Chemistry 1B-AL
Fall 2016

adventures ~~lectures~~ 7-8

Zumdahl
(pp. 571-582*[atomic properties]*),
606-609*[ionic radii]*)

1

Chemistry 1B –AL

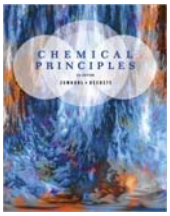
Electronic Structure

and

Periodic Properties of

Atoms

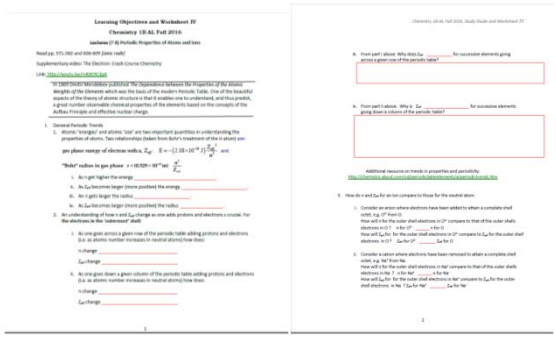
2



Zumdahl
(pp. 571-582*[atomic properties]*),
606-609*[ionic radii]*)

3

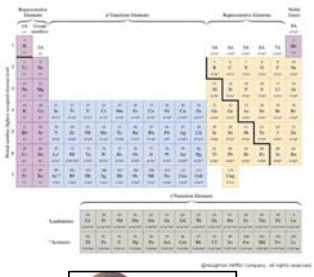
worksheet IV- sections I.1-I.3 and upcoming clickeroos



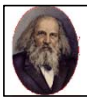
4

periodicity (figure 12.29)


Lavoisier
1789




Newlands
1863


Mendeleev
1869

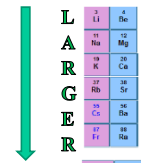
5

EXPLAIN THIS !!!! (atomic radii, fig. 12.38)

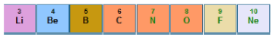
increase atomic number of atom

atomic radii (10^{-12} m):

Li *152*
Na *186*
K *227*
Rb *247*
Cs *265*
Fr *270*



but
Li *152* Be *113* B *88* C *77* N *70* O *66* F *64* Ne *69**



S M A L L E R

6

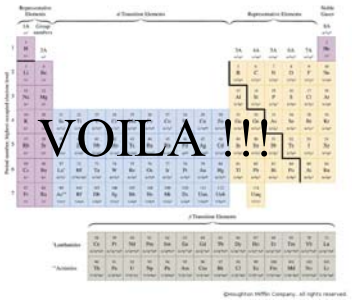
explain this

$$Na\ (s) + \tfrac{1}{2}Br_2\ (\ell) \rightarrow Na^+Br^-\ (s)$$

why Na^+ ?
why Br^- ?

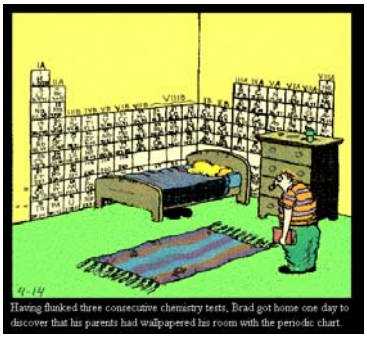
7

periodicity (figure 12.29)



8

bad joke



http://www.uky.edu/~holler/html/comics.html

9

periodic properties of atoms and their ions

gas phase energy of electron with n, Z_{eff}

$$E \approx -\left(2.18\times10^{-18}\ J\right)\frac{Z_{eff}^{\ 2}}{n^2}$$

$$IE = +\left(2.18\times10^{-18}\ J\right)\frac{Z_{eff}^{\ 2}}{n^2}$$

"Bohr" radius in gas phase

$$r \approx (0.529\times10^{-10}m)\frac{n^2}{Z_{eff}}$$

$$r \approx (52.9pm)\frac{n^2}{Z_{eff}}$$

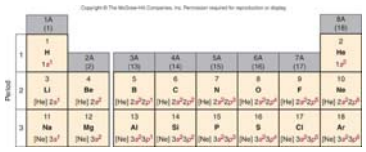
$$pm = 10^{-12}m\ \text{(picometer)}$$

10

basic trends for n and Z_{eff} in periodic table (figure 8.9, Silberberg)

