p" e^- do not screen "s" e^-

The "s" e^- do screen "p" e^- somewhat due to a probability for these e^- to be nearer the nucleus

- penetration





A) General Trends

1) Across Row

Z_{eff} inc. by ~1 as each atom has added 1 proton to nucleus and 1 e^- to valence shell (which does not screen)

Z_{eff} inc.

2) Down Column

Z_{eff} inc. slightly as valence shell e^- can penetrate better

Li	Be	B	C	N	O	F	Ne
1.3	2	3	4	5	6	7	8
Na							
2.5							
K							
3.3							

III) Atomic and Ionic Radii

A) Atomic Radii

1) Nonbonding

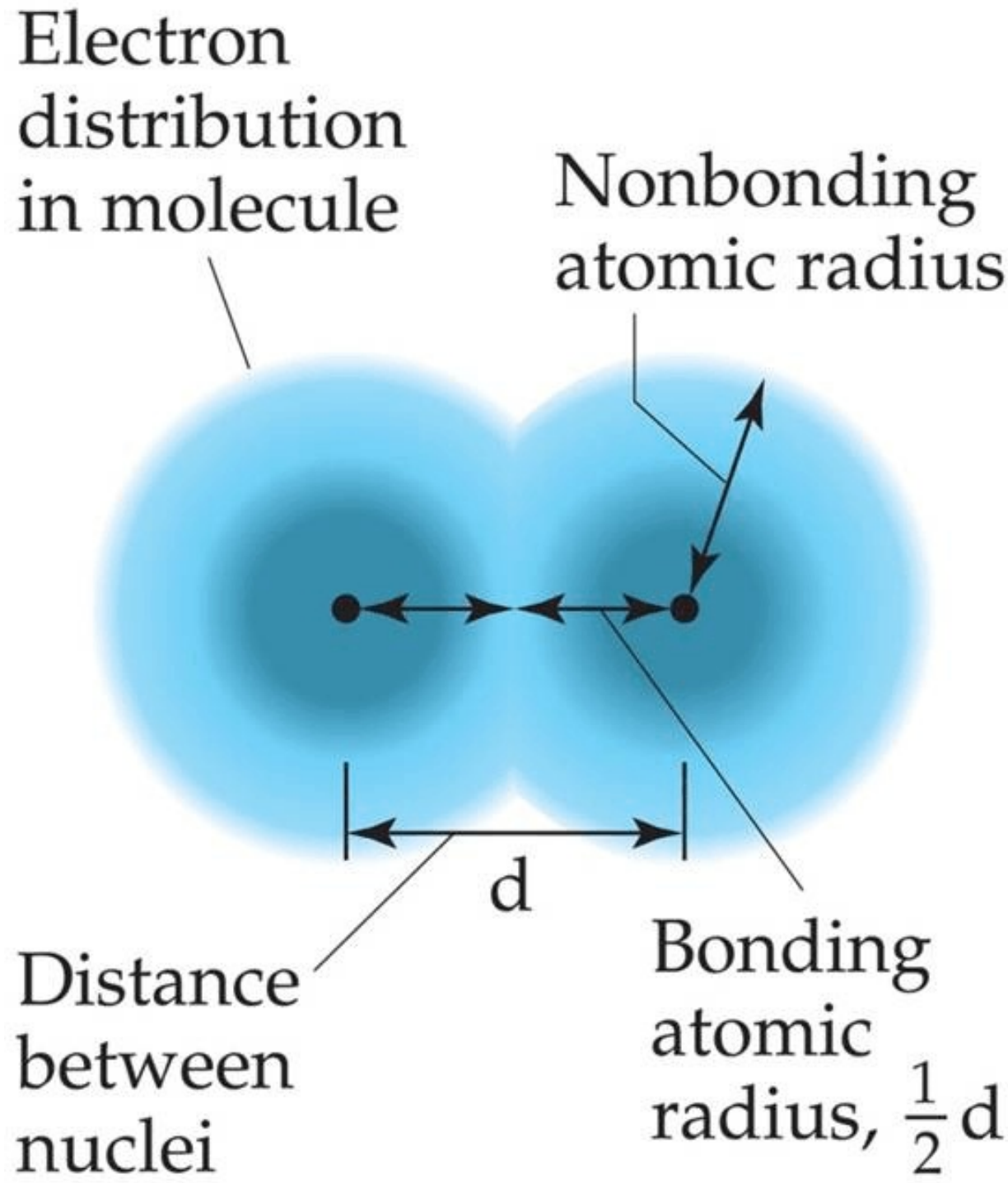
Closest approach of atoms based on gas phase collisions or crystal structures

2) Bonding Atomic Radius

Bond Length:

Distance between atoms in a covalently bound cmpd., averaged over many cmpds.

b.a.r = ½ bond length



3) Size inc. down a group

e^- occupy a higher energy level w. each element down a group & n determines size of orbital and avg. radius

