Week 8
PART 1

CHEM 1061-003 9 MARCH 2015
WEEK 8, PART 1 NOTES

ANNOUNCEMENTS:

THIS WEDNESDAY IS EXAM 2,
9:00 - 10:00 PM

ROOM ASSIGNMENTS ARE IDENTICAL TO THOSE FOR EXAM 1 AND ARE ACCORDING TO THE FIRST LETTER OF YOUR LAST NAME (OR SURNAME):

PHYSICS 150 A-L

(TATE LAB OF PHYSICS 150)

STSS 230 M-Z

DO NOT TAKE THE EXAM IN THE WRONG ROOM!

→ SEE HANDOUT FOR DETAILS ON THE EXAM. IT WILL COVER CH 5-7 AND HAVE SOME Q's BASED ON CH 2-4.

NO QUESTIONS WILL INVOLVE SECTION 7.3 OF CH 7.

WEDNESDAY'S *OPTIONAL* LECTURE WILL INVOLVE REVIEW OF SELECTED Q's FROM PRACTICE EXAM 2 OF 2014.
Please E-MAIL ME ANY REQUESTS:
ellis@umn.edu

TOPICS TODAY:
(NONE OF THIS STUFF WILL BE ON EXAM 2- BUT IT WILL BE ON EXAM 3!!)

1. G.S. ELECTRONIC CONFIG OF POLYELECTRONIC ATOMS

   (i) RULES FOR FILLING ORBITALS
   (ii) HUND'S RULES: MAXIMIZING THE NUMBER OF UNPAIRED ELECTRONS IN A PARTIALLY FILLED SUBSHELL

2. CORE AND VALENCE ELECTRONS

3. KEY IMPORTANCE OF VALENCE ELECTRONS

4. ATOMIC STRUCTURE, CHEMICAL PROPERTIES AND SELECTED FAMILIES OF ELEMENTS IN THE PERIODIC TABLE

   (i) ALKALI METALS (gp 1)
   (ii) ALKALINE EARTHS (GP 2) AND A LITTLE ABOUT ALUMINUM (GP 3)
   (iii) HALOGENS

5. SOME DIMERIZATION REXNS OF PARAMAGNETIC ATOMS

   ↑ ATOMS WITH UNPAIRED ELECTRONS

FROM LAST FRIDAY

GROUND STATE ELECTRONIC CONFIGURATIONS OF POLYELECTRONIC ATOMS

1s<2s<2p<3s<3p<4s<3d<4p<5s

RULES FOR DETERMINING THE MOST STABLE ELECTRONIC CONFIGURATIONS OF NEUTRAL ATOMS

a. ELECTRONS ARE ADDED TO ORBITALS IN ORDER OF INCREASING ENERGY. EACH LEVEL IS USUALLY FILLED COMPLETELY BEFORE BEGINNING THE NEXT ONE. E.G.,

$_{28}$**Ni** $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{Ar} 4s^2 3d^8$

or $[Ar]\,\underline{4s^2 3d^8}$

[Ar] ← CORE; $4s^2 3d^8$ VALENCE

$_{37}$**Rb** $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6}_{Kr} 5s^1$

or $[Kr]\,5s^1$ ← VALENCE

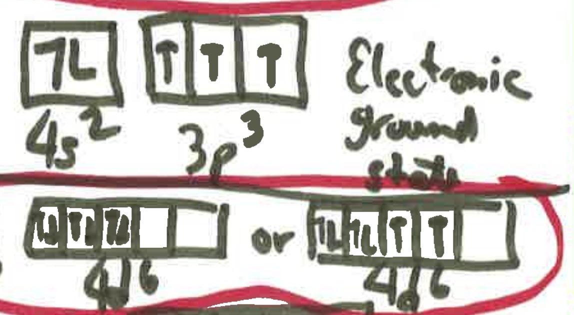
[Kr] ← CORE

1s<2s<2p<3s<3p<4s<3d<4p<5s

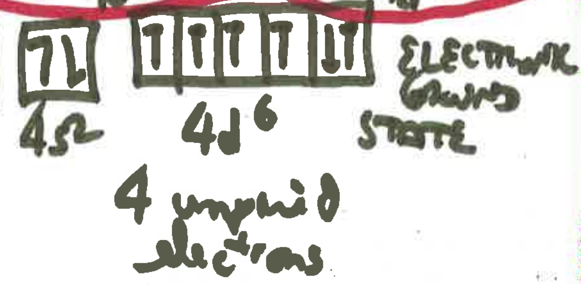
b. HUND'S RULE: ELECTRONS ARE ADDED TO SUBSHELLS WITH PARALLEL OR ALIGNED SPINS TO THE MAXIMUM POSSIBLE EXTENT TO MINIMIZE INTERELECTRONIC REPULSIONS. THUS, HUND'S RULE MUST BE SATISFIED FOR AN ATOM TO ACHIEVE ITS MOST STABLE OR GROUND ELECTRONIC STATE

EXAMPLES:

$_{15}$P $[Ne]\,3s^2 3p^3$ ≡ [Ne]



$_{26}$Fe $[Ar]\,4s^2 3d^6$ ≡ [Ar]



ATOMS OR MOLECULES WITH UNPAIRED ELECTRONS ARE ATTRACTED TO A MAGNETIC FIELD AND ARE SAID TO BE ***PARAMAGNETIC***

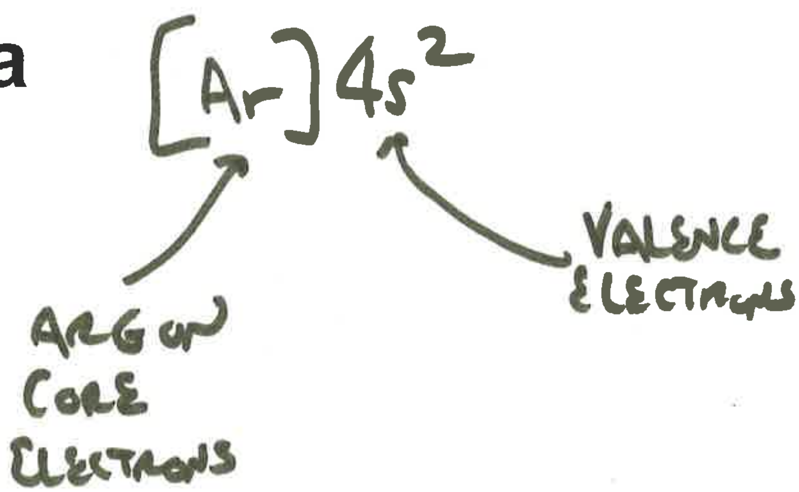
CORE AND VALENCE ELECTRONS

a. CORE ELECTRONS ARE ELECTRONS IN COMPLETELY FILLED SHELLS (n = 1, 2, ...) AND/OR HAVE THE SAME ELECTRONIC CONFIGURATIONS AS THE ESPECIALLY STABLE INERT GASES IN NEUTRAL OR CATIONIC ATOMS

COMPLETELY FILLED SHELLS ARE ESPECIALLY STABLE AND THUS CORE ELECTRONS HAVE VERY HIGH IONIZATION ENERGIES AND ARE RARELY LOST (OR SHARED) IN CHEMICAL REXNS; I.E., THEY ARE VERY TIGHTLY BOUND TO THE NUCLEI OF ATOMS.

EXAMPLE:

$_{20}Ca$



CORE AND VALENCE ELECTRONS

b. COMPLETELY FILLED d and f-SUBSHELLS ALSO USUALLY FUNCTION AS CORE ELECTRONS IN ATOMS

EXAMPLE:

CORE ELECTRONS

$_{34}$**Se** [Ar] $4s^2$ $3d^{10}$ $4p^4$

VALENCE ELECTRONS

$-6e^-$ ⇸ Se^{+6} [Ar]$4s^2 3d^8$ PARAMAGNETIC ION

$-6e^-$ → Se^{+6} [Ar]$3d^{10}$ DIAMAGNETIC ION (FAVORED) IN SeO_4^{2-}

c. ELECTRONS IN PARTIALLY FILLED SHELLS (OR SUBSHELLS) ARE CALLED VALENCE ELECTRONS, WHICH ARE OFTEN LOST OR SHARED IN REXNS.