n Z_{eff} → across

↓ down



11

basic trends for n and Z_{eff} in periodic table (figure 8.9, Silberberg)

n Z_{eff} → across

for each sequential atom a proton and an electron **in same shell** is added:

for an outermost (valence) electron:

n: stays the same as one goes across a row

Z_{eff}: add +1 to Z (actual nuclear charge), increases attraction
add electron in same shell; repulsion shields other electron
but not full -1 repulsion since in same shell

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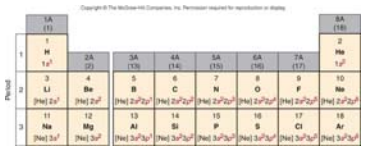
basic trends for n and Z_{eff} in periodic table (figure 8.9, Silberberg)

Z_{eff} *increases across row (period)*

n is not changing



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basic trends for n and Z_{eff} in periodic table (figure 8.9, Silberberg)

n Z_{eff}

for each sequential atom, complete **inner shells** are added:

for an outermost (valence) electron:

n: increases by 1 as one goes down a column

Z_{eff}: add same number of protons and electrons (e.g. 8 in going period 2→3)

but electrons are inner shell so 'almost' complete shielding so nuclear attraction and electron repulsion (shielding) cancel

down

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basic trends for n and Z_{eff} in periodic table (figure 8.9, Silberberg)

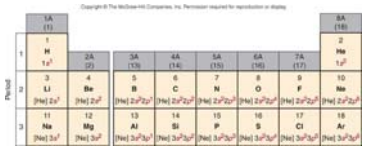
n

increases down column (group)

Z_{eff} *increases across row (period)*

n is not changing

Z_{eff} *is 'relatively' constant*



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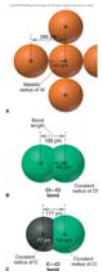
Estimating atomic radii (metallic and covalent) (figs. Zumdahl 12.37, Silberberg 8.14)



for metals

for nonmetals-
can vary from compound to compound

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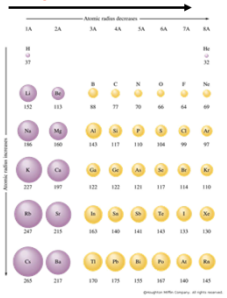
covalent and metallic atomic radii periodic trends (fig. 12.38)

n Z_{eff}



gas phase 'Bohr' radius

$r \approx (0.529 \times 10^{-10}\ m)\ \frac{n^2}{Z_{eff}}$

don't take formula too 'literally' for metallic/covalent radii

but :

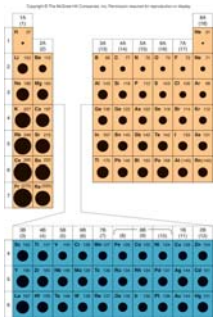
larger n ⇒ larger r

larger Z_{eff} ⇒ smaller r

17

atomic radii (Silberberg fig. 8.15) numerical values differ slightly from Zumdahl

n Z_{eff}



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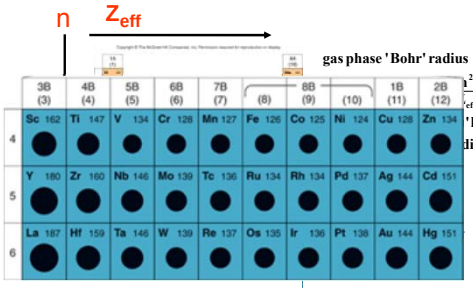
18

atomic radii (Silberberg fig. 8.15) *numerical values differ slightly from Zumdahl*



transition metals
(special considerations)

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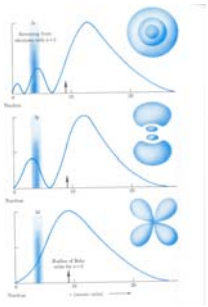
radii for transition metal (neutral) atoms in 4th period

Even though the $E_{4s} < E_{3d}$ (due to penetration effects), the average position (radius) of the 3d oribtals is somewhat smaller.