∴ Inc. n ⇛ Inc. atomic size

4) Size generally dec. across a period from left to right

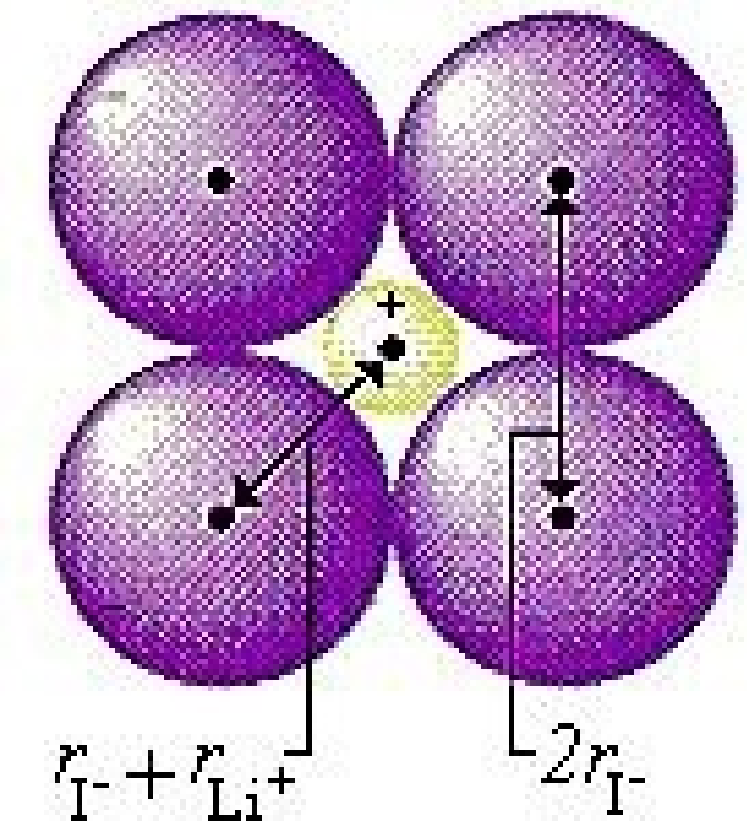
- e^- added to same shell
- nuclear charge, Z_{eff}, inc. which pulls whole shell closer

5) Overall Trend

B) Ionic Radii

Determined from crystal structure of ionic cmpds.

Averaged interatomic distance from multiple cmpds.