EXAMPLES:

$_{17}$**Cl** [Ne]$3s^2 3p^5$ [↑↓] [↑↓|↑↓|↑]

$+e^-$ → Cl^- ← ARGON-LIKE ELECTRONIC STRUCTURE [Ne]$3s^2 3p^6$

$-7e^-$ → Cl^{7+} in ClO_4^- [Ne] NEON-LIKE ION IN ClO_4^-

$_{25}$**Mn** [Ar]$4s^2 3d^5$ [↑↓] [↑|↑|↑|↑|↑]

$+e^-$ ⇸ Mn^- UNSTABLE — NO ELECTRONIC STABILITY, UNLIKE FOR Cl^-.

$-7e^-$ → Mn^{7+} in MnO_4^- ARGON-LIKE ION IN MnO_4^-

SO NON-METALLIC Cl AND METALLIC Mn BOTH FORM RELATED COMPOUNDS CONTAINING ATOMS WITH O.N. = +7, BECAUSE IN DOING SO THEY BOTH BECOME NOBLE-GAS LIKE!

CORE AND VALENCE ELECTRONS

d. THE OUTERMOST ELECTRONS IN ANIONIC ATOMS (H(1-), O(2-), F(1-), S(2-), Cl(1-), ETC.) WITH COMPLETELY FILLED SHELLS (OR SUBSHELLS) ARE CONSIDERED TO BE VALENCE ELECTRONS BECAUSE THESE ARE OFTEN SHARED OR LOST IN REXNS.

EXAMPLES:

$_1$H(1-): $1s^2$ (A SUPER-BASE) $H:^-$ —$H^+(aq)$→ H_2 ; —H_2O→ H_2 + OH^-

HELIUM-LIKE — BUT FAR MORE REACTIVE!

$_{16}$S(2-) : [He]$2s^2 2p^6$ —$H^+(aq)$→ SH^- (SULFUR ANALOG OF OH^-) ; —BACTERIAL OXIDATION; $-8e^-$, 4[O]→ SO_4^{2-} SULFATE ION CONTAINING S +6

NEON-LIKE — BUT $2s^2 2p^6$ ARE VALENCE ELECTRONS!

HOWEVER, THE OUTERMOST ELECTRONS IN CATIONIC ATOMS THAT ARE ISOELECTRONIC WITH THE INERT GASES (He, Ne, Ar, Kr, Xe) ARE CORE ELECTRONS

EXAMPLES:

$_{13}$Al(3+) [Neon]-like core ($1s^2 2s^2 2p^6$), BUT EVEN MORE RESISTANT THAN NEON TOWARDS LOSING OR SHARING ITS CORE ELECTRONS.

$_{19}$K(1+) ARGON-LIKE CORE, $1s^2 2s^2 2p^6 3s^2 3p^6$, BUT K CATION HOLDS ONTO ITS CORE ELECTRONS MORE TIGHTLY THAN ARGON.

SUMMARY OF IMPORTANT POINTS ON THE ELECTRONIC CONFIGURATIONS OF ATOMS (OR ATOMIC STRUCTURE)

1. ELECTRONS ARE ADDED TO ORBITALS ACCORDING TO THEIR RELATIVE ENERGIES: THE MOST STABLE ORBITALS (I.E., THE ONES CLOSEST TO THE NUCLEUS) ARE FILLED FIRST

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p...

NOTE UNUSUAL ORDERs:

You need to know this

4s<3d<4p and
5s<4d<5p

You will not be examined on this explanation!

4s FILLS BEFORE 3d DUE TO A GREATER PENETRATION OF THE 4s ORBITAL INTO THE INNER "ARGON CORE" [Ar] ELECTRONS, BECAUSE, ON AVERAGE, ELECTRONS IN THE 4s ORBITAL ARE CLOSER TO THE NUCLEUS THAN THOSE IN THE 3d ORBITALS.

SIMILARLY, 5s FILLS BEFORE 4d

SUMMARY OF IMPORTANT POINTS

2. HUND'S RULE IS IMPORTANT IN DETERMINING THE MOST STABLE OR GROUND STATE OF AN ATOM WITH A PARTIALLY FILLED SUBSHELL. THE ATOM WILL ALWAYS CONTAIN THE MAXIMUM NUMBER OF UNPAIRED ELECTRONS (WITH SAME m_s VALUE) TO MINIMIZE INTERELECTRONIC REPULSIONS. (NUMBER OF UN-PAIRED ELECTRONS = "# upe")

EXAMPLES:

EXCITED STATES (VIOLATION OF HUND'S RULE): [↑↓ | ↑↓ |] or [↑↓ | ↑ | ↓]

$_8$O [He] $2s^2 2p^4$

[↑ | ↑ | ↓↑]

most stable $2p^4$ configuration

note that [↑↓ | ↑ | ↑] and [↑ | ↑↓ | ↑] are also equally stable.

$_{23}$V

[Ar] $4s^2 3d^3$ most stable: [↑ | ↑ | ↑ | |]

$3d^3$

3 unpaired electrons

SUMMARY OF IMPORTANT POINTS

3. CORE ELECTRONS ARE SO TIGHTLY HELD BY NEUTRAL OR CATONIC ATOMS THAT THEY ARE NOT LOST OR SHARED IN CHEMICAL REACTONS (EXCEPT WITH THE BARE PROTON, H(1+), A SUPER-REACTIVE SUB-ATOMIC PARTICLE THAT IS ONLY LONG-LIVED IN A HIGH VACUUM)

a. INERT GAS CONFIGURATIONS FOR NEUTRAL AND CATIONIC ATOMS:

TOTALLY INERT TOWARDS CHEMICAL ATTACK UNDER NORMAL CONDITIONS

$_{2}$He $1s^2$ or $_{3}Li^{+}$ $1s^2$

$_{10}$Ne $[He]2s^2 2p^6$ or $_{12}Mg^{2+}$ $[He]2s^2 2p^6$ = "[Ne]"

$_{18}$Ar $[Ne]3s^2 3p^6$ or $_{20}Ca^{2+}$ $[Ne]3s^2 3p^6$ = "[Ar]"

b. COMPLETELY FILLED d-ORBITALS FOR NON-TRANSITION METALS (INCLUDING METALLOIDS AND NON-METALS)

CORE

$_{33}$As $[Ar]4s^2 3d^{10} 4p^3$ $\xrightarrow{-5e^-}$ $[Ar]3d^{10}$

VALENCE

As^{5+} in AsO_4^{3-}

SUMMARY OF IMPORTANT POINTS

4. ELECTRONS ON AN ATOM THAT ARE LOST OR SHARED IN CHEMICAL REXNS ARE CALLED VALENCE ELECTRONS. VALENCE ELECTRONS ARE ALWAYS IN THE OUTERMOST ORBITALS OF AN ATOM.

a. ELECTRONS IN PARTIALLY FILLED SHELLS/SUBSHELLS ON ANY ATOM

$_{25}$**Mn** $[Ar]\ 4s^2 3d^5$ — CORE: [Ar]; VALENCE (7 e): $4s^2 3d^5$

$_{35}$**Br** $[Ar]\ 4s^2 3d^{10} 4p^5$ — CORE: [Ar] $3d^{10}$; VALENCE (7 e): $4s^2 4p^5$

b. ELECTRONS IN COMPLETELY FILLED OUTERMOST SHELLS/SUBSHELLS IN ANIONIC ATOMS

$_1$**H(1-)** [He]-LIKE BUT BOTH ELECTRONS IN $H^{\ominus}$ ARE VALENCE ELECTRONS!

$_7$**N(3-)** $1s^2 2s^2 2p^6$ — CORE: [He] ($1s^2$); VALENCE ELECTRONS: $2s^2 2p^6$

NEON-LIKE, BUT N(3-) CONTAINS 8 VALENCE ELECTRONS — SO N(3-) CAN BE CONVERTED TO NO_3^-, WHICH CONTAINS N(5+), AN 8 ELECTRON OXIDATION!