Thus, in terms of atomic size, the 4s is the "outermost" orbital for all of the atoms; and as one goes across the period, successive e's are added to "inner" 3d orbitals and the radii are relatively constant.



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radii of ions (F vs F⁻) $r \approx 52.9\ n^2/Z_{eff}$ pm

how would the radius of F compare to that of F⁻ ?

- **F $1s^2 2s^2 2p^5$ F⁻ $1s^2 2s^2 2p^6$**
- **outer electron n=2 for both, $Z_{nuclear}$=+9 for both**
- **how does Z_{eff} for 2p in F compare to Z_{eff} for 2p in F⁻ ?**
  - **2p e in F is shielded by ? electrons in same subshell**
  - **2p e in F⁻ is shielded by ? electrons in same subshell**
  - **$(Z_{eff})_F$? $(Z_{eff})_{F^-}$**
- **radius (F) ? radius (F⁻)**
- **Experiment: F: r=64 pm F⁻: r=136 pm**

(fig. 12.38) *(fig. 13.8)*

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For today

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no rest for the weary !!


Monday, 17 October !!!
after midterm

iClicker-Check-Up Video 4
Study Guide 4 I-IV
the whole thing !

How's your CHEM1B-AL health?

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worksheet IV : how do Z_{eff} and n vary across and down periodic table?

I. General Periodic Trends

1. Atomic 'energies' and atomic 'size' are two important quantities in understanding the properties of atoms. Two relationships (taken from Bohr's treatment of the H atom) are:

gas phase energy of electron with n, Z_{eff}: $E \approx -(2.18 \times 10^{-18}\ J)\frac{Z_{eff}^2}{n^2}$ and

"Bohr" radius in gas phase $r \approx (0.529 \times 10^{-10} m)\ \frac{n^2}{Z_{eff}}$

i. As n get higher the energy _____.
ii. As Z_{eff} becomes larger (more positive) the energy _____.
iii. An n gets larger the radius _____.
iv. As Z_{eff} becomes larger (more positive) the radius _____.

2. An understanding of how n and Z_{eff} change as one adds protons and electrons s crucial. For **the electrons in the 'outermost' shell**:

i. As one goes across a given row of the periodic table adding protons and electrons (i.e. as atomic number increases in neutral atoms) how does:

n change _____
Z_{eff} change _____

ii. As one goes down a given column of the periodic table adding protons and electrons (i.e. as atomic number increases in neutral atoms) how does:

n change _____
Z_{eff} change _____

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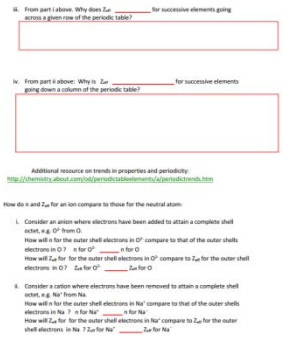
worksheet IV: how do Z_{eff} and n compare for neutrals and ions?



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more examples of comparing radii

- Na vs Na^+
- Ne vs Na^+

(note experimental data for Na^+, fig. 13.8 and Ne, fig. 12.38 not comparable see)

- O^{2-} vs F^-
- O^{2-} vs F

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ionization energies (IE's)

energy required to remove an electron from a gaseous atom (ion)

$X(g) + (\text{energy}=IE) \rightarrow X(g)^+ + e^-$

as in chapter 9:

energy positive (+) when absorbed in reaction *(endothermic)*

energy negative (–) when released in reaction *(exothermic)*

IE's generally positive

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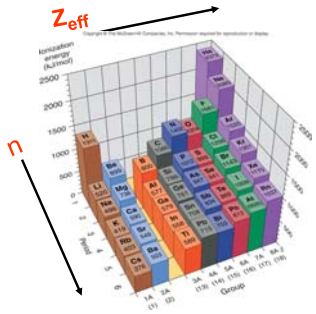
ionization energies (Zumdahl fig. 12.35, Silberberg, fig. 8.18)



gas phase energy of electron with n, Z_{eff}

$E \approx -(2.18\times10^{-18}\ J)\frac{Z_{eff}^2}{n^2}$

IE = –E

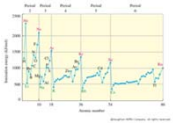
larger n ⇒ smaller IE

larger Z_{eff} ⇒ larger IE

exceptions

N > O, P > S, As ≈ Se why?

