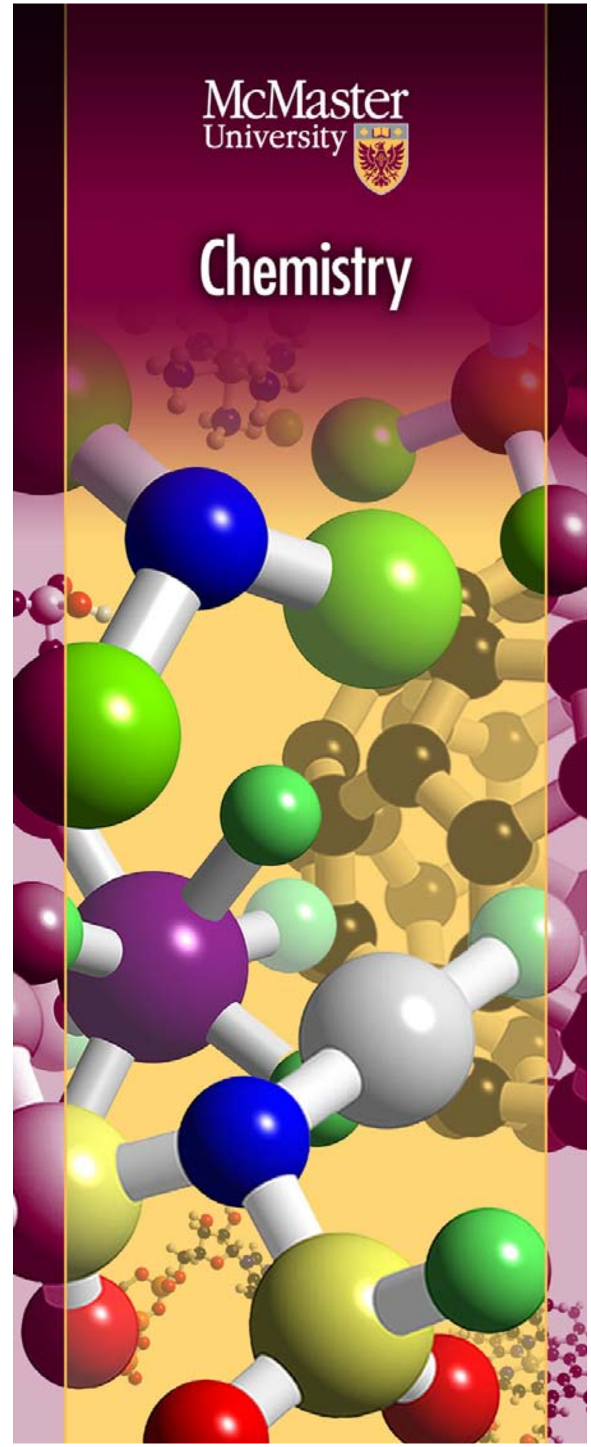
CHEM 1A03: Intro. Chemistry I



Essential Elements: Chemistry, Life & Health

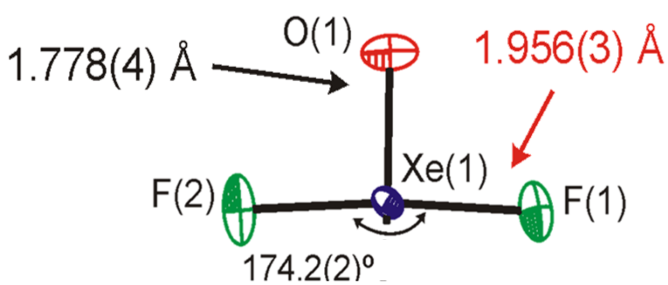
Ch.9: The Periodic Table and Some Atomic Properties

Noble gases, Group 18 (8A)

- *ns*^{2}*np*^{6} stable electron configurations
- Other elements try to attain these configurations

- Considered chemically “inert” until 1962
  - many noble gas compounds known, including
    e.g. KrF_2, XeF_2, XeF_4, XeF_6
    XeO_3, $XeOF_2$#, $XeOF_4$, XeO_2F_4

Much of this research based at McMaster!

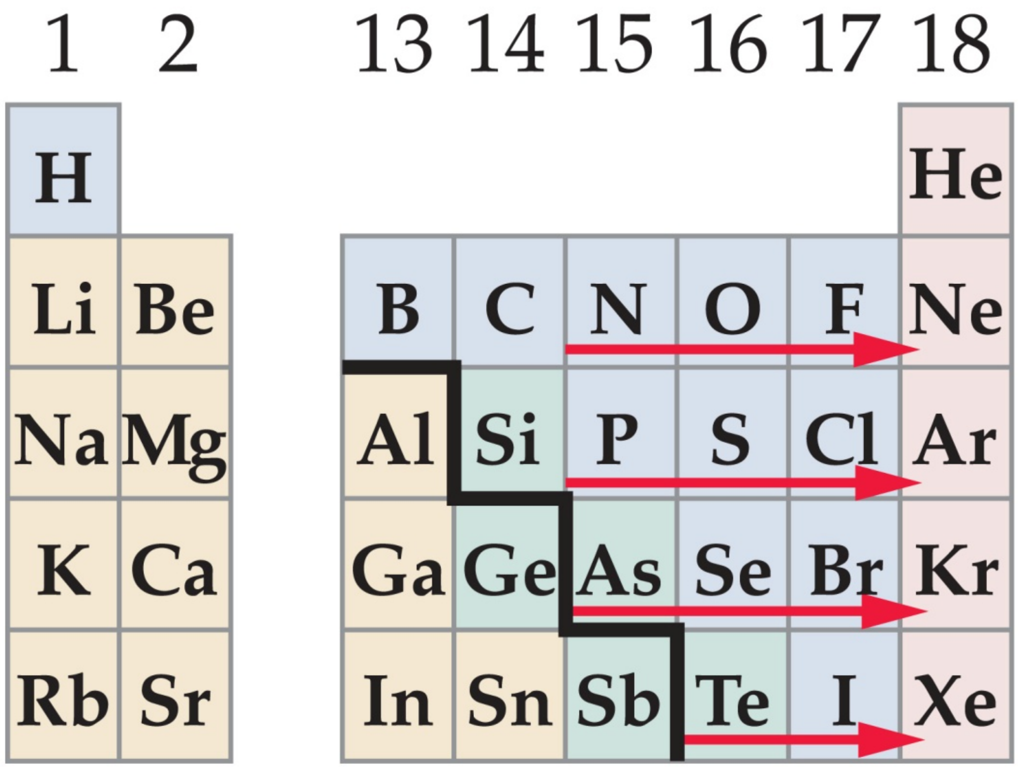


p. 365 (344, 9th ed.)

#**Brock, D. S., *et al.*, *J. Am. Chem. Soc.*, *129*, 2007, 3598-3611.**

Non-metals

- Main group (s and p block) non-metals tend to gain electrons



p. 366 10th (345, 9th ed.)