IMPORTANCE OF VALENCE ELECTRONS:

THE CHEMICAL PROPERTIES OF FAMILIES OF ELEMENTS,E.G., THE ALKALI METALS (GP 1) OR THE HALOGENS (GP 17) ARE OFTEN QUITE SIMILAR BECAUSE THEY HAVE IDENTICAL NUMBERS OF VALENCE ELECTRONS. THESE SIMILARITIES INSPIRED DMITRY MENDELEEV IN THE LATE 19th CENTURY TO CREATE THE PERIODIC TABLE OF THE ELEMENTS.

WE WILL EXPLORE THESE IDEAS NEXT.

ATOMS, VALENCE ELECTRONS, THE PERIODIC TABLE ....WOW!

ATOMIC STRUCTURE, CHEMICAL REACTIVITY AND FAMILIES OF ELEMENTS IN THE PERIODIC TABLE

a. ALKALI METALS (group 1)
(i) ALL HAVE THE ELECTRONIC CONFIG:
[INERT GAS CORE] ns^1 , n>1
(ii) ALL READILY LOSE ONE e(-) IN CHEMICAL REXNS TO PRODUCE SALTS CONTAINING ALKALI METAL CATIONS, M(+).
EXAMPLES:

$_{3}$Li [He] $2s^1$ ← HIGHEST IONIZATION ENERGY

$_{11}$Na [Ne] $3s^1$

$_{19}$K [Ar] $4s^1$

$$M \rightarrow M^+ + e^-$$

$_{37}$Rb [Kr] $5s^1$

$_{55}$Cs [Xe] $6s^1$

$_{87}$Fr [Rn] $7s^1$

$_{119}$Uue* [Uuo] $8s^1$ ← PROBABLY LOWEST IONIZATION ENERGY (OF ANY ELEMENT)

(*unknown to date)

a. SOME CHEMICAL REXNS OF ALKALI METALS

(i) ALL ARE VERY STRONG REDUCING AGENTS AND READILY DISPLACE HYDROGEN GAS FROM WATER TO GIVE ALKALI METAL HYDROXIDES.

e.g.,

$$K(s) + H_2O \xrightarrow{H_2O} K^+(AQ) + OH^-(AQ) + \frac{1}{2}H_2(g)$$

(ii) ALL REDUCE HALOGENS TO GIVE ALKALI METAL HALIDES

$$K(s) + \frac{1}{2}Cl_2 \longrightarrow K^+ \ Cl^-$$

BOTH ARGON-LIKE ELECTRONIC STRUCTURES

(iii) SIMILAR REXNS OCCUR WITH ELEMENTAL S AND P TO PRODUCE EXPECTED SULFIDE, S(2-), AND PHOSPHIDE, P(3-), SALTS

e.g.,

$$2K(s) + \frac{1}{8}S_8 \longrightarrow 2K^+ S^{2-}$$

or

K_2S, where

BOTH K^+ AND S^{2-} ARE STABILIZED BY HAVING AN ARGON-LIKE ELECTRONIC CONFIG. $[Ne]3s^2 3p^6$

b. ALKALINE EARTH METALS (gp 2)
(i) ALL HAVE THE ELECT. CONFIG.:
[INERT GAS CORE] ns ; n>1
(ii) ALL READILY LOSE 2 ELECTRONS IN REXNS TO PRODUCE SALTS CONTAINING M(2+) IONS (HOWEVER, Be(2+) COMPOUNDS ARE OFTEN MUCH LESS IONIC IN CHARACTER THAN ANALOGOUS ONES WITH THE LARGER GP 2 ELEMENTS)

$_{4}$Be [He] $2s^2$ ← WEAKEST REDUCING AGENT OF THE Gp 2 METALS: HIGHEST IONIZATION ENERGIES

$_{12}$Mg [Ne] $3s^2$

$_{20}$Ca [Ar] $4s^2$

$_{38}$Sr [Kr] $5s^2$

$_{56}$Ba [Xe] $6s^2$ ← STRONGEST REDUCING AGENT OF THE NON-RADIOACTIVE GP 2 METALS

$_{88}$Ra [Rn] $7s^2$

$$M \rightarrow M^{2+} + 2e^-$$

Activity Series of Metals

Li
K
Ba
Ca
Na
Mg
Al
Mn
Zn
Cr
Fe
Cd
Co
Ni
Sn
Pb
H_2
Cu
Hg
Ag
Au

EXAMPLE OF REXN OF CALCIUM WITH WATER (SHOWN EARLIER IN CLASS):

$$Ca_{(s)} + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

(CALCIUM HYDROXIDE

Ca^{2+} $2OH^-$

c. HALOGENS (gp 7 or 17)

(i) ALL HAVE THE ELECT. CONFIG:
[INERT GAS CORE] ns^2np^5; n>1 *

* BUT Br + I ALSO CONTAIN $(n-1)d^{10}$ CORE ELECTRONS — e.g.;

Br: [Ar] $4s^2$ $3d^{10}$ $4p^5$
I: [Kr] $5s^2$ $4d^{10}$ $5p^5$
(core)

(ii) ALL READILY GAIN ONE e(-) IN MANY REXNS WITH METALS TO PRODUCE COMPOUNDS CONTAINING HALIDE IONS, OR X(-), WHERE THE LATTER HAS THE FAVORED ELECTRONIC STRUCTURE OF AN INERT GAS

e.g.: $Br + e^- \longrightarrow Br^-$ ⟵ krypton-like — i.e.; [Ar] $4s^2 3d^{10} 4p^6$

(iii) ALL EXCEPT FLUORINE CAN BE OXIDIZED TO PRODUCE CMPDS CONTAINING HALOGENS IN THEIR MAX O.N. OF +7; ESPECIALLY IMPORTANT ONES: THE PER-HALATE ANIONS, $[XO_4](1-)$, PERCHLORATE, PERBROMATE AND PERIODATE ANIONS.

FLUORINE NEVER LOSES ANY VALENCE ELECTRONS IN CHEMICAL REXNS — IN THIS SENSE IT RESEMBLES He, Ne, + Ar

IN THIS FASHION, Cl, Br and I FORMALLY LOSE ALL OF THEIR 7 VALENCE ELECTRONS IN CHEMICAL COMBINATIONS

c. EXAMPLES OF REXNS INVOLVING HALOGENS (NOTE: MOLECULAR HALOGENS, X_2, ARE USED AS SOURCES OF ATOMIC X IN THESE REXNS)

• REDUCTION OF HALOGENS BY METALS (ALL METALS REACT READILY WITH HALOGENS, INCLUDING GOLD, Au, AND PLATINUM, Pt, AT ROOM T.)

EXAMPLE WITH ALUMINUM $Al(s) + \frac{3}{2} F_2(g) \longrightarrow AlF_3$ (CONTAINING $Al(3+)$ AND $3\ F(-)$)

• OXIDATION OF THE HEAVIER HALOGENS IS EASIEST FOR I, MORE DIFFICULT FOR Cl, Br.

OUTERMOST VALENCE ELECTRONS ON IODINE ARE MORE EASILY LOST BY IODINE VS Cl OR Br.

MOST INTERESTING IS THE OXIDATION OF I_2 BY Cl_2 TO PRODUCE PERIODATE SALTS:

I_2 + 7 Cl_2 + 16 OH(-)-----> 2 IO_4(-) + 14 Cl(-) + 8 H_2O

***THIS REXN WILL NOT APPEAR ON AN EXAM!!!

NOTE: IODINE IS A REDUCING AGENT IN THIS REXN! (UNUSUAL FOR A HALOGEN)

d. BRIEF INTRODUCTION TO THE DIMERIZATION REXNS OF ATOMS HAVING UNPAIRED ELECTRONS: THE STRONG TENDENCY OF ESPECIALLY NONMETALLIC ATOMS TO FORMALLY ACHIEVE THE ELECTRONIC CONFIGURATION OF AN INERT GAS BY SHARING OF ELECTRONS!