Be > B, Mg > Al, Ca ≈ Ga why?



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successive gas phase ionization energies in kJ/mol (p572; S6)

Al ([He]$2s^2 2p^6 3s^2 3p^1$) → Al^+ ([He]$2s^2 2p^6 3s^2$) + e^- IE_1=580

Al^+ ([He]$2s^2 2p^6 3s^2$) → Al^{2+} ([He]$2s^2 2p^6 3s^1$) + e^- IE_2=1815

Al^{2+} ([He]$2s^2 2p^6 3s^1$) → Al^{3+} ([He]$2s^2 2p^6$) + e^- IE_3= 2740

Al^{3+} ([He]$2s^2 2p^6$) → Al^{4+} ([He]$2s^2 2p^5$) + e^- IE_4= 11,600

- successive IE's get larger (positively charged ions have greater Z_{eff})
- large jumps in IE when n of electron removed changes

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electron affinities (EAs, pp 576-577)

the energy of the reaction when an electron is added to an atom

$X(g) + e^- \rightarrow X^-(g) + (\text{energy} = EA)$

negative EA means energy given off (exothermic)

positive EA means ion unstable relative to neutral atom

(some older texts use opposite)

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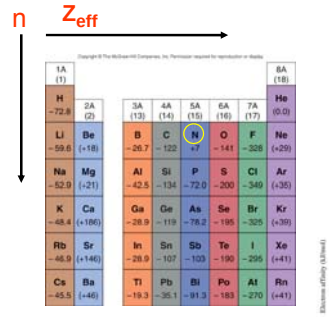
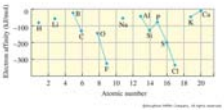
electron affinities (Zumdahl fig 12.36; Silb fig. 8.20)



higher n ⇒ smaller (less negative) EA

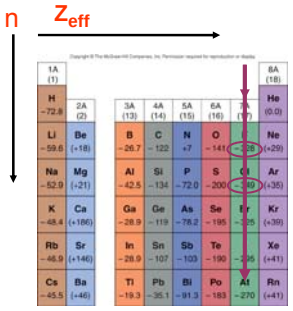
larger Zeff ⇒ larger (more negative) EA

positive EA ⇒ negative ion unstable



[harder to measure and "less regular " tha I.E.'s]

F vs Cl electron affinities (Zumdahl p 577)



higher n ⇒ smaller (less negative) EA

small size of F^-

HW #3
Prob 27a

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Journal of Fluorine Chemistry 2002

ELSEVIER

Journal of Fluorine Chemistry 116 (2002) 35–39

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

How anomalous are the anomalous properties of fluorine? Ionization energy and electron affinity revisited☆

Eric D. Balighian, Joel F. Liebman*

Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, MD 21250, USA

Received 23 January 2002; received in revised form 7 March 2002; accepted 7 March 2002

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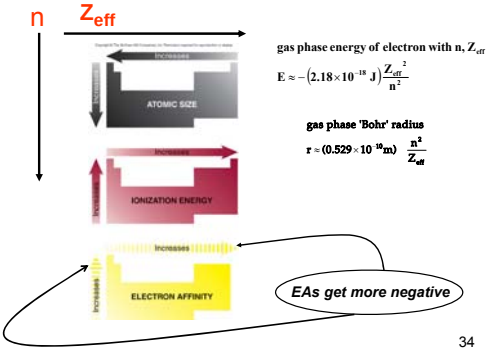
summary (Silb, fig. 8.21)