Example: Descriptive Halogen Chemistry

1) Ability to <u>oxidize</u> increases up the group (towards F). For example:

YES: $Cl_2(g) + 2\ I^-(aq) \rightarrow I_2(aq) + 2\ Cl^-(aq)$

NO: $Br_2(l) + Cl^-(aq) \rightarrow$ no rxn

Fig. 9-17 (9-16, 9^{th} ed.)

2) They react with metals to form salts! e.g. NaCl

$2\ Na(s) + Cl_2(g) \rightarrow 2\ NaCl(s)$

Fig. 9-16 (9-15, 9^{th} ed.)

p. 384 10^{th} (362, 9^{th} ed.)

Example: Descriptive Halogens Chemistry

3) Halogen mp/bp increases down group 17A (more on this in Ch 12 – Chem 1AA3)

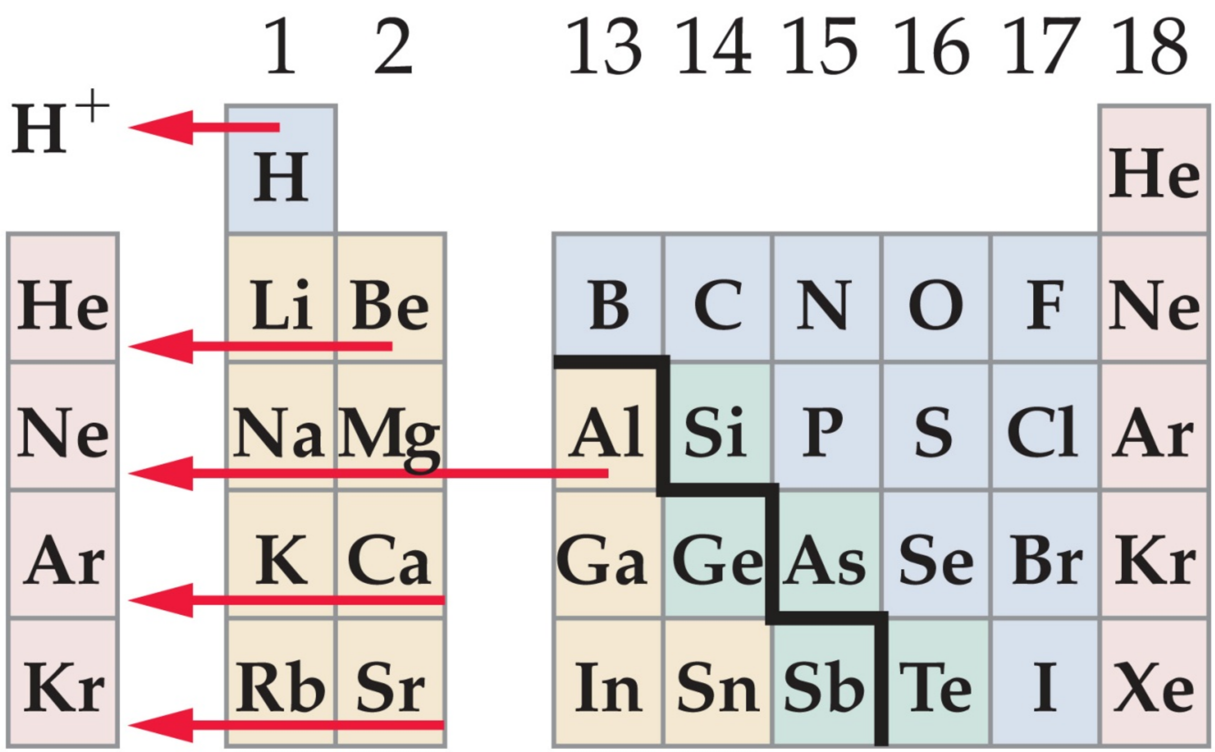
Cl_2(g), Br_2(l), I_2(s)

Fig. 9-13 (9-12, 9th ed.)

p. 382 (360, 9th ed.)

Metals

- Main group (s and p block) metals (and H) tend to lose electrons



p. 365 (344, 9th ed.)

Example: Group 1 and 2 metals

- Alkali metals (Group 1) oxidize more readily than alkaline earth metals (Group 2)
- Both oxidize easily in water [Fig. 9-15 (9-14, 9th ed.)]

(a)

K

(b)

Ca, with added phenolphthalein

Make sure you can write these reactions!

p. 384 (361, 9th ed.)

General trends in physical properties

Across a period:

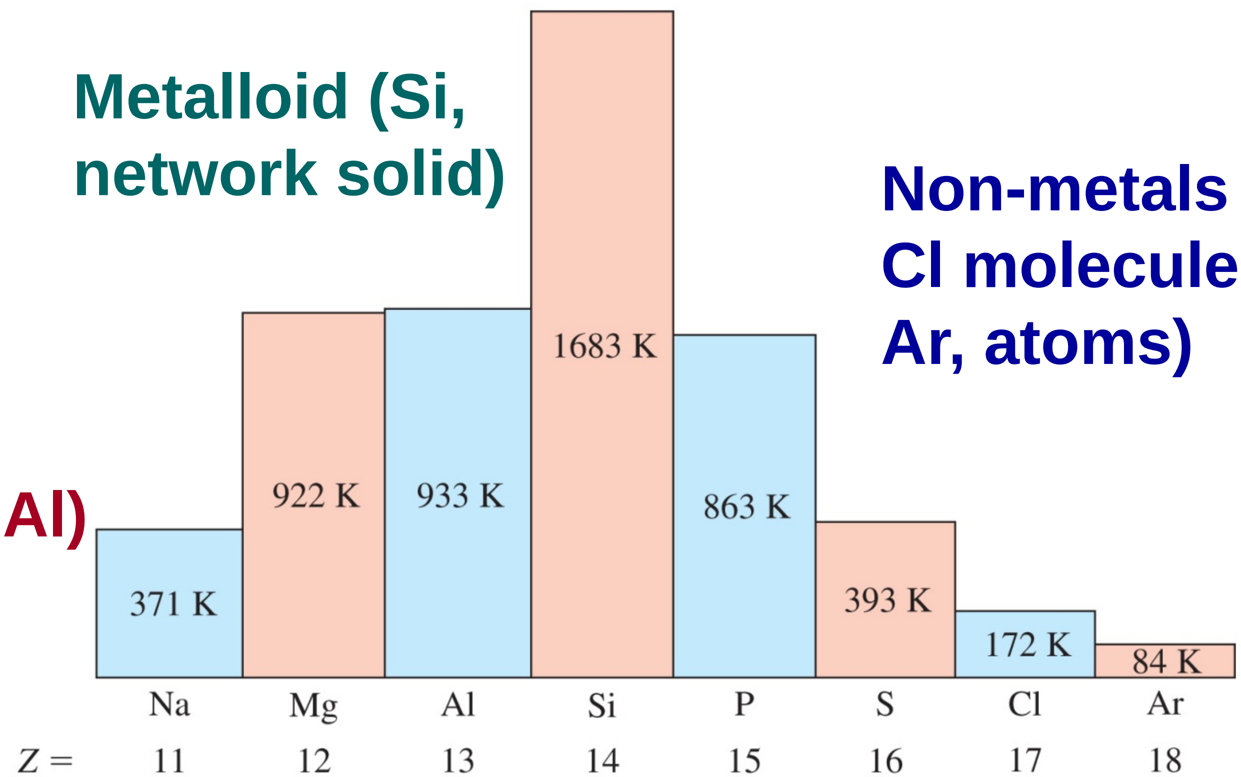
– Metallic properties <u>decrease</u>

– melting point (mp) <u>varies</u> with **type of bonding:**

Metalloid (Si, network solid)