1) Cations

always smaller than parent atom

Cs^+ smaller than Cs

a) Size decreases with increasing ionic charge

$Fe^{3+} < Fe^{2+}$; $Cu^{2+} < Cu^+$

2) Anions

always larger than parent atom

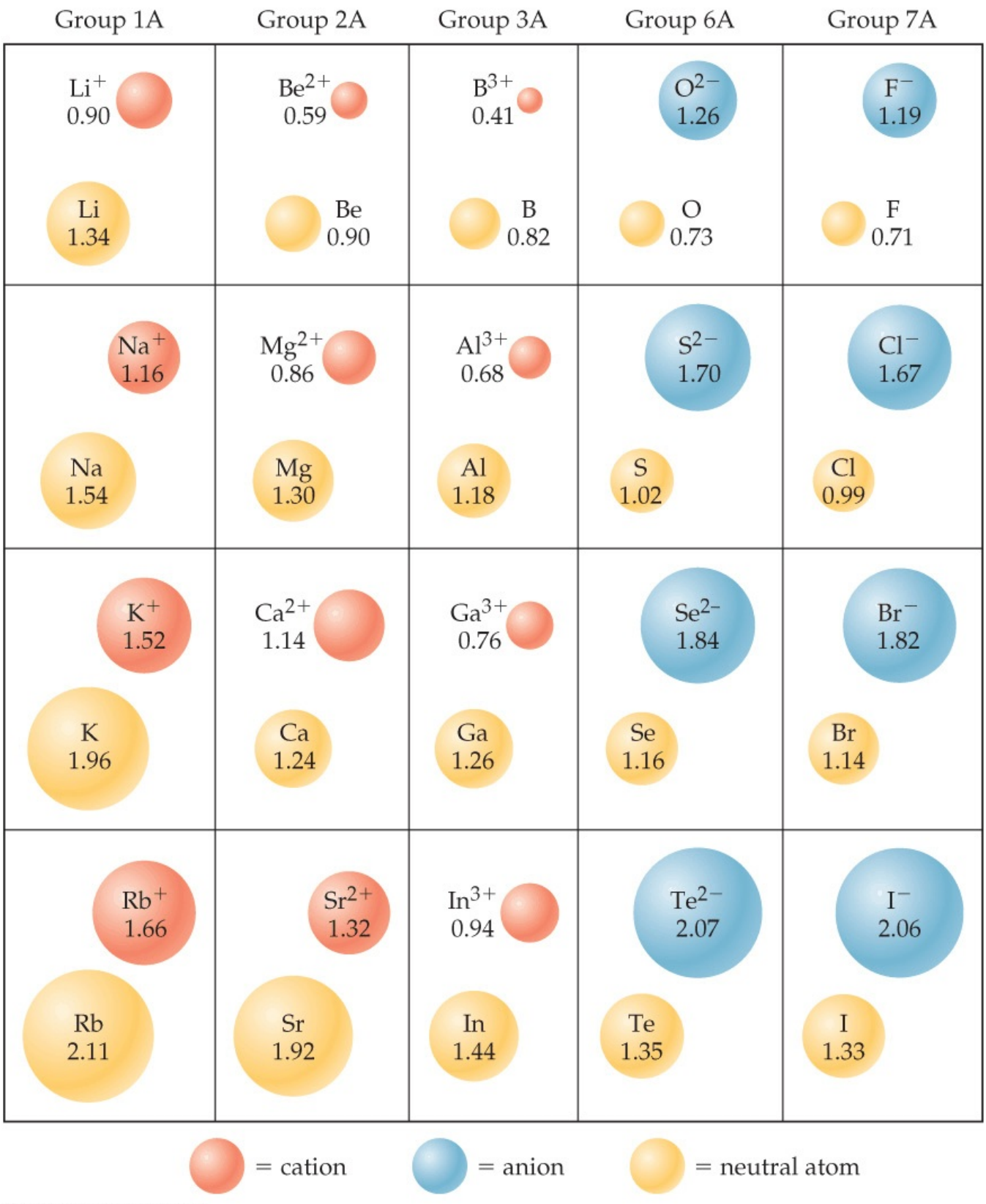
$Br^- > Br$ $S^{2-} > S$

3) Isoelectronic Series

Same # e^-

$_{16}S^{2-} > {}_{17}Cl^- > {}_{19}K^+ > {}_{20}Ca^{2+}$

Z_{eff} inc., radius dec.



IV) Ionization Energy , I.E.

Ionization: removal of an e^-

I.E. : energy required to remove e^- from gaseous atom or ion

$Na \rightarrow Na^+ + e^-$ 5.1 eV

$Cs \rightarrow Cs^+ + e^-$ 3.9 eV

e^- removed is from highest energy level (highest n & ℓ)

I.E. depends on avg. distance from the nucleus.

First I.E, I_1

Energy req. to remove the highest energy e^- from neutral atom

$Mg\,(g) \rightarrow Mg^+\,(g)$ $\quad I_1 = 738$ kJ/mol

Second I.E $\quad I_2$

Energy req. to remove the next highest energy e^- from ion

$Mg^+\,(g) \rightarrow Mg^{2+}\,(g)$ $\quad I_2 = 1450$ kJ/mol

Successive I.E. inc. in magnitude

- # e^- dec. (less repulsion)
- Z (# p^+) same (greater attraction)

	I_1	I_2	I_3	I_4	I_5
Na	496 [Ne]	4560		inner-shell e^-	
Mg	738 $3s^1$	1450 [Ne]	7730		
Al	577 $3s^2$	1816 $3s^1$	2744 [Ne]	11,600	
Si	786 $3s^2 3p^1$	1577 $3s^2$	3228 $3s^1$	4354 [Ne]	16,100
P	1060 $3s^2 3p^2$	1890	2905	4950	6270
S	999 $3s^2 3p^3$	2260	3375	4565	6950

I.E. for removing e^- beyond valence e^- greater than energy involved in chem. rxns & bonding

- only e^- outside noble-gas core involved in chem. change

Remember:

Atoms tend to lose or gain e^- to get filled outer shell

- e^- config. of a noble gas

Note

I.E. depends on avg. distance from nucleus & Z_{eff}

I.E. $\propto Z_{eff}$ I.E. $\propto 1/r$

A) Up a Group

Dec. atomic radius

e^- held more tightly

I.E. Inc.