(i) ATOMS WITH ONE UNPAIRED ELECTRON EACH DIMERIZE TO GIVE A DIATOMIC MOLECULE CONTAINING A SINGLE BOND BETWEEN THE ATOMS:

(a) 2 H• -------> H:H (EACH H ATOM BECOMES "HELIUM-LIKE") or H-H

BY SHARING VALENCE ELECTRONS

(b) 2 :C̈l• -------> :C̈l:C̈l: or :C̈l—C̈l:

EACH Cl BECOMES "ARGON-LIKE" BY SHARING TWO ELECTRONS

(c) H• + :C̈l• -----> H—C̈l: or H:C̈l:

H BECOMES "HELIUM-LIKE"

Cl BECOMES "ARGON-LIKE" BY SHARING ELECTRONS

(ii) ATOMS WITH TWO UNPAIRED ELECTRONS EACH WILL DIMERIZE TO GIVE A DIATOMIC MOLECULE CONTAINING A DOUBLE BOND BETWEEN THE TWO ATOMS:

(a) 2:Ö• -----> 

← Each oxygen becomes neon-like by sharing 4 electrons

(b) 2:Ṡ• ------> 

← S_2 is actually unstable to S_8 at 25°C, 1 atm P.

(iii) ATOMS WITH THREE UNPAIRED ELECTRONS WILL DIMERIZE TO FORM A DIATOMIC MOLECULE HAVING A TRIPLE BOND BETWEEN THE TO ATOMS:

(a) 2 •Ṅ• ------> 

Each N becomes "neon-like" by sharing 6 electrons

(b) 2 •Ṗ• -------> 

Each P atom becomes "argon-like" by sharing 6 electrons in the triple bond. — i.e., Each P is said to satisfy the "octet rule"

WEEK 8
PART 2

CHEM 1061-003 13 MARCH 2015

WEEK 8, PART 2 NOTES

(NOTE: THE 11 MAR LECTURE INVOLVED A REVIEW OF EXAM 2 TOPICS)

AVG SCORE ON EXAM 2: 66%

BRIEF DISCUSSION OF THE EXAM RESULTS

TOPICS TODAY:

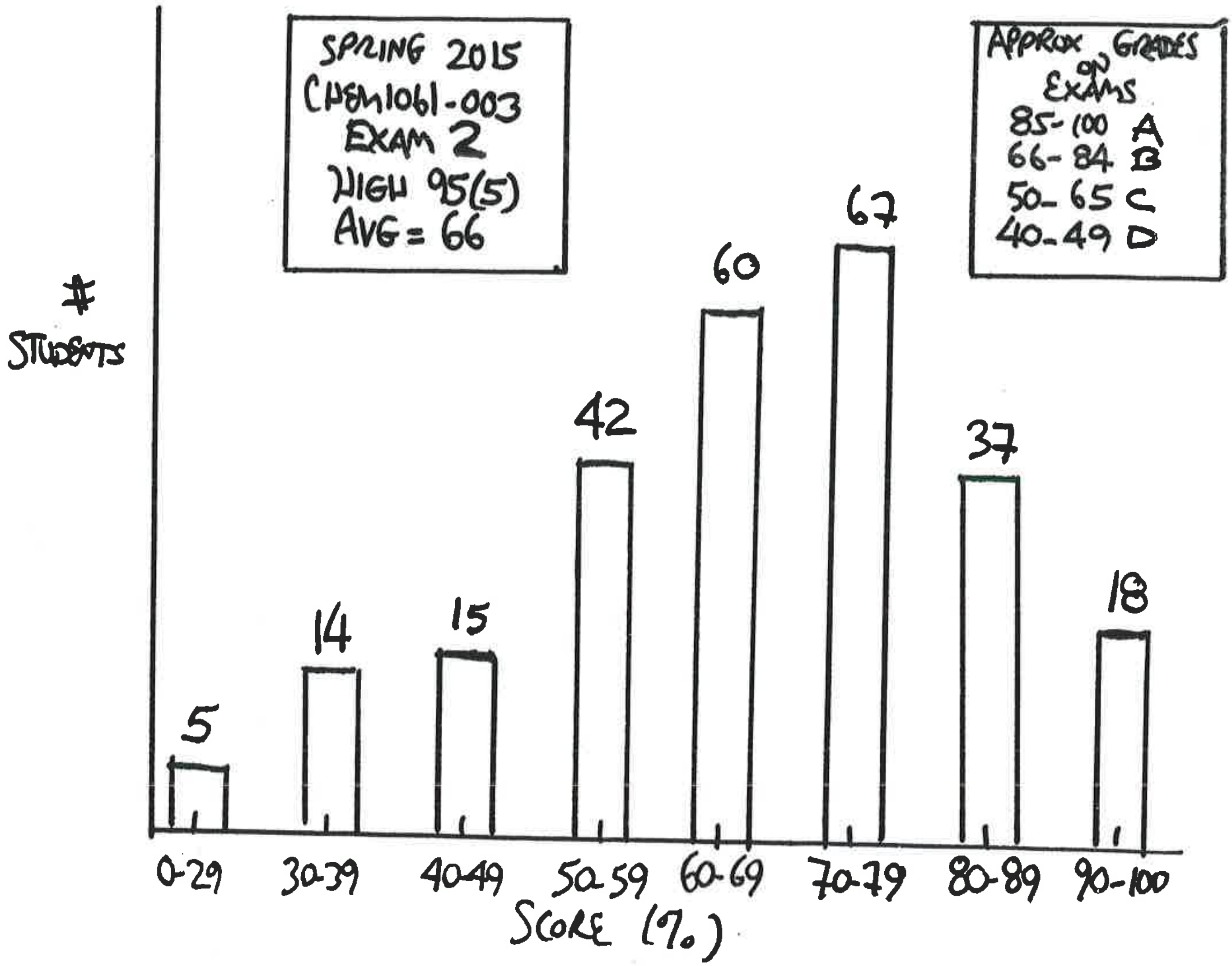
1. FINISH CH 8
   a. GROUND ELECTRONIC CONFIGS OF ATOMIC IONS OF MAIN GROUP (s,p block) ELEMENTS.
   b. IMPORTANT PROPERTIES OF POLYELECTRONIC ATOMS
      (i) SIZE OF NEUTRAL ATOMS
      (ii) IONIZATION ENERGIES OF VALENCE AND CORE ELECTRONS
      (iii) ELECTRON AFFINITY (which is NOT the same as "electronegativity")
      (iv) COMPARISONS OF THE SIZES OF ATOMIC NEUTRALS, CATIONS, AND ANIONS.
2. INTRO TO CH 9: "MODELS OF CHEMICAL BONDING"
   a. IONIC OR ELECTROSTATIC BONDS
   b. COVALENT BONDING
   c. METALLIC BONDING

AFTER BREAK!

DEMO FINALE: ACETONE PEROXIDE BATTLES THE GREEN DRAGON

RESULTS ON EXAM 2 GENERALLY QUITE GOOD- EXCEPT ON Q's INVOLVING MERCURY(I) CHLORIDE, WHICH CONTAINS $Hg_2(2+)$, (Answer was on last page of exam under "Solubility Guidelines") AND SELECTING THE MOST STABLE FORM OF AN ELEMENT AT 25°C (liquid Br_2) AND NOT $I_2(g)$ THIS WAS A DEMO!

ANNOTATED ANSWER SHEET WILL BE POSTED ON/BEFORE MARCH 17 (WITH WEEK 8 NOTES)



HOW ARE YOU DOING SO FAR IN LECTURE?

SUM OF SCORES ON EXAMS 1 AND 2	VERY APPROXIMATE GRADES
171-200	A- TO A
136-170	B- TO B+
100-135	C- TO C+
80-99	D TO D+

IF YOUR TOTAL SCORE IS < 100 YOU WILL NEED TO REDOUBLE YOUR EFFORTS TO RECEIVE A SATISFACTORY GRADE IN 1061

HOWEVER, THERE IS HOPE(!) BECAUSE EXAM 3 AND THE FINAL COUNT FOR 60% OF YOUR TOTAL REMAINING POINTS, SO THERE IS A CONSIDERABLE OPPORTUNITY OF IMPROVING YOUR GRADE. (ESPECIALLY ON THE FINAL, WHICH REPRESENTS 40% OF YOUR SCORE) HOWEVER, BE CAREFUL SINCE MANY OF THE REMAINING TOPICS (CH 8-12, 15) INVOLVE QUALITATIVE OR DESCRIPTIVE ASPECTS OF CHEMISTRY, WHICH MANY OF YOU HAVE STRUGGLED WITH ON 1061 EXAMS.