Non-metals (P, S, Cl molecules, and Ar, atoms)

Metals (Na, Mg, Al)



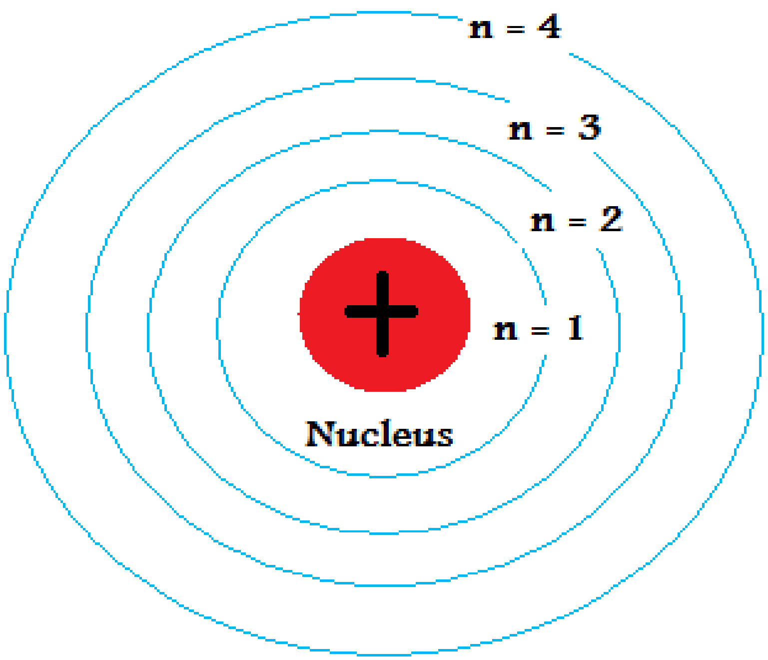
p. 382 (360, 9th ed.)

Fig. 9-14 (9-13, 9th ed.)

A key idea for periodic trends:

- How are electrons held?

- Electrostatic interactions of the nucleus (positive) and electrons (negative)



$$E = \frac{k\,Q_{nucleus}}{r^2}$$

E = electric field
$Q_{nucleus}$ = Charge on nucleus
r = electron distance

A key idea for periodic trends:

- As ***r*** increases (electrons are placed in further shells, n increases), electric field decreases and valence electrons are not held as strongly
- As we go across a period, ***r*** remains relatively constant, but $\boldsymbol{Q_{nucleus}}$ increases with greater number of protons. Thus electric field increases and valence electrons are held more strongly

A key idea for periodic trends: Screening

- Outer e^- of an atom are screened by the core e^- from feeling the full attractive charge (Z) from the nucleus

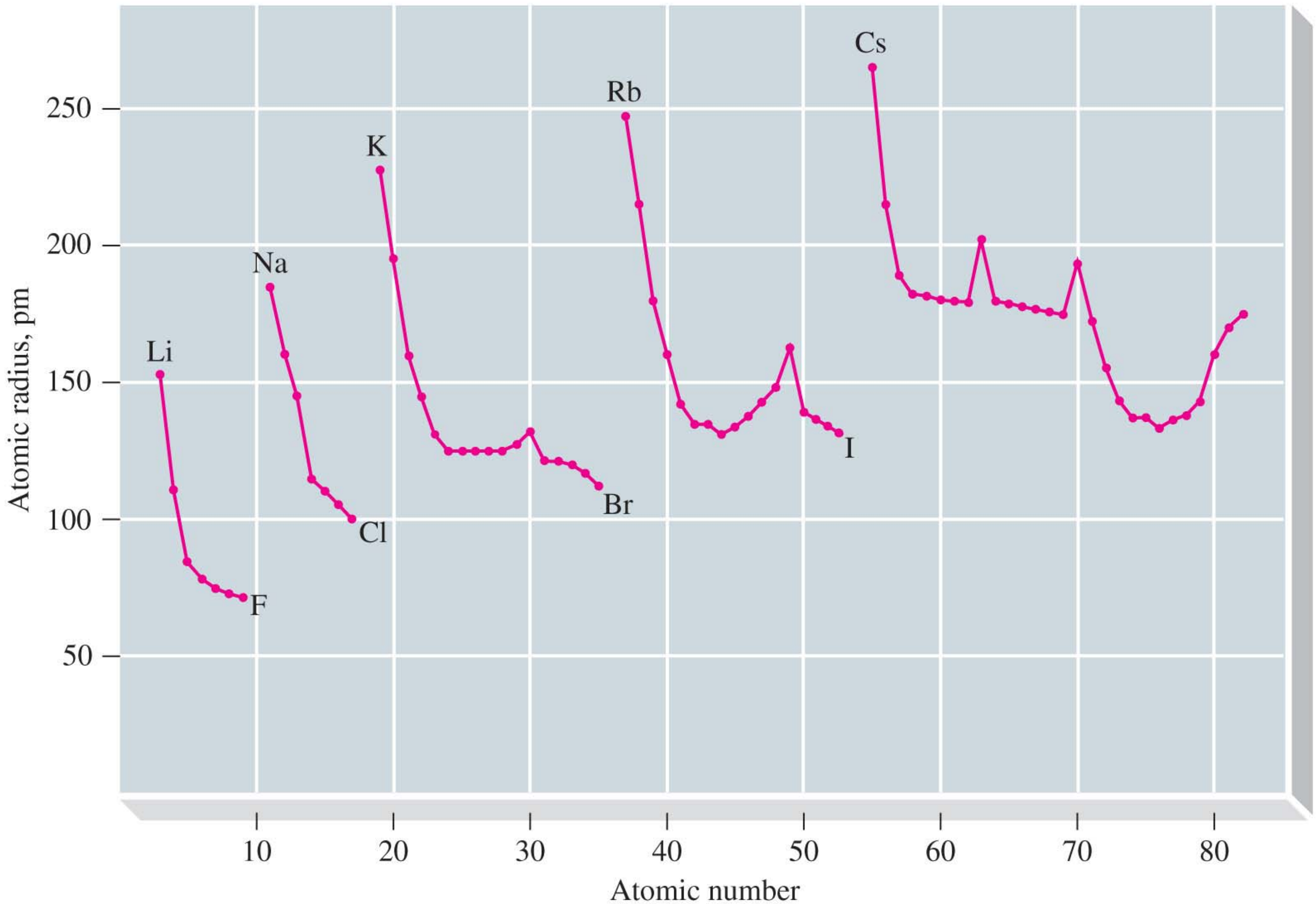
- Outer e^- feel an effective nuclear charge, $Z_{effective}$

- Simply, $Z_{eff} = Z - S$, where S = # core e^-

- In reality, s, p and d e^- are screened to different extents; outer e^- also screen each other
  [note: omit eq. 9.5]

p. 368 (348, 9th ed.)