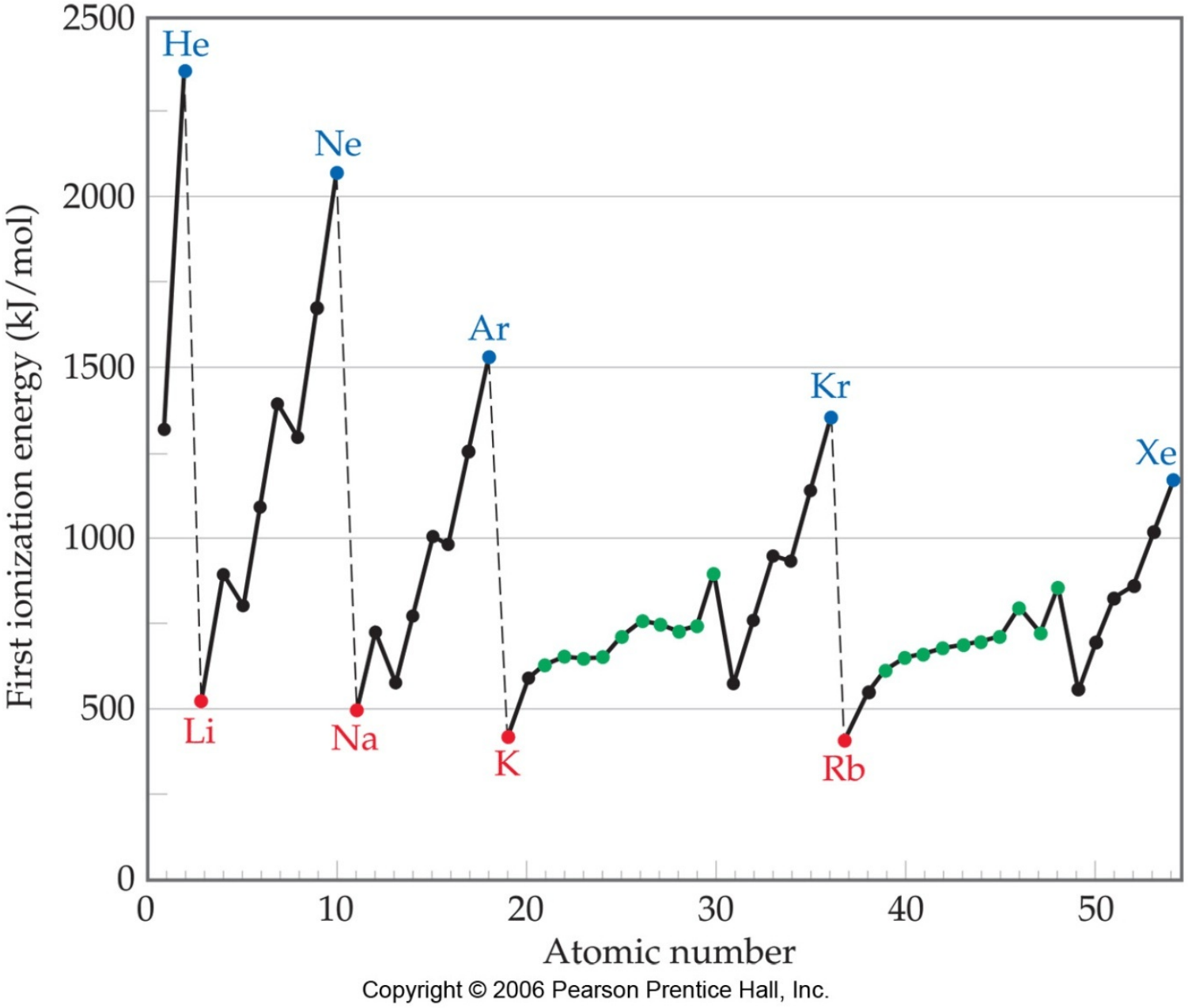
B) Across a Period

Dec. atomic radius

Z_{eff} inc. e^- held more tightly

I.E. Inc

C) Summary



D) Irregularities

e^- config. accounts for irregularities

Li → Ne, generally inc.

However,

Be ($1s^2\ 2s^2$) > B ($1s^2\ 2s^2\ 2p^1$)

N ($1s^2\ 2s^2\ 2p^3$) > O ($1s^2\ 2s^2\ 2p^4$)

½-filled & filled subshells more stable

Elements at end of each transition series, Zn, Cd & Hg have higher I.E. than following element

pseudo-noble-gas

Highest I.E. for noble gases
- filled s & p subshells

E) Electron Config. of Ions

1) Representative Ions

a) Metals

Form Cations

1) s - block

Groups 1A & 2A

All valence e^- removed
- noble-gas config.

Na $1s^2\ 2s^2\ 2p^6\ 3s^1$

Na^+ $1s^2\ 2s^2\ 2p^6$ [Ne]

1) p - block

Groups 3A - 5A

Lose p e^- fairly readily

(group # - 2)

Often req. too much energy to remove all val. e^-

(group #)

Pb [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

Pb^{2+} [Xe] $4f^{14}\ 5d^{10}\ 6s^2$

Pb^{4+} [Xe] $4f^{14}\ 5d^{10}$

Pb^{2+} more common than Pb^{4+}

b) NonMetals

Monatomic anions

charge = (group # - 8)

- add e^- to obtain noble-gas e^- config.