(FOR EXAMPLE, ON THE 3rd EXAM, ONLY 2-4 QUESTIONS WILL LIKELY REQUIRE A CALCULATOR).

LAST PAGE OF EXAM 2 -4-

Activity Series of Metals

Li
K
Ba
Ca
Na
Mg
Al
Mn
Zn
Cr
Fe
Cd
Co
Ni
Sn
Pb
H_2
Cu
Hg
Ag
Au

ZINC IS A GOOD REDUCING AGENT AND READILY DISPLACES H_2 FROM $H^+(aq)$

Solubility Guidelines for Ionic Compounds in Water

Soluble	Exceptions
NH_4^+	None
Na^+	None
K^+	None
NO_3^-	None
ClO_4^-	None
$C_2H_3O_2^-$	None
Cl^-, Br^-, I^-	Cu^+, Ag^+, Hg_2^{2+}, and Pb^{2+} compounds
SO_4^{2-}	Ba^{2+}, Sr^{2+}, Ca^{2+}, Ag^+, and Pb^{2+} compounds

Hg_2^{2+} GIVES INSOLUBLE Hg_2Cl_2!

Insoluble	Exceptions
OH^-	Li^+, Na^+, K^+, Ba^{2+}, Sr^{2+}, Ca^{2+} compounds
S^{2-}	Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, Li^+, Na^+, K^+, NH_4^+ compounds
CO_3^{2-}	Li^+, Na^+, K^+, NH_4^+ compounds
PO_4^{3-}	Li^+, Na^+, K^+, NH_4^+ compounds

speed of light = $c = 2.9979 \times 10^8$ m/s

Planck's constant = $h = 6.626 \times 10^{-34}$ J•s

$E_n = -2.178 \times 10^{-18}$ J(Z^2/n^2)/atom = -1312.0 kJ (Z^2/n^2)/mol

$E = 1.197 \times 10^5/\lambda$ for E in kJ/mol, λ in nm

$E = 2.31 \times 10^{-19}$ kJ•pm (Q_1Q_2/d); $E_{molar} = 1.39 \times 10^5$ kJ•pm (Q_1Q_2/d).

$PV = nR_{gas}T$

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$R_{gas} = 0.0821$ L•atm•mol^{-1}•K^{-1} = 8.314 J•K^{-1}•mol^{-1}

molar volume of an ideal gas at STP = 22.414 L

STP = 0 °C and 1 atm pressure; 0 K = -273.2 °C

1 atm = 101.3 kPa = 14.7 lb/in^2 = 760 torr

$\Delta H°_{rxn} = \Sigma n_p \Delta H_f°$ (products) - $\Sigma n_r \Delta H_f°$ (reactants)

$\Delta H°_{rxn} = \Sigma BE$ (reactant bonds broken) - ΣBE (product bonds formed)

PERIODIC CHART OF THE ELEMENTS

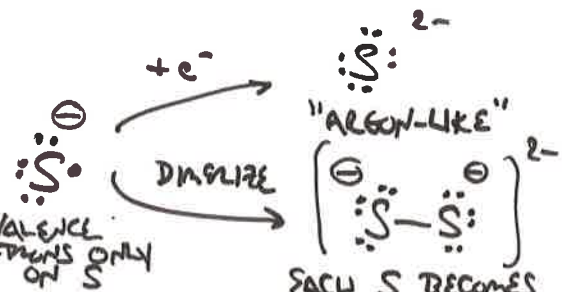
IA IIA IIIB IVB VB VIB VIIB VIII IB IIB IIIA IVA VA VIA VIIA INERT GASES

1 H ... 1 H 2 He

WHY IS Hg^+ UNSTABLE RELATIVE TO Hg_2^{2+}? SAME REASON WHY H• DIMERIZES TO GIVE H_2. BOTH Hg^{+}• AND H• ARE FREE RADICALS!

1. **FOR MAIN GROUP ATOMS (GPS 1A-7A) ELECTRONS ARE REMOVED FROM OR ADDED TO THE VALENCE SHELL OF THE NEUTRAL ATOMS. ALWAYS REMOVE/ADD ELECTRONS FROM/TO THE OUTERMOST SUBSHELL FIRST (np BEFORE ns; ns BEFORE (n-1)d)e.g., 4s BEFORE 3d. EXAMPLES: DETERMINE THE MOST STABLE EC's AND # UPE's OF:**

	EC	#UPE's
$_{12}$Mg(0) - e(-) ------> Mg(+)		
	$[Ne]3s^2 - e^- \longrightarrow [Ne]3s^1$	1
$_{16}$S(0) + e(-) ------> S(-)		
	$[Ne]3s^2 3p^4 + e^- \longrightarrow [Ne]3s^2 3p^5$ (CHLORINE-LIKE) or	
$_{31}$Ga(0) - 2 e(-)-----> Ga(2+)		
	$[Ar]4s^2 3d^{10} 4p^1 \xrightarrow{-2e^-} [Ar]4s^1 3d^{10}$	1
$_{34}$Se(0) - e(-) ------> Se(+)		
	$[Ar]4s^2 3d^{10} 4p^4 \xrightarrow{-e^-} [Ar]4s^2 3d^{10} 4p^3$	3



For Ga: CORE (n = 3 SHELL FILLED ENTIRELY)

d SUBSHELL REMAINS FILLED (DUE TO SPECIAL STABILITY OF COMPLETELY FILLED n = 3 SHELL)

For Se: HUND'S RULE PREDICTS THE HALF-FILLED 4p SUBSHELL WILL HAVE 3 SPIN ALIGNED ELECTRONS IN DIFFERENT ORBITALS ; i.e.

2. THE MOST STABLE IONS IN CMPDS OF MAIN GROUP ELEMENTS (s,p- BLOCK) HAVE EITHER NOBLE GAS OR "PSEUDO-NOBLE GAS" EC's, e.g. [Ar]$3d^{10}$

RESULTS:

(i) Gp 1A , 2A METALS AND ALUMINUM ARE REDUCING AGENTS IN MOST OF THEIR CHEMISTRY

ALSO: $_{30}Zn$

[Ar] $4s^2$ $3d^{10}$ (valence electrons: $4s^2$; core electrons: [Ar] $3d^{10}$)

$\xrightarrow{-2e^-}$ [Ar] $3d^{10}$ = Zn^{2+} ⟸ MOST STABLE FORM OF Zn^{2+} IS DIAMAGNETIC, WITH $3d^{10}$ SUBSHELL

$\not\rightarrow$ [Ar] $4s^2 3d^8$ ⟵ THIS HIGHLY UNSTABLE FORM OF Zn^{2+} WOULD BE PARAMAGNETIC WITH 2 UNPAIRED ELECTRONS IN THE $3d^8$ SUBSHELL

(ii) Gp 6A and 7A NONMETALS ARE OXIDIZING AGENTS WHEN THEY REACT WITH METALS

ALSO NOTE:

$_6C$ [He] $2s^2 2p^2$

$_{14}Si$ [Ne] $3s^2 3p^2$

$_{32}Ge$ [Ar] $4s^2$ $3d^{10}$ $4p^2$ (core: [Ar] $3d^{10}$)

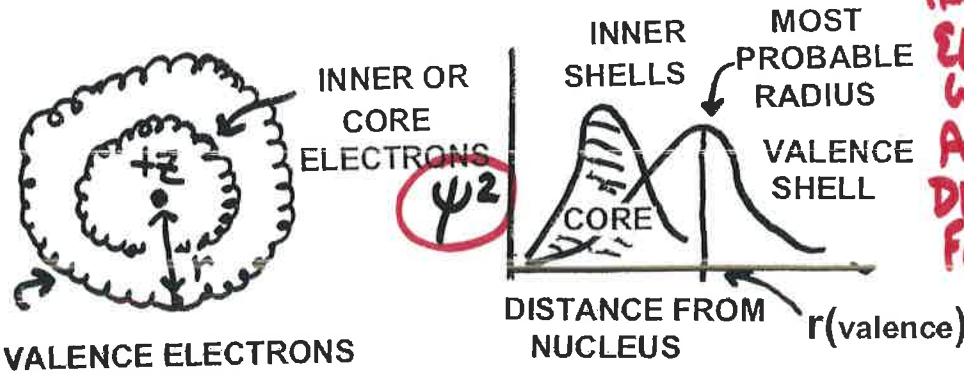
$_{50}Sn$ [Kr] $5s^2$ $4d^{10}$ $5p^2$ (core: [Kr] $4d^{10}$)