Atomic radius (Fig. 9-4)



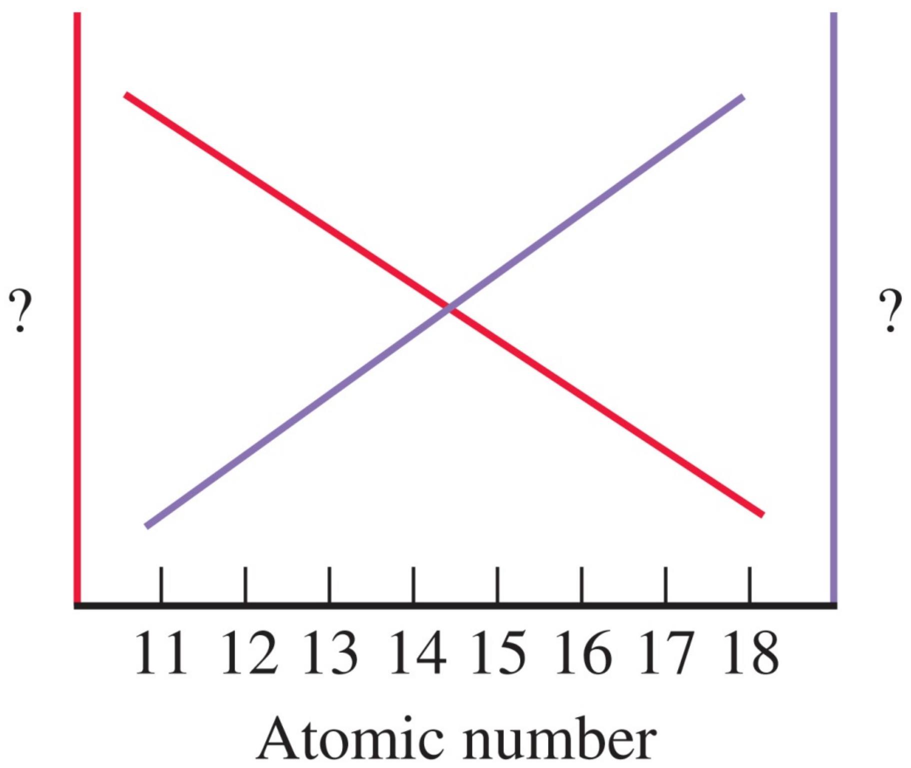
p. 367-371 (347-350, 9th ed.)

Atomic radius – general trends

- Decreases across a period
  - Z increases, but e^- are added to same n valence shell
  - These outer e^- feel stronger attraction to nucleus (higher Z_{eff})
- Increases down a group
  - e^- are added to new n shells
  - On average e^- are farther away but Z_{eff} does not change much down a group, thus valence e^- have weaker attraction to the nucleus

i-Clicker Question #1

The graph below represents the variation of Z_{eff} and atomic radius with atomic number. Which axis (and line) corresponds to Z_{eff}, which to atomic radius?

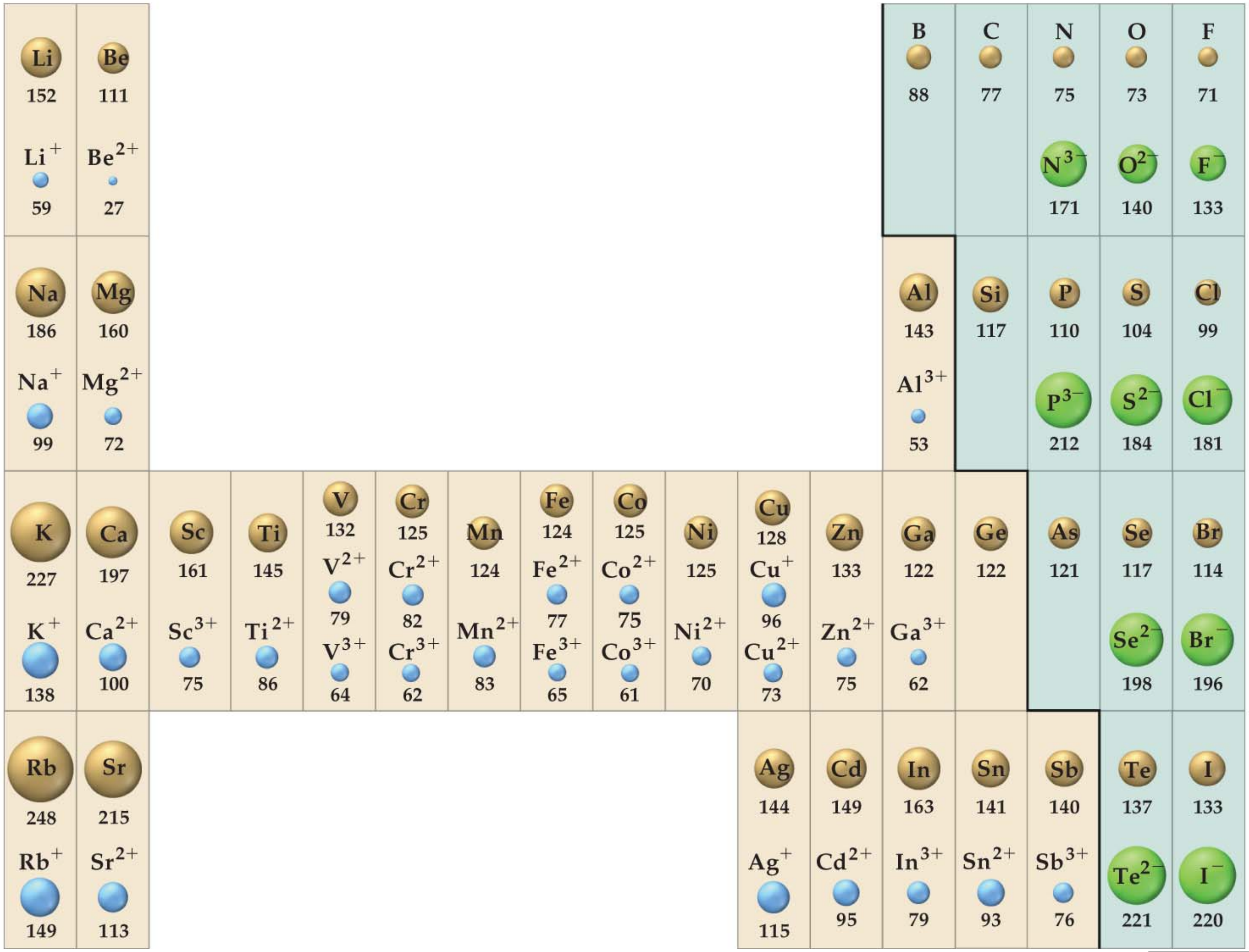


(a) Red line – Atomic radius
Grey line – Z_{eff}

(b) Red line – Z_{eff}
Grey line – Atomic radius

(c) None of the above is correct

Ionic radius - Fig. 9-9 (9-8, 9th ed.)



p. 372-374 (351-352, 9th ed.)

