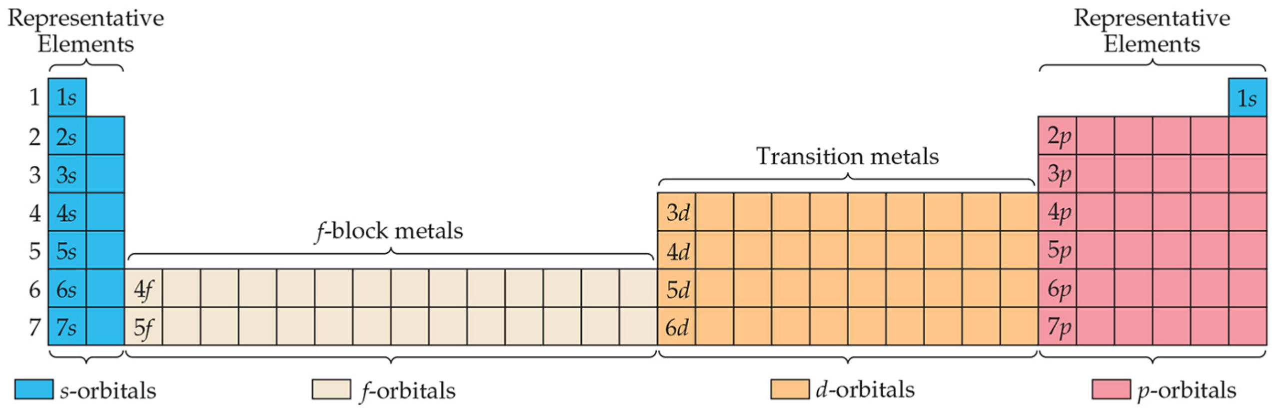
Chapter 7

PERIODICITY

Periodic Table

- We fill orbitals in increasing order of energy.
- Different blocks on the periodic table correspond to different types of orbitals: *s* = blue, *p* = pink (*s* and *p* are representative elements); *d* = orange (transition elements); *f* = tan (lanthanides and actinides, or inner transition elements)
- The *s* and *p* blocks are called the **main-group elements**.



PERIODICITY

Diamagnetic vs. Paramagnetic species:

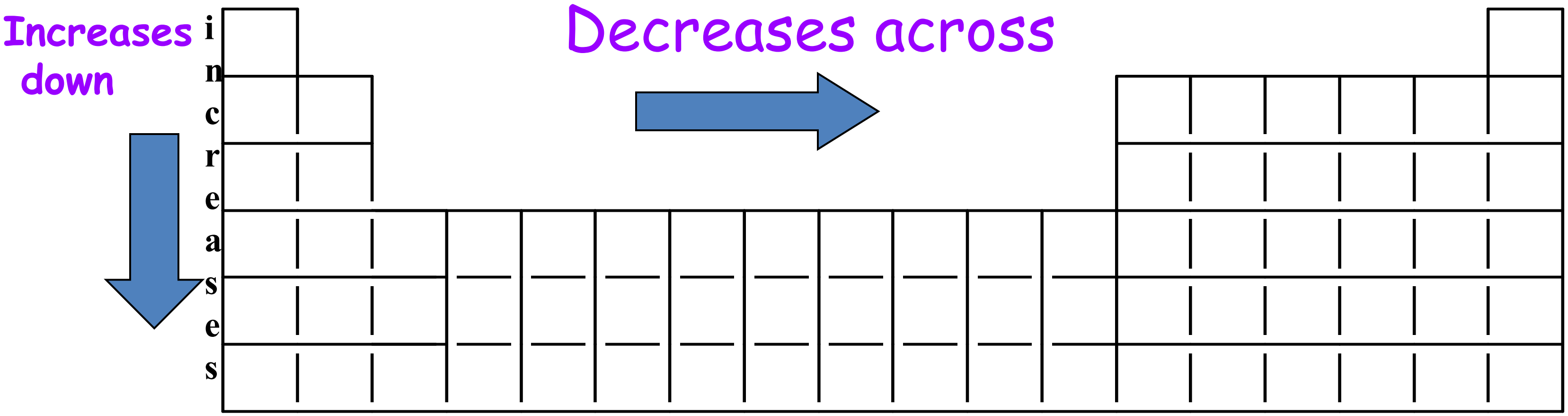
Diamagnetic has all its electrons paired and is slightly repelled by a magnetic field

Paramagnetic has one or more unpaired electrons and is attracted into a magnetic field.

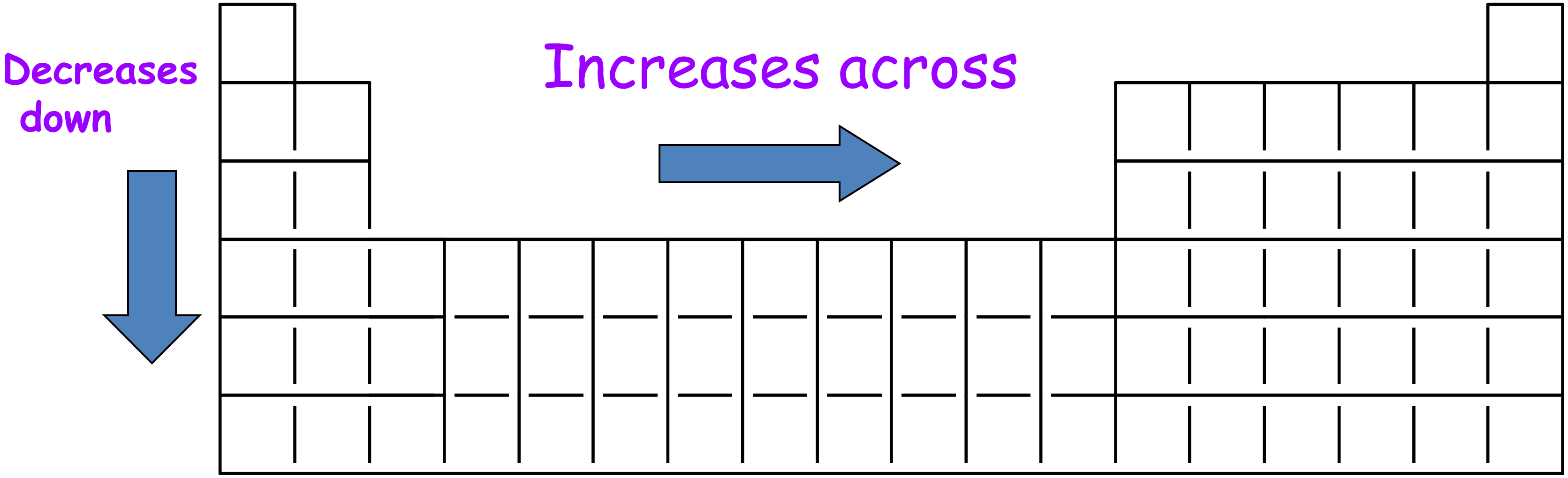
Which group(s) on the periodic table will have elements that are always diamagnetic?

Periodic Trends

1. Atomic Radius