$_{82}Pb$ [Xe] $6s^2$ $4f^{14} 5d^{10}$ $6p^2$ (core: [Xe] $4f^{14} 5d^{10}$)

THUS, ALL GP 4 (14) FAMILY OF ELEMENTS HAVE THE SAME NUMBER AND TYPES OF VALENCE ELECTRONS: $ns^2 np^2$

ψ^2 : "psi 2" PROBABILITY THAT AN ELECTRON WILL BE A CERTAIN DISTANCE FROM THE NUCLEUS

3. ATOMIC SIZE IS DETERMINED BY THE DISTANCE OF THE OUTERMOST ELECTRONS FROM THE NUCLEUS



"CARTOON" OF ELECTRON SHELLS IN ATOM

E.g., $_3Li$ $1s^2 2s$ — $1s^2$: CORE; $2s$: VALENCE

a. FOR ATOMS OF THE SAME FAMILY OF ELEMENTS (GP 1, GP 2, ETC) AND CHARGE, Q, THE ATOMS BECOME LARGER AS ONE GOES DOWN A COLUMN: E.G.,

Li < Na< K < Rb < Cs (largest)

OUTERMOST (VALENCE) ORBITAL: 2 3 4 5 6

b. FOR ATOMS OF SAME CHARGE, Q, AND SAME SHELL (value of n) THE ATOMS BECOME SMALLER AS THE NUCLEAR CHARGE, Z, INCREASES; E.G.,

Li> Be> B> C> N > O> F > Ne (smallest)

n = 2 SHELL

Z = +3   Z = +10

TRENDS IN ATOMIC RADII OF NEUTRAL ATOMS

NOTE THE LARGEST ATOMS FOR A GIVEN SHELL

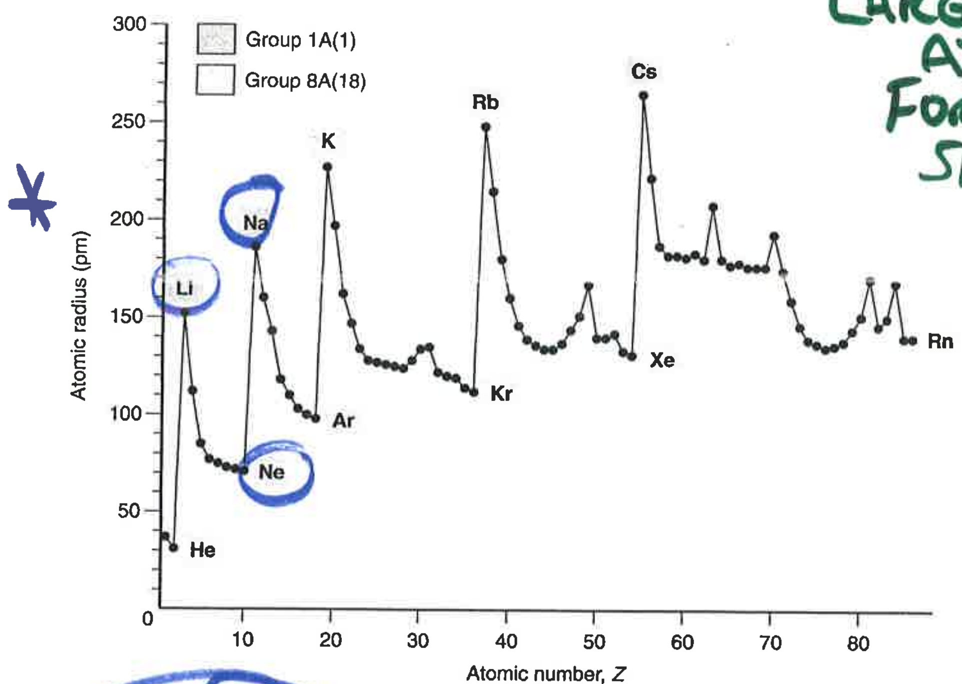


FIG. 8.16 Periodicity of atomic radius. A plot of atomic radius of elements in periods 1-6 shows a periodic change: the radius usually decreases through a period (except for transition metals-don't worry about these!) to the noble gas and then increases suddenly at the next alkali metal

BOTTOM LINE: FOR A GIVEN SHELL OR PERIOD (value of n) GP 1 METALS ARE THE LARGEST AND NOBLE GASES ARE THE SMALLEST FOR NEUTRAL ATOMS