Ionic radius – general trends

- Cations <u>smaller</u> than their neutral atoms
  - Same Z but as remove e^- less repulsion/screening
  - Might even remove all e^- from valence shell

    e.g. r_{Na} = 186 pm r_{Na+} = 99 pm

- Anions <u>larger</u> than their neutral atoms
  - Same Z but as add e^- increase repulsion/screening

    e.g. r_F = 71 pm r_{F-} = 133 pm

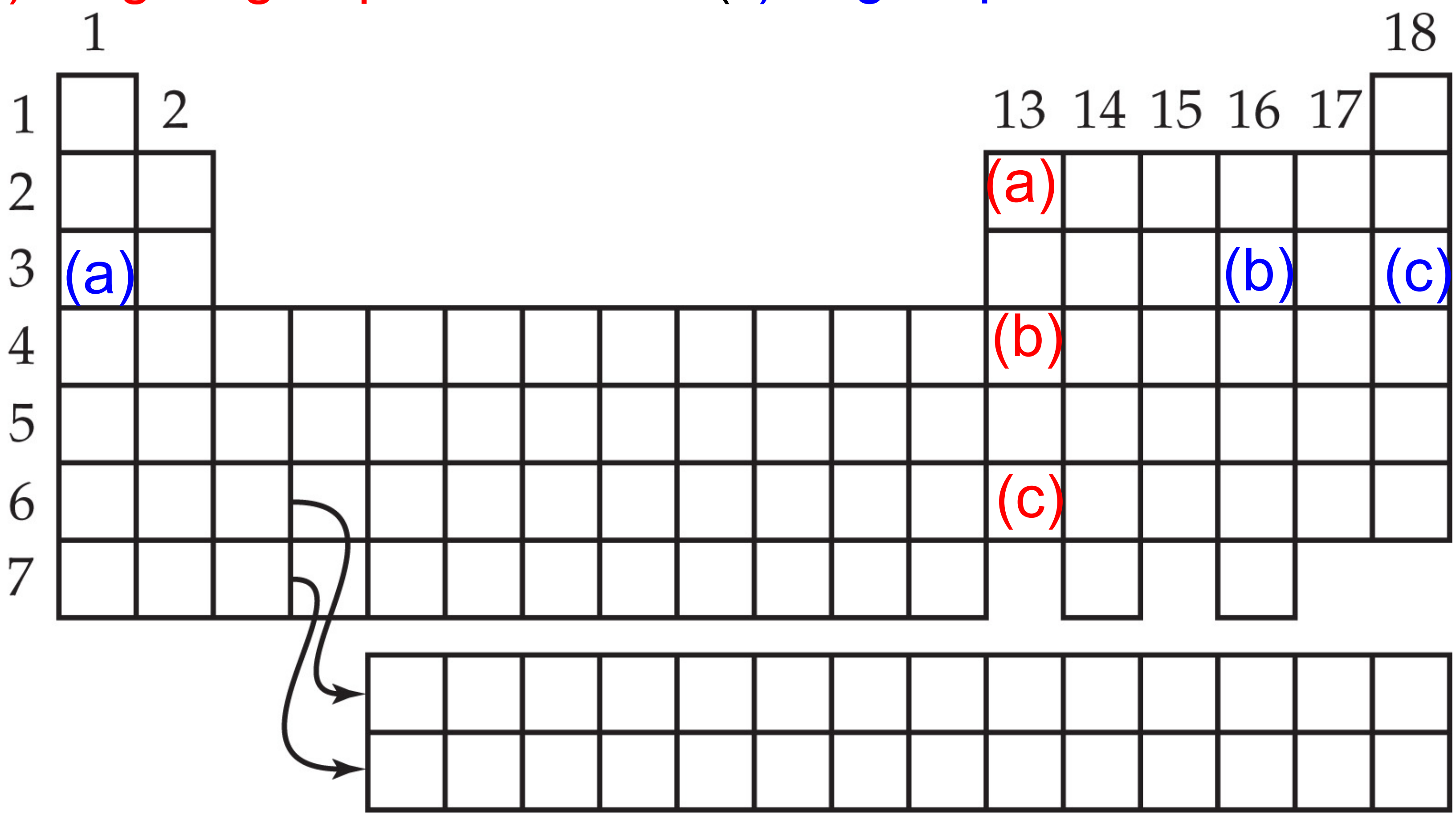
- Isoelectronic ions/atoms
  - Size decreases as Z increases

    e.g. F^- > Ne > Na+

i-Clicker Question #2

On the blank periodic table, locate:

(i) largest group 13 atom (ii) largest period 3 atom



p. 373 (352, 9th ed.)

Essential Elements: Tooth Enamel

- Principal mineral in tooth enamel is hydroxyapatite, $Ca_5(PO_4)_3OH$

- Crystal structure:
- http://webmineral.com/jpowd/JPX/jpowd.php?target_file=Hydroxylapatite_3.jpx

- The hydroxide ions reside in channels

What ions can we substitute?

- Why is fluoride ion is added to drinking water?

- Fluoride ions (F^{-}) can substitute into spaces vacated by hydroxide ions (OH^{-}) in tooth enamel

- Why are there spaces?
  - Teeth decay
  - Plaque causes acids
  - OH^{-} is a base….it's acid-base chemistry.

Teeth!