gas phase energy of electron with n, Z_{eff}

$$E \approx -(2.18 \times 10^{-18}\ J)\frac{Z_{eff}^2}{n^2}$$

gas phase 'Bohr' radius

$$r \approx (0.529 \times 10^{-10} m)\ \frac{n^2}{Z_{eff}}$$

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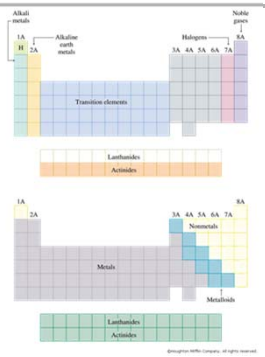
Zumdahl (section 12.16, figure 12.39)



not responsible for pp. 580-582

BUT

35

reactivity and periodic structure (Silberberg figure 8.22)

metallic vs non-metallic behavior

- IE and EA ➡
- melting point and conductivity ➡
- acid-base behavior of oxides *(not responsible 1B before 1A)*

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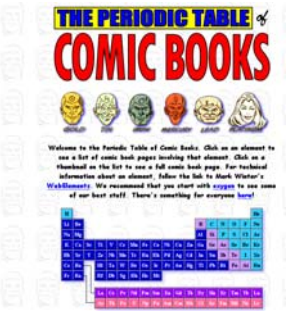
periodic table of comic books

http://www.uky.edu/Projects/Chemcomics/



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$$IE = +\left(2.18\times10^{-18}\ \text{J}\right)\frac{Z_{eff}^{\ 2}}{n^2}$$

$$r \approx (0.529\times10^{-10}\text{m})\frac{n^2}{Z_{eff}}$$

END OF ~~LECTURES~~ ADVENTURES 7-8

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comparing Na^+ to Ne (similar experimental measures)

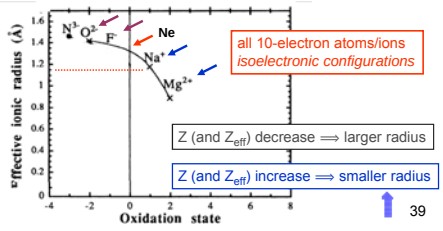
American Mineralogist, Volume 80, pages 670–675, 1995

Atomic radii of noble gas elements in condensed phases

TABLE 1. Radii (in ångströms) of noble gas elements given in the literature

Ref.	Description	He	Ne
1	univalent radii	0.93	1.12
2	radii in crystal lattice	1.78	1.60
3	van der Waals radii	1.22	1.60
4	covalent radii	~0.325	0.69
5	covalent radii	—	0.76

Zum fig 12.38



Zum ~ fig 13.8
Na^+ 95 pm

all 10-electron atoms/ions
isoelectronic configurations

Z (and Z_{eff}) decrease ⟹ larger radius

Z (and Z_{eff}) increase ⟹ smaller radius

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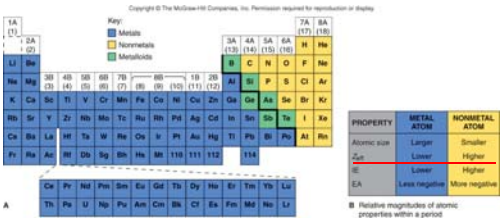
figure Silberberg 9.1



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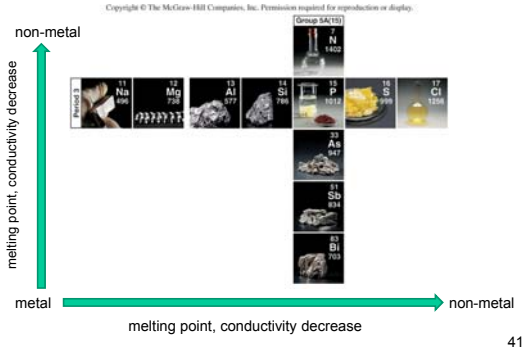
Silberberg figure 8.23



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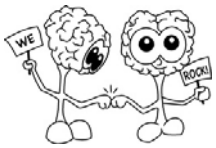
team ***2-minute*** *max section explanations*

exceptions to ionization potential trend of increasing as one 'goes across periodic table' !!

exceptions

N > O, P > S, As ≈ Se why? *team 1 in each section*

Be > B, Mg > Al, Ca ≈ Ga why? *team 2 in each section*



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