* PM = PICOMETER = 10^{-12} METER

"1 TRILLIONTH" OF A METER

MORE CONVENTIONAL DIAGRAM SHOWING THE CHANGE IN ATOMIC RADII AS THE NUCLEAR CHARGE INCREASES ACROSS A SHELL

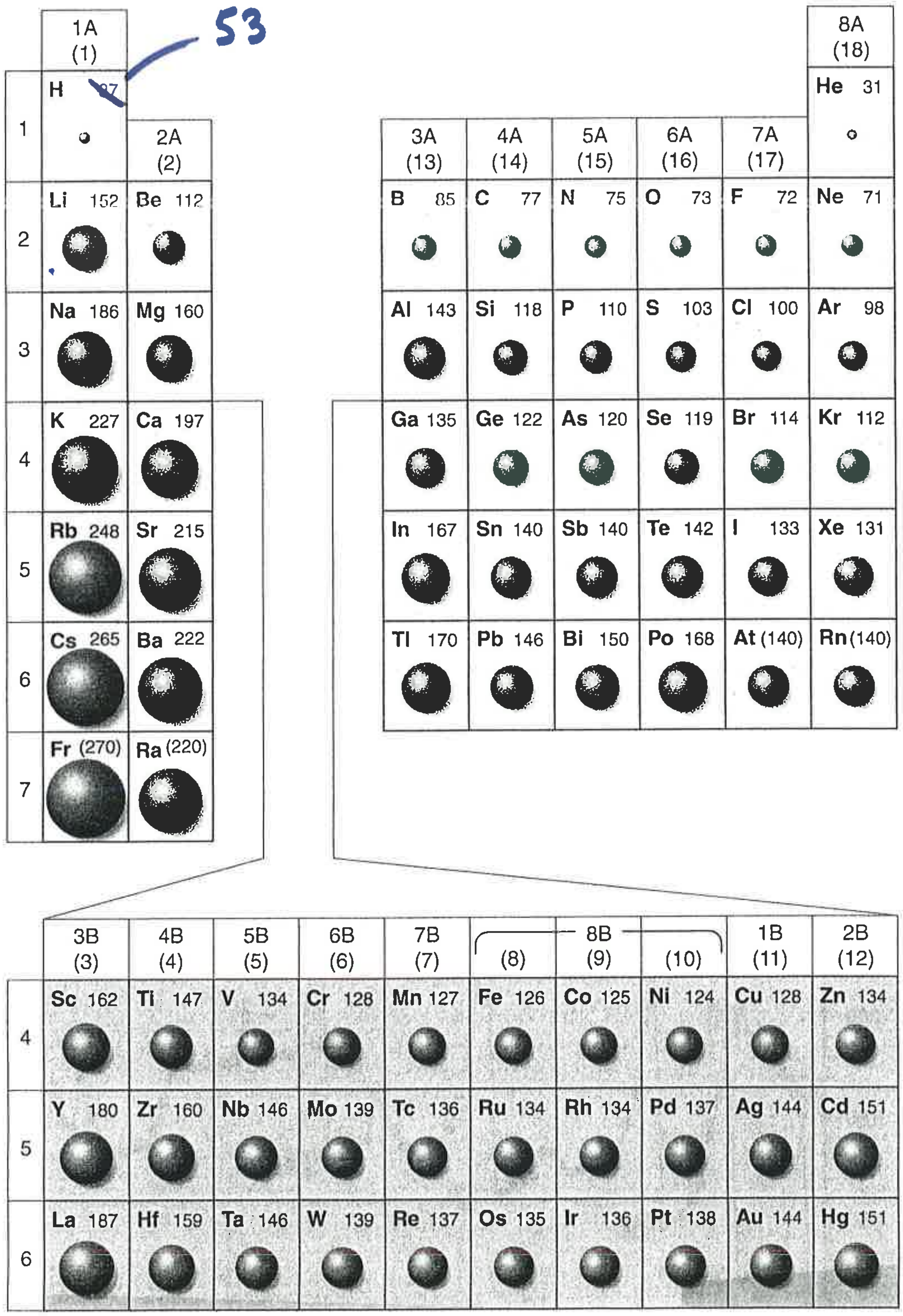


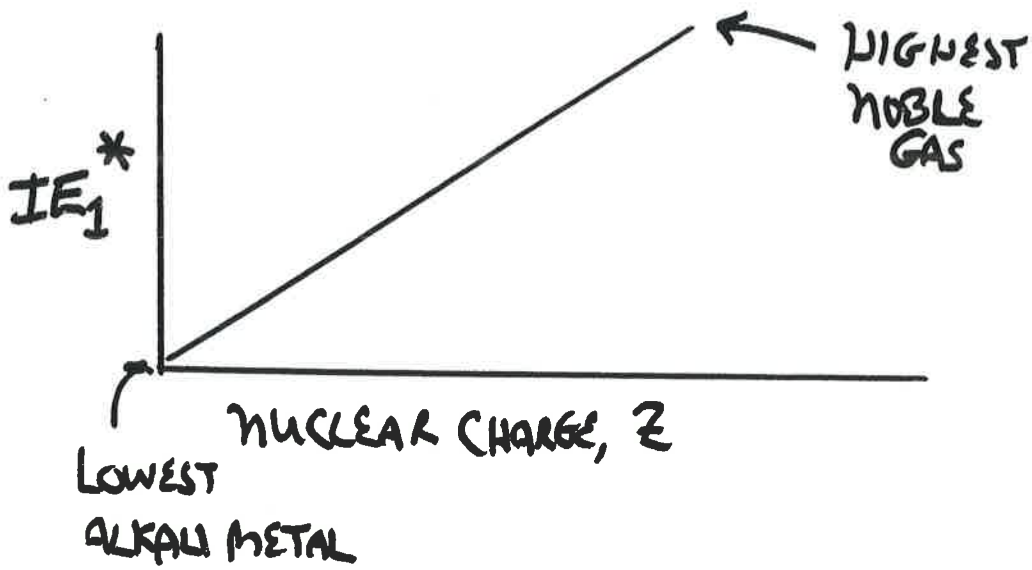
Figure 8.15 Atomic radii of the main-group and transition elements.

RADII IN PICOMETERS = 10^{-12} m

4. FIRST IONIZATION ENERGY, IE_1, IS THE ENERGY REQUIRED TO REMOVE THE WEAKEST BOUND OR OUTERMOST ELECTRON FROM AN ATOM IN THE GAS PHASE. THIS VALUE IS ALWAYS POSITIVE (REQUIRES ADDITION OF ENERGY) FOR NEUTRAL ATOMS RECALL $H\cdot_{n=1} \longrightarrow H^+ + e^-$ $IE_1 = +1312$ kJ/mol

A(g) ------> A(+) + e(-) ; $IE_1 > 0$

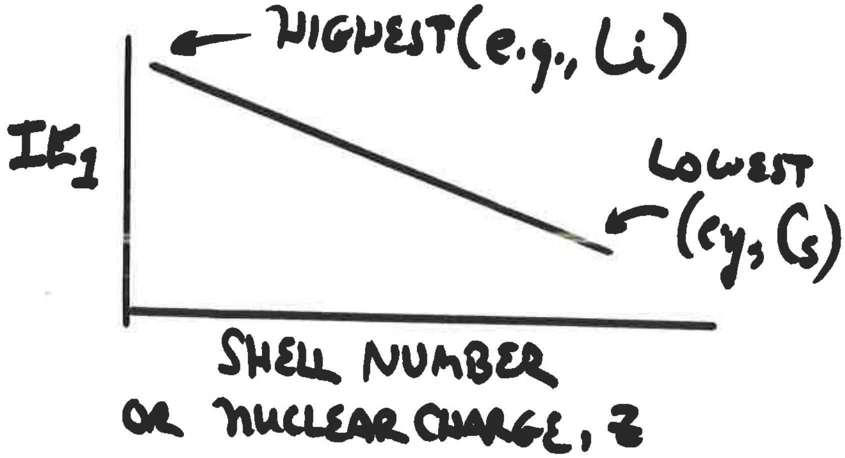
a. TRENDS FOR IE_1 VALUES FOR MAIN GROUP ATOMS ACROSS A ROW



*THERE ARE SOME EXCEPTIONS IN IE_1 TRENDS NOT SHOWN IN THIS PLOT, DUE TO THE SPECIAL STABILITY OF HALF-FILLED np SUBSHELLS IN ATOMS (WE WILL ONLY WORRY ABOUT N vs O)

b. TRENDS FOR IE_1 OF MG ELEMENTS DOWN A COLUMN OF THE PERIODIC TABLE

IE_1	
H	1312 kJ/mol
Li	520 "
Na	496 "
K	419 "
Rb	403 "
Cs	376 "



THUS, AS THE VALUE OF n INCREASES, THE OUTERMOST ELECTRONS BECOME LESS TIGHTLY BOUND TO THE ATOM. IE_1 TRENDS DOWN A COLUMN: (AS SHELL # INCREASES)

CALLING HYDROGEN A GP 1 ELEMENT

H >> Li > Na > K > Rb > Cs

* 1681 kJ/mol → F > Cl > Br > I > At

He> Ne > Ar > Kr > Xe > Rn

* 2372 kJ/mol *2080 kJ/mol

NEUTRAL * ATOMS WITH HIGHEST IE_1 VALUES!

YOU SHOULD REMEMBER THAT He HAS THE HIGHEST IE_1 OF ANY NEUTRAL ATOM!

PLOT OF IE_1 OF GASEOUS ATOMS AS A FUNCTION OF ATOMIC NUMBER

$$A(g) \text{ ----------> } A(+) + e(-) \quad \Delta E = IE_1$$

SHELL #	NOBLE GAS
1	He
2	Ne
3	Ar
4	Kr
5	Xe
6	Rn

H.