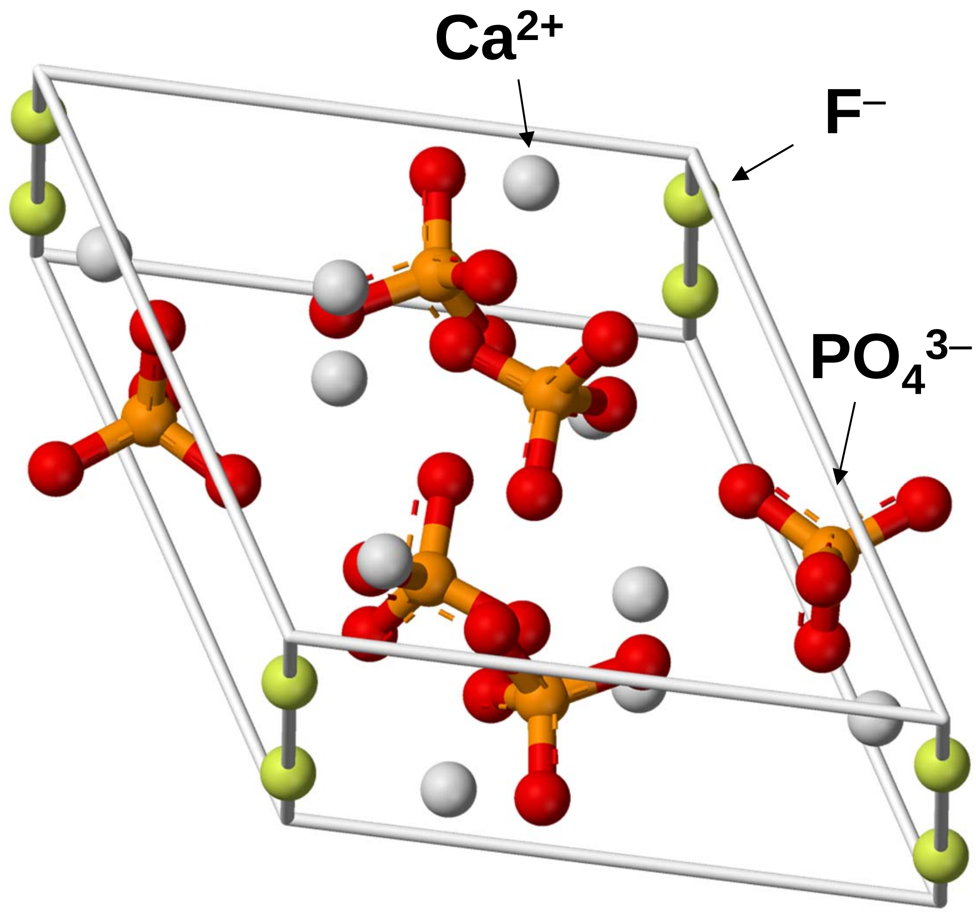
- So, why does F^- substitute so well into spaces vacated by hydroxide ions (OH^-) in tooth enamel?

[Fluorapatite $Ca_5(PO_4)_3F$]

OH^- and F^- charges match (1:1 substitution)

O^{2-} r = 140 pm *vs.*
F^- r = 133 pm
(F^- is slightly smaller – its similar size fits!)

Can deliver F^- to teeth (water, toothpaste)



Ionization Energy (IE) – general trends

- Energy required to remove e^- from gaseous atom

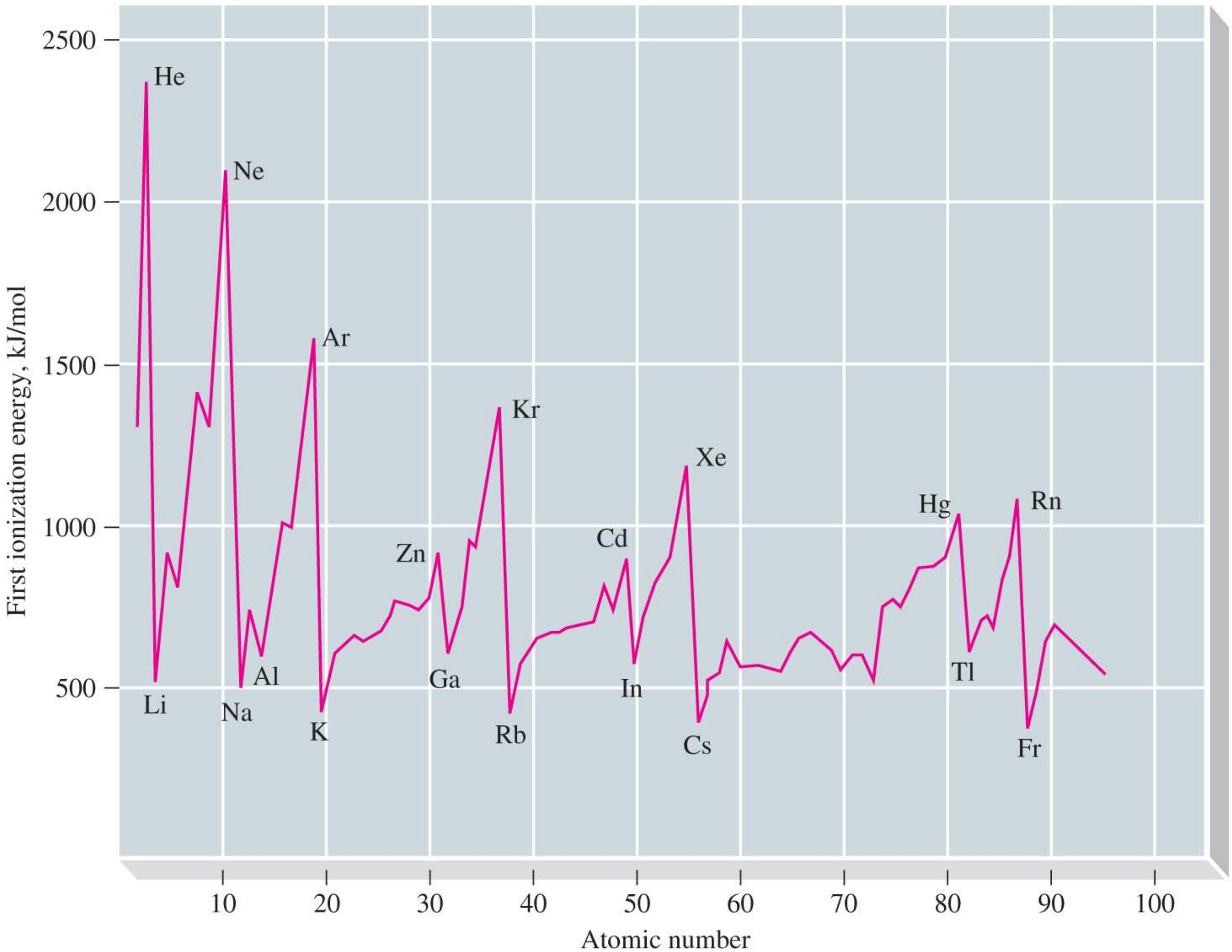
$$X(g) \rightarrow X^+(g) + e^- \qquad U = IE_1$$

- IE <u>de</u>crease as atomic radii <u>in</u>crease
  - IE increase left to right across a period (same n, Z_{eff} increases so outer e^- held more tightly)
  - IE decrease down a group (n increases so outer e^- further away, Z_{eff} increases little)

e.g.

e.g.	IE_1 (Na) =	495.8 kJ mol^{-1}
	IE_1 (K) =	418.8 kJ mol^{-1}
	IE_1 (Ar) =	**1,520.6 kJ mol^{-1}**

Ionization Energy - Fig. 9-10 (9-9, 9th ed.)



p. 374-377 (353-356, 9th ed.)

Ionization Energy - Table 9-4

TABLE 9.4 Ionization Energies of the Third-Period Elements (in kJ/mol)

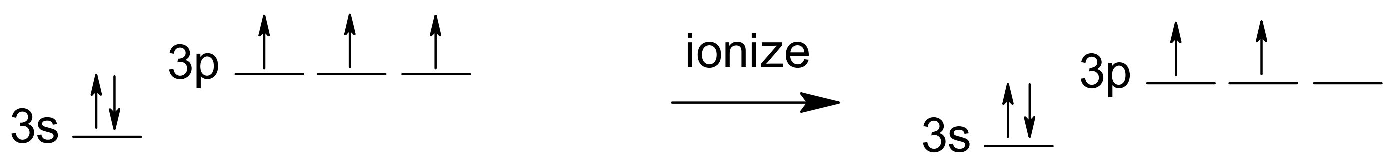
	Na	Mg	Al	Si	P	S	Cl	Ar
I_1	495.8	737.7	577.6	786.5	1012	999.6	1251.1	1520.5
I_2	4562	1451	1817	1577	1903	2251	2297	2666
I_3		7733	2745	3232	2912	3361	3822	3931
I_4			11,580	4356	4957	4564	5158	5771
I_5				16,090	6274	7013	6542	7238
I_6					21,270	8496	9362	8781
I_7						27,110	11,020	12,000

- I_1 = first ionization energy
- I_2 = second ionization energy, etc.

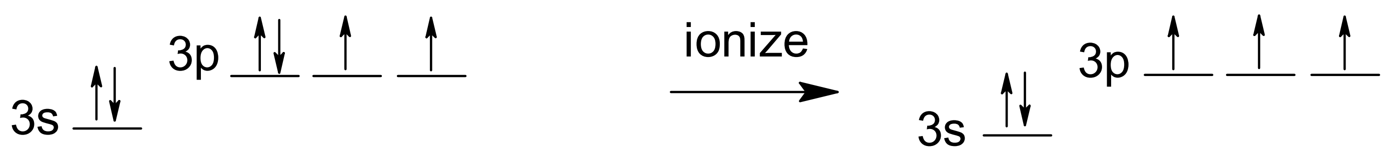
Filled & Half-filled Subshell Effect in IE

IE_1 (Al) < IE_1 (Mg) (also IE_1 (B) < IE_1 (Be))

IE_1 (S) < IE_1 (P) (also IE_1 (O) < IE_1 (N))



outer subshell of **P** is half-filled
- this has a special stability



outer subshell of **S** has one more electron - increased repulsion

outer subshell is now half-filled

Trend in successive IE's

$IE_1(Mg) < IE_2(Mg) << IE_3(Mg)$

$\uparrow$

e^- is taken a core shell of Mg

Similarly,

$IE_1(Al) < IE_2(Al) < IE_3(Al) << IE_4(Al)$

Al has three valence electrons – it is the fourth that is taken from a core shell

Alkali metals in water

- Demos: Na, K

  IE_1 (Na) = 495.8 kJ mol^{-1} IE_1 (K) = 418.8 kJ mol^{-1}

- Observations:
  - production of gas (bubbles, fizzing)
  - fast, vigorous reaction (K more vigorous than Na)
  - K shows a burst of flame when reacting with water

- Reactions:

$$Na(s) + H_2O(l) \rightarrow NaOH(aq) + \tfrac{1}{2} H_2(g)$$

$$K(s) + H_2O(l) \rightarrow KOH(aq) + \tfrac{1}{2} H_2(g)$$

- http://video.google.ca/videoplay?docid=-2134266654801392897&q=sodium+explosion

Electron Affinity - Fig. 9-11 (9-10, 9th ed.)

1	2	13	14	15	16	17	18
H −72.8							He >0
Li −59.6	Be >0	B −26.7	C −121.8	N +7	O −141.0	F −328.0	Ne >0
Na −52.9	Mg >0	Al −42.5	Si −133.6	P −72	S −200.4	Cl −349.0	Ar >0
K −48.4	Ca −2.37	Ga −28.9	Ge −119.0	As −78	Se −195.0	Br −324.6	Kr >0
Rb −46.9	Sr −5.03	In −28.9	Sn −107.3	Sb −103.2	Te −190.2	I −295.2	Xe >0
Cs −45.5	Ba −13.95	Tl −19.2	Pb −35.1	Bi −91.2	Po −186	At −270	Rn >0

p. 378-379 (356-357, 9th ed.)

Electron Affinity – general trends

- Energy change that occurs when e^- is added to a gaseous atom

  $$X(g) + e^- \rightarrow X^-(g) \qquad U = EA$$

- Very irregular trend, but approximately:
  - Magnitude increases across a period
  - Magnitude increases up a group
  - See subshell effect (Groups 1/2, 14/15)

Take-home practice problem

Electron Affinity subshell effect: Explain why the magnitude of EA for the Group 15 elements is much smaller than for Group 14.

Half-filled Subshell Effect in EA

Analogous to half-filled subshell effect in IE trend (but it happens one element earlier because we are adding an e^- rather than taking one away. There is also a filled subshell effect in EA.

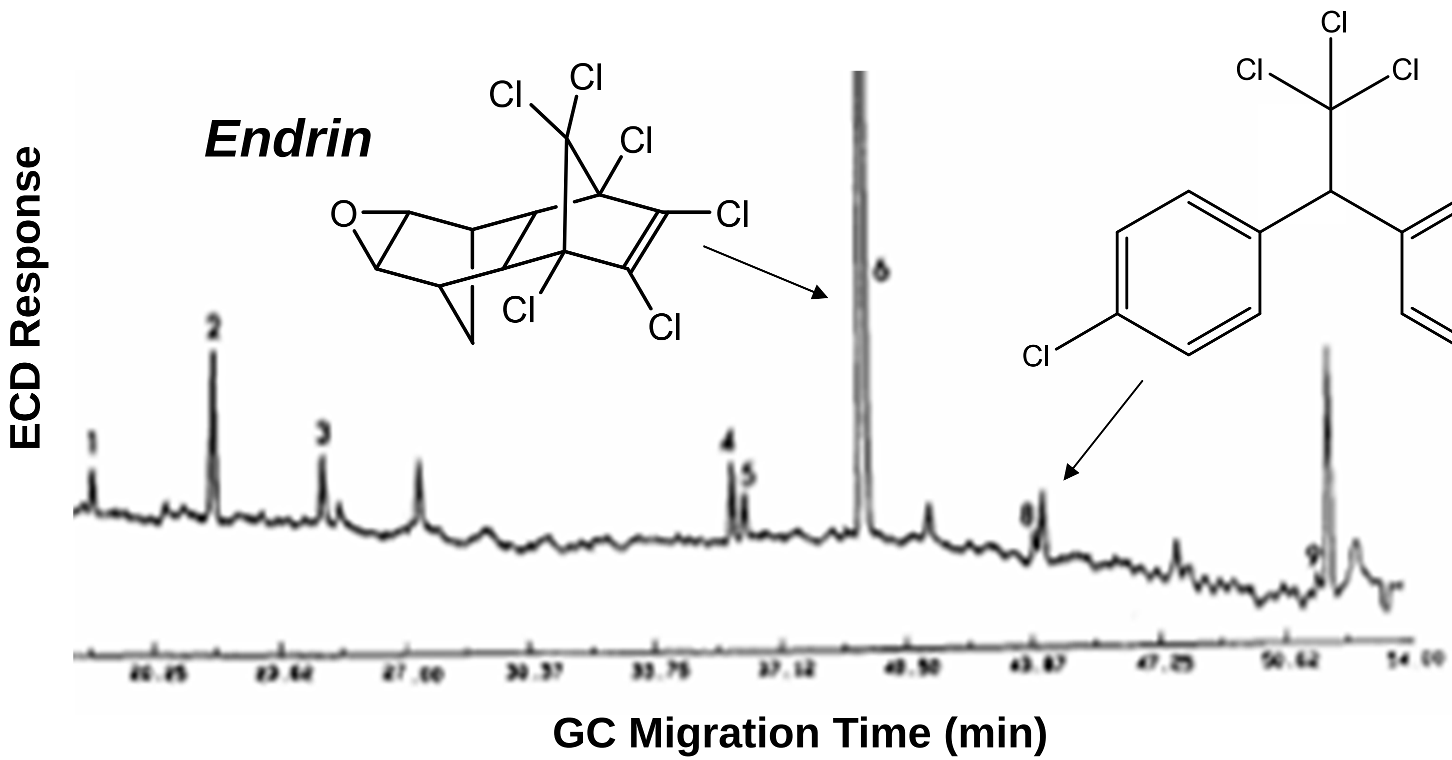
For example, in Period 3:

In Group 15 the outer electrons are in 3s (filled) and 3p (half-filled) orbitals. The next electron added will also occupy a 3p orbital, and now it must **pair** with one of the electrons already there.

Restricting two electrons to the same orbital results in significant repulsion and makes electron affinity much less favourable. It is actually positive for N. This corresponds to a metastable anion.

Electron Affinity of *Molecules*: **Pesticides Analysis of Blood from Agricultural Workers**

- Exposure to high levels of pesticides → Disease
- Analysis of complex mixtures of chlorinated pesticides by gas chromatography-electron capture detection (GC-ECD)
- Polyhalogenated molecules readily capture electrons (EA)



Identify, quantify trace amounts

Trends and Descriptive chemistry - Oxides

- Metal oxides: basic

  react with water to produce OH^-

- Non-metal oxides: acidic

  react with water to produce H_3O^+

- Amphoteric oxides?

  Some metalloids and near-metalloids

  react with acid and with base

1	2	13	14	15	16	17
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Ga	Ge	As	Se	Br
Rb	Sr	In	Sn	Sb	Te	I
Cs	Ba	Tl	Pb	Sn	Po	At

Fig. 9-18 (9-17, 9th ed.)

p. 385 (362-363, 9th ed.)

Oxides - Example Reactions

Basic: $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

base

Ionic bonding

Acidic: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

acid

Covalent bonding

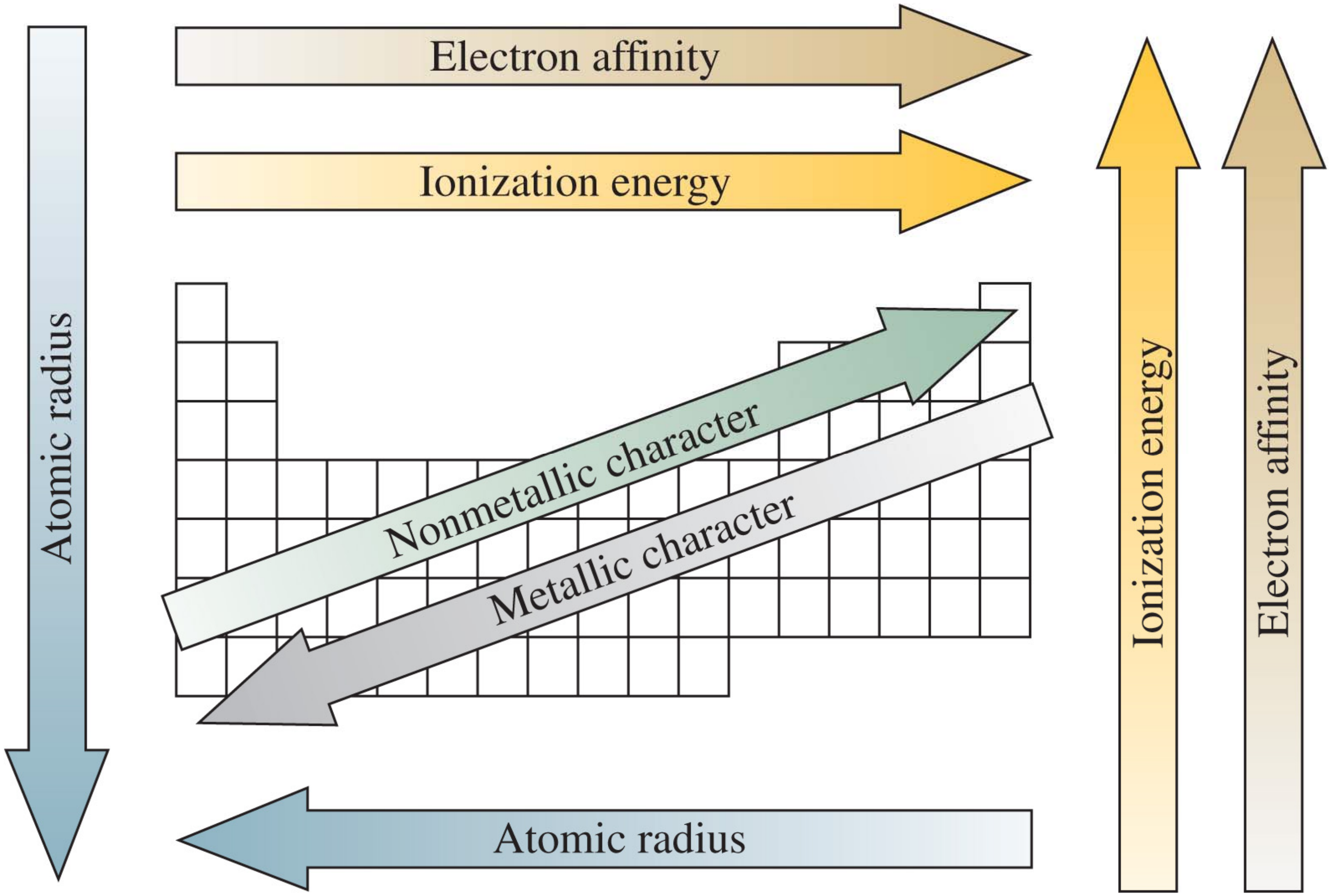
Amphoteric: reacts with acid or base

$Al_2O_3(s) + 6\ HCl(aq) \rightarrow 2\ AlCl_3(aq) + 3\ H_2O(l)$

$Al_2O_3(s) + 2\ NaOH(aq) + 3\ H_2O(l) \rightarrow 2\ Na[Al(OH)_4](aq)$

Atomic properties – Summary

Fig. 9-12 (9-11, 9th ed.)



p. 381 (359, 9th ed.)