S [Ne] $3s^2\ 3p^4$

S^{2-} [Ne] $3s^2\ 3p^6$

Cl [Ne] $3s^2\ 3p^5$

Cl^- [Ne] $3s^2\ 3p^6$

2) Transition Metal Ions

Generally, only highest energy e^- lost

Outer s-subshell e^-

Many tran. metals form +2 cations

- lose both s-subshell e^-

For ions of higher charge
d-subshell e^- are lost

a) Ex 1:

Group 2B

Zn, Cd, Hg

$(n-1)d^{10}\ ns^2 \rightarrow (n-1)d^{10}$

Zn^{2+}, Cd^{2+}, Hg^{2+}

b) Ex 2:

Fe [Ar] $4s^2\ 3d^6$

Fe^{2+} [Ar] $3d^6$

Fe^{3+} [Ar] $3d^5$

V) Electron Affinity, EA

Energy associated with the gain of an e^- by a gaseous atom or ion

A) First EA

$Cl\ (g) + e^- \rightarrow Cl^-\ (g)$ EA = −349 kJ/mol

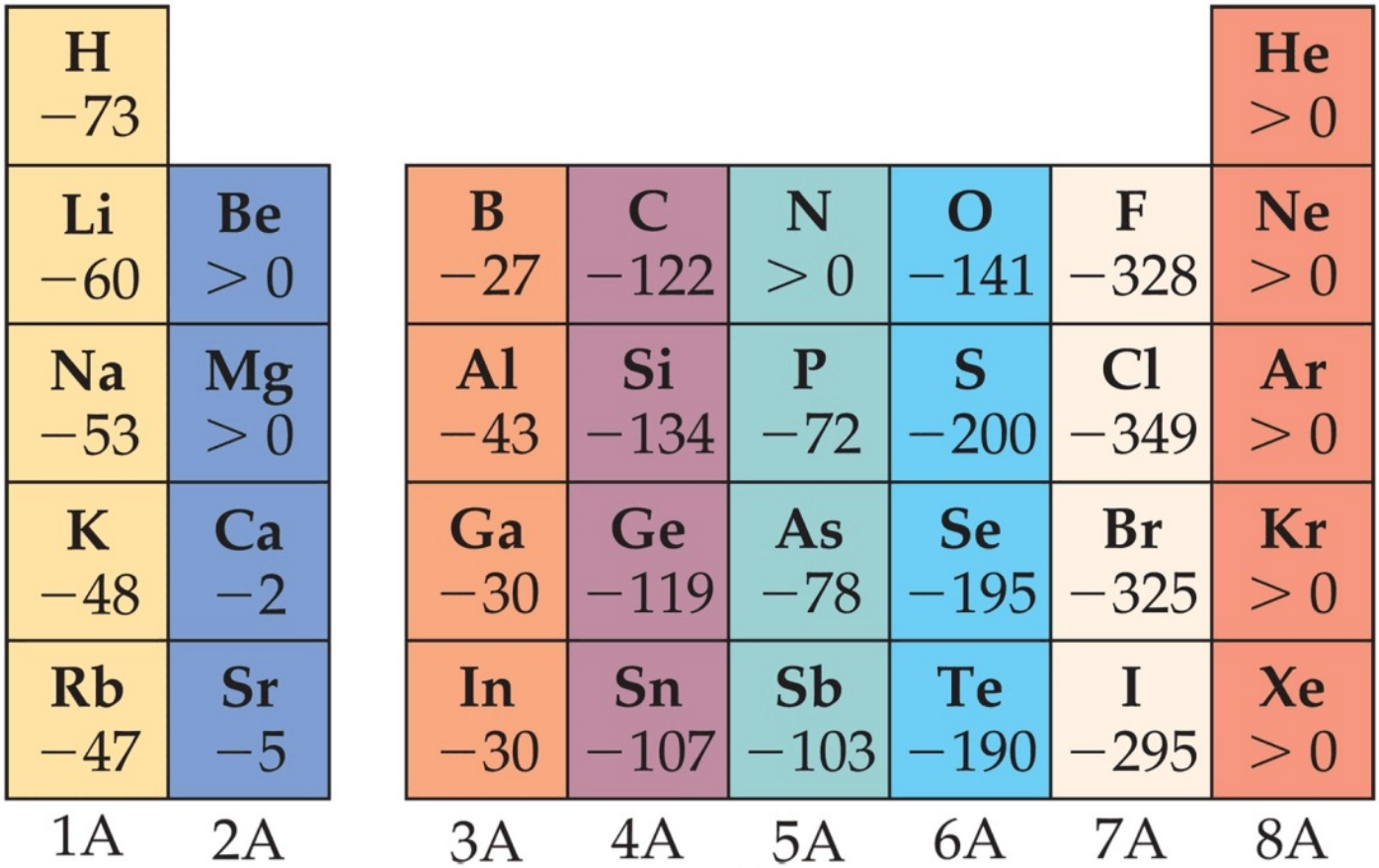
Energy released for most neutral atoms & all positive ions

greater attraction for e^- ⇒ more neg. EA

B) Second EA

$O^-\ (g) + e^- \rightarrow O^{2-}\ (g)$ EA = +710 kJ/mol

2^{nd} e^- must be forced onto a neg. charged ion which requires energy



A) Periodic Trends in EA

Generally, parallels variation in atomic size

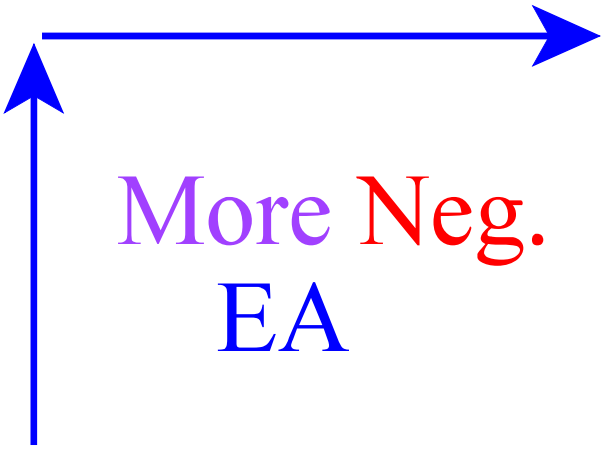
- not as well-established as other trends (exceptions)

e^- placed into outer shell

- closer it gets to nucleus & greater Z_{eff}

larger neg. EA

C) Summary



1) Exceptions

a) 2nd period

F: −328 kJ/mol Cl: −349 kJ/mol

True for other 2nd period elements

Small size of 2nd period elements

e^- enters small outer shell

Adding an e^- places it very close to other 2s and 2p e^- resulting in stronger e^- - e^- repulsions.

b) Other Exceptions

Adding an e^- to stable e^- - config.

1) Group 2A

full s subshell

added e^- goes into p subshell

2) Group 5A

½ - filled p valence subshell

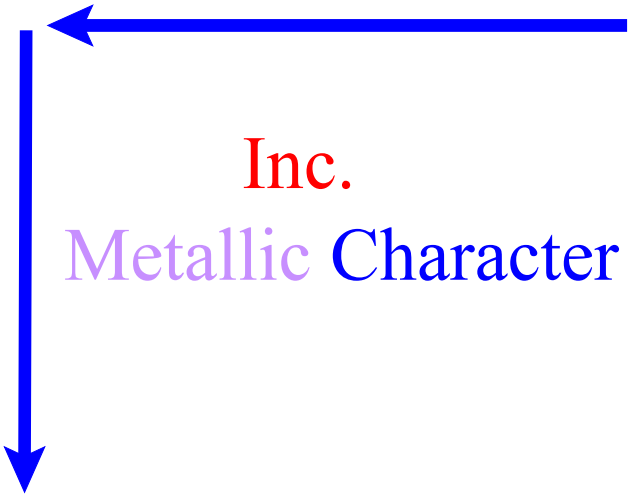
added e^- pairs w. another e^- in occupied p orbital & experiences repulsions

3) Group 8A

filled valence shell

e^- goes into next higher shell

VI) Metals, Nonmetals, Metalloids



metals

Low IE

Low EA

form cations

oxides are basic

B

Si

Ge As

Sb Te

Po At

nonmetals

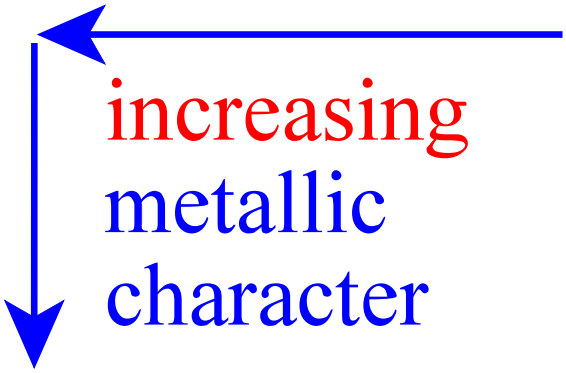
Large IE

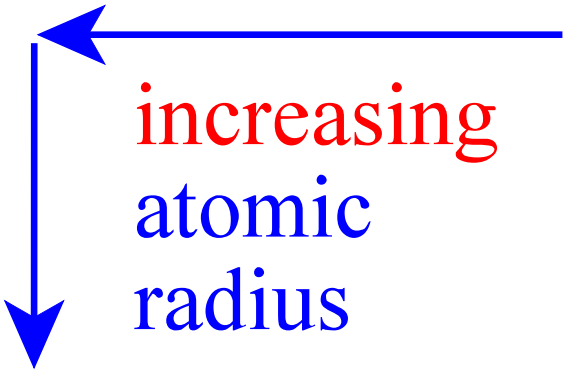
Large EA

form anions

oxides are acidic

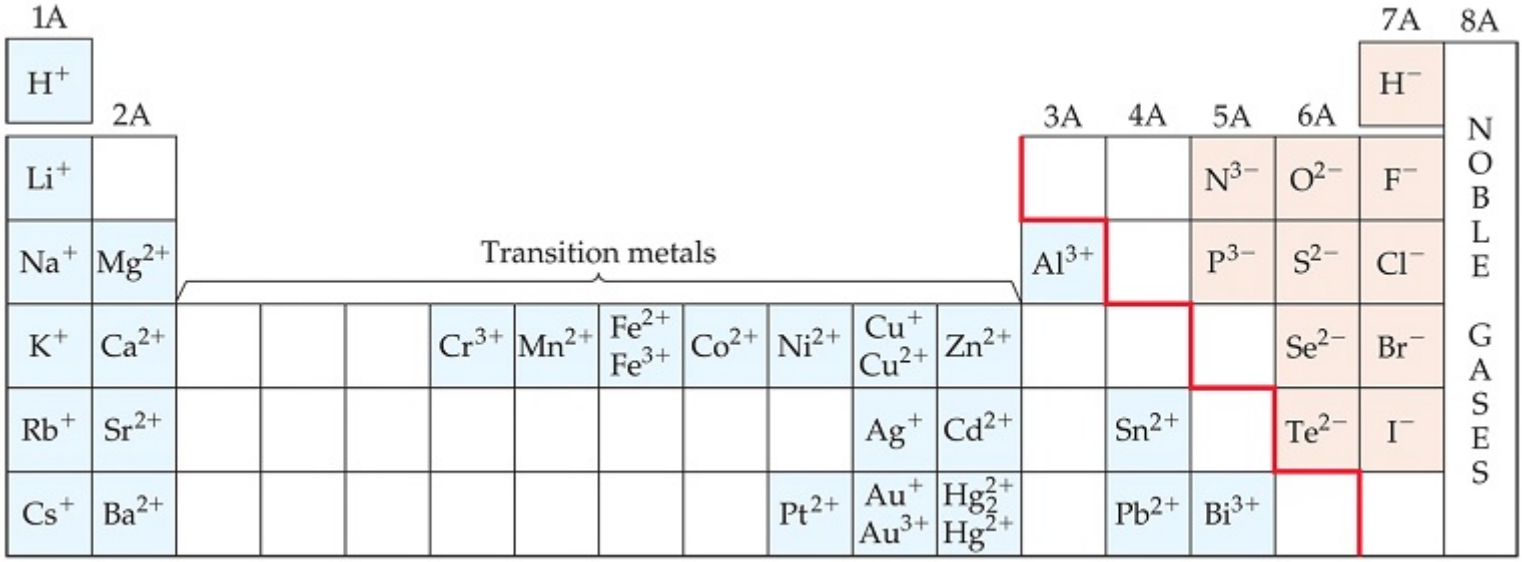
Summary of Periodic Trends





A) Metals

- chgs for 1A & 2A ions = grp #
- for p-block chgs = grp# or (grp# - 2)
- transition metals: highly variable



1) Reactions with nonmetals

- form ionic cmpds

$$Zn + S \rightarrow ZnS$$

or

$$2\,Ca + O_2 \rightarrow 2\,CaO$$

Note: these are redox reactions, metal is oxidized (loses e^-) due to low IE and nonmetal is reduced (gains e^-) due to do high EA.

2) Metal oxides are basic

$$CaO(s) + H_2O(\ell) \rightarrow Ca(OH)_2(aq)$$

Metal oxide + water → metal hydroxide

$$ZnO(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(\ell)$$

Metal oxide + acid → salt + water

3) Other Properties:

- luster (shiny)

- malleable (pound into thin sheets)

- ductile (drawn into a wire)

- good conductors of
  heat & electricity

B) Nonmetals

1) React with metals to give ionic cmpds

2) React w. other nonmetals to give molecular cmpds:

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

3) Oxides are acidic

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4$$

4) Other Properties:

- not lustrous (dull)

- vary widely in color & appearance

- not malleable & ductile

- poor conductor of heat & elect.

C) Metalloids

Located between metals & nonmetals

- have prop. of both

- Don't form ions easily

  IE too high to form cations

  EA not neg. enough to form anions

- form molecular cmpds w. nonmetals

VII) Grp 1A & 2A - Active Metals

A) Grp 1A: Alkali Metals

1) soft & low densities (Li, Na & K are less dense than water) due to the large size of the atoms.

2) valence shell e^- configuration is ns^1 one e^- easily lost to form M^+ ions with a noble gas e^- configuration.

3) react rapidly with O_2 and H_2O so must be stored under oil

Reactivity with H_2O inc. down grp

3) Preparation

- Reduction of salt
  req. elect. energy

$$2\ LiCl(\ell) \rightarrow 2\ Li(s) + Cl_2(g)$$

Li is used in Al alloys for aircrafts and in batteries.

- Na used in replacement rxns to produce other reactive metals

$$Na(\ell) + KCl(\ell) \rightarrow NaCl(\ell) + K(\ell)$$

4) Reaction w. nonmetals

Ionic cmpds

$2\ Li(s) + Cl_2(g) \rightarrow 2\ LiCl(s)$

$2\ Na(s) + H_2(g) \rightarrow 2\ NaH(s)$

$2\ K(s) + S(s) \rightarrow K_2S(s)$

5) Reaction w. Oxygen

$4\ Li + O_2 \rightarrow 2\ Li_2O$ oxide

$2\ Na + O_2 \rightarrow Na_2O_2$ peroxide

$K + O_2 \rightarrow KO_2$ superoxide

B) Grp 2A: Alkaline Earth Metals

1) harder, more dense, less reactive than grp 1A due to smaller size & larger Z_{eff}.

2) valence shell configuration is ns^2 and loss of 2 e^- results in a M^{2+} ion with a [NG] e^- configuration.

3) Mg, Ca most abundant & impt.

4) Rxn with O_2

All produce expected oxide, except Ba, i.e.

$$2\ Ca + O_2 \rightarrow 2\ CaO$$

Ba forms the peroxide:

$$Ba + O_2 \rightarrow BaO_2$$

5) Rxn with H_2O

$$Ca(s) + H_2O(\ell) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

Reactivity increases down the group:
Be (no reaction), Mg slowly, Ca more rapid.
Heat generated.

6) Rxn with H_2: Ionic Hydrides

$$Ca(s) + H_2(g) \rightarrow CaH_2(s)$$

VIII) Selected Nonmetals

A) Hydrogen

1) H_2 bond energy, 463 kJ/mol - stable

2) Isotopes

^{1}H (99.9%) protium
^{2}H (0.01%) deuterium, labels
^{3}H tritium, radioactive

3) High IE (1312 kJ/mol)

Shares e^- in covalent bonds

4) Gains e^-

Forms hydrides, H^-

B) Oxygen

1) O_2 - odorless, colorless gas

21% of air

2) allotropes

O_2 and O_3 (ozone)

$3\ O_2(g) \rightarrow 2\ O_3(g) \quad \Delta H° = 284.6\ kJ$

3) Ions

O^{2-} oxides

O_2^{2-} peroxides (unstable)

$2\ H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g) + 196.1\ kJ$

O_2^- superoxides (rescue masks)

C) Sulfur

S_8 - ring, yellow solid

S^{2-} sulfides

$S(s) + O_2(g) \rightarrow SO_2(g) \rightarrow SO_3(g)$

Acid rain

D) Nitrogen

N_2 - odorless, colorless gas

78% of air, very stable

1) Cmpds with H

NH_3, N_2H_4 (hydrazine, rocket fuel)

2) Cmpds with O

NO, NO_2, N_2O, N_2O_4, HNO_2, HNO_3

Formed in Combustion, Acid rain

E) Phosphorous

P_4 - strained tetrahedral, solid

found in rocks, sand, soft drinks
- generally as phosphates

P_4O_6, P_4O_{10}, H_3PO_3, H_3PO_4

- ADP, adenosine diphosphate

- ATP, adenosine triphosphate

- energy storage in biology

F) Halogens (X_2)

High EA, form X^-

$F_2(g)$, $Cl_2(g)$, $Br_2(\ell)$, $I_2(s)$ - redox rxns

Fluorocarbons, ChloroFluorocarbons

CFCs : CF_3CF_3, CCl_2F_2

- Refrigerants, greenhouse gases

Teflon - CF_2CF_2, Roy Plunkett (Ohio)

$Cl_2(g) + H_2O(\ell) \rightarrow HCl(g) + HOCl(aq)$

OCl^- hypochlorite used in pools

$F_2(g)$ - very reactive, exothermic rxns

$2\ F_2(g) + H_2O(\ell) \rightarrow 4\ HF(g) + O_2(g)$

$2\ F_2(g) + SiO_2(s) \rightarrow SiF_4(g) + O_2(g)$

G) Carbon

Solid - covalent bonding

diamonds, graphite, C_{60} ("buckyball")

CO, CO_2, H_2CO_3 (blood buffer)

Hydrocarbons - CH4, C2H6, etc.

Biological molecules

H) Silicon

Solid

Semiconductors

SiO_2 - sand, glass

Silicates - SiO_4^{2-} (asbestos)

Silicones - $(SiOR_2)_n$ - caulk, implants

I) Boron

Octet exception

Rocket fuel

Diborane -

$B_2H_6 + O_2 \rightarrow B_2O_3 + H_2O + 2030\ KJ$

J) Noble Gases

Monatomic

Full s and p subshells

High IE, dec. moving down grp

- mostly unreactive, except Xe

XeF_2, XeF_4, XeF_6, XeO_3, XeO_4