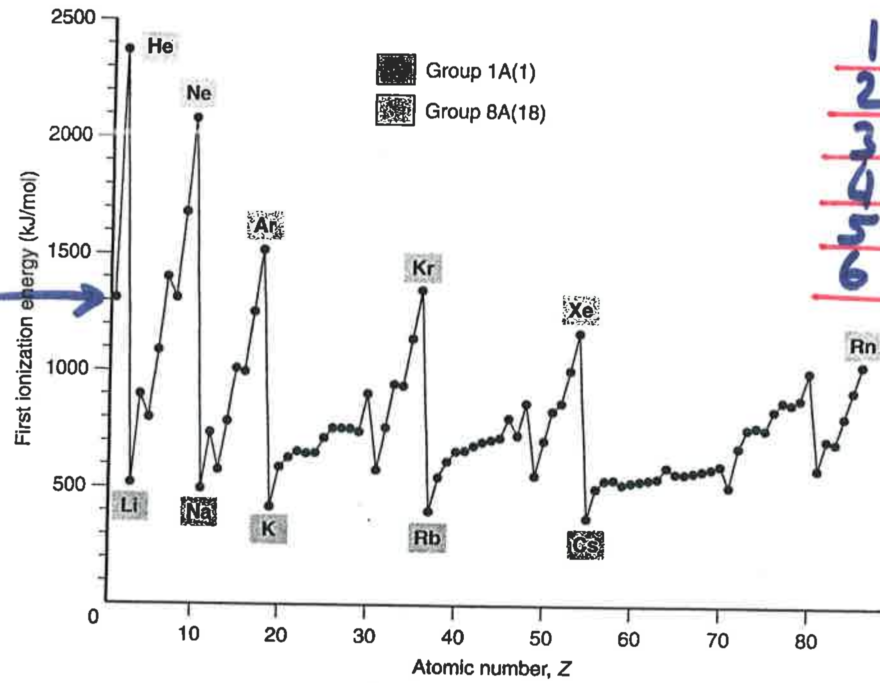
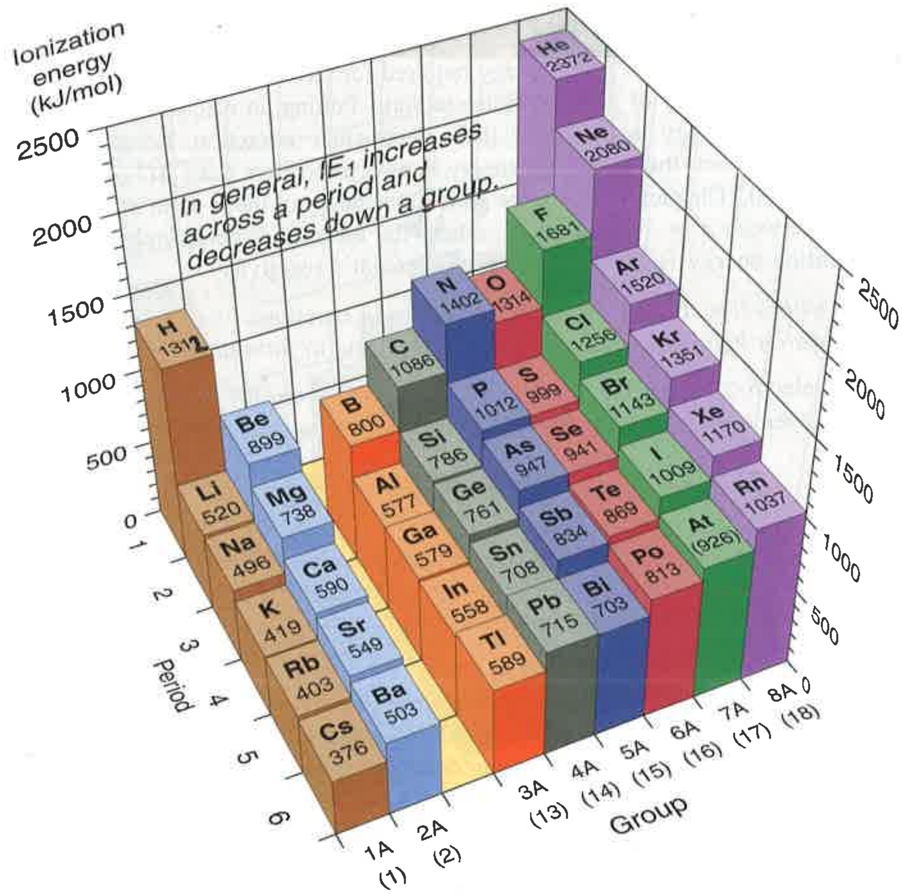


Fig. 8.17 A plot of IE_1 VS ATOMIC NUMBER FOR THE ELEMENTS OF PERIODS 1-6 SHOWS A PERIODIC PATTERN: THE LOWEST VALUES OCCUR FOR GP 1 METALS AND THE HIGHEST FOR THE NOBLE GASES. NOTICE THE "FUNNY BUSINESS" IN Be vs B and N vs O.

NOTE THAT IE_1 VALUES FOR THE NOBLE GASES ARE ALWAYS THE HIGHEST FOR A GIVEN SHELL (n = 1, 2, 3 . . . etc.) – ATTESTING TO THEIR ESPECIALLY STABLE ELECTRONIC GROUND STATES

SIMILAR PLOT OF IE₁ VS Z SHOWING DIFFERENCES OF IE₁ WITHIN COLUMNS (FAMILIES OF ELEMENTS)



*NOTE THE UNUSUALLY HIGH IE₁ OF ATOMIC N, ARISING FROM THE SPECIAL STABILITY OF ITS HALF-FILLED 2p SUBSHELL

- K+

SAMPLE QUESTIONS:

PREDICT WHICH ATOM HAS THE LARGEST IE_1 VALUE (THIS IS THE ATOM THAT IS MOST DIFFICULT TO IONIZE)

(i) B, O, or F

HIGHEST VALUE OF Z

(ii) N, P, or As

LOWEST VALUE OF n

(iii) C, N, or O (careful!)

ESPECIALLY STABLE $2p^3$ SUBSHELL OF ATOMIC $N^{(0)}$ GIVES IT AN UNUSUALLY HIGH IE_1 VALUE

ALSO, ONE MAY CONSIDER THE IE_1 OF ATOMIC O TO BE RELATIVELY LOW BECAUSE WHEN IT LOSES AN ELECTRON, THE PRODUCT O^+, HAS AN ESPECIALLY STABLE HALF-FILLED $2p^3$ SUBSHELL, LIKE NEUTRAL N!

IMPORTANT!!

COMPARISON OF IONIZATION ENERGIES OF CORE AND VALENCE ELECTRONS

EXAMPLE: Na and Mg (VALUES IN kJ/mol)

IE_n n =	1	2	3 ....
Na [Ne]$3s^1$	496	4560	......
Mg [Ne]$3s^2$	738	1445	7330

VALENCE | CORE

NET RESULTS:

Na(0) -------> Na(+) + e(-) ; IE_1 VALENCE ELECTRON REMOVAL (OK!)

Na(+) --X--> Na(2+) + e(-) ; IE_2 TOO HIGH!

Mg(0) -------> Mg(1+) + e(-); IE_1 } REMOVAL OF VALENCE e^-

Mg(+) -------> Mg(2+) + e(-); IE_2 }

Mg(2+)--X--> Mg(3+) + e(-); IE_3 TOO HIGH!

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CONCLUSIONS:

IONIZATION ENERGIES FOR REMOVAL OF CORE ELECTRONS ARE SO HIGH THAT THE MAX POSSIBLE O.N.'s OF AN ATOM IN A CMPD NEVER EXCEEDS ITS "GROUP FAMILY NUMBER"

	1A	2A	3A	4A	5A	6A	7A	8A
n = 5	Rb	Sr	In	Sn	Sb	Te	I	Xe
MAX O.N.	+1	+2	+3	+4	+5	+6	+7	+8

HOWEVER, THE IONIZATION ENERGIES FOR VALENCE ELECTRONS OF THE FOLLOWING ATOMS ARE SO HIGH THAT THEY NEVER ACHIEVE MAX. O.N.'s IN COMPOUNDS:

He, O, F, Ne, Ar, Kr ← all are noble gases, except for O + F!

EXAMPLES:

(1/8) S_8 + xcess F_2 -------> SF_6

BUT O_2 + xcess F_2 -------> no rexn (20°C)

Xe + xcess F_2 ------> XeF_2(20°C, sun)

BUT Kr +xcess F_2 ---->no rexn (20°C)

For F: The max O.N. of Fluorine in compounds is always −1 (by definition!)

DEMO FINALE FOR SPRING BREAK!!!!!

ACETONE PEROXIDE BATTLES THE "GREEN DRAGON" FOR FLAME AND GLORY.

LET'S HOPE THAT OUR GREEN DRAGON DOES NOT FIZZLE OUT (OR THAT THE HIGH HEAT PRODUCED, GIVING "YELLOW LIGHT," OVERWHELMS OR OBSCURES THE GREEN LIGHT!)

IGNITION OF A TRAIL OF ACETONE PEROXIDE MEETS UP WITH A BALLOON CONTAINING TRIMETHYLBORATE, AKA, OUR RATHER WIMPY VERSION OF THE "GREEN DRAGON"

DEMO GETS A GRADE OF C+ - IT WAS TOO HOT!

HEY, ALL OF YOU HAVE A FANTASTIC BREAK!!! SOME OF YOU MIGHT EVEN "THINK GOOD THOUGHTS ABOUT CHEMISTRY"

* IN FACT, THE FLAME FROM THE BALLOON WAS A "WASHED-OUT" GREEN (MAINLY YELLOW) – BUT WHEN THE GREEN BALLOON BROKE, LIQUID B(OMe)$_3$ DID GIVE A GREEN FLAME (ON THE CARPET) AS IT BURNED, SO THE DEMO WAS A C+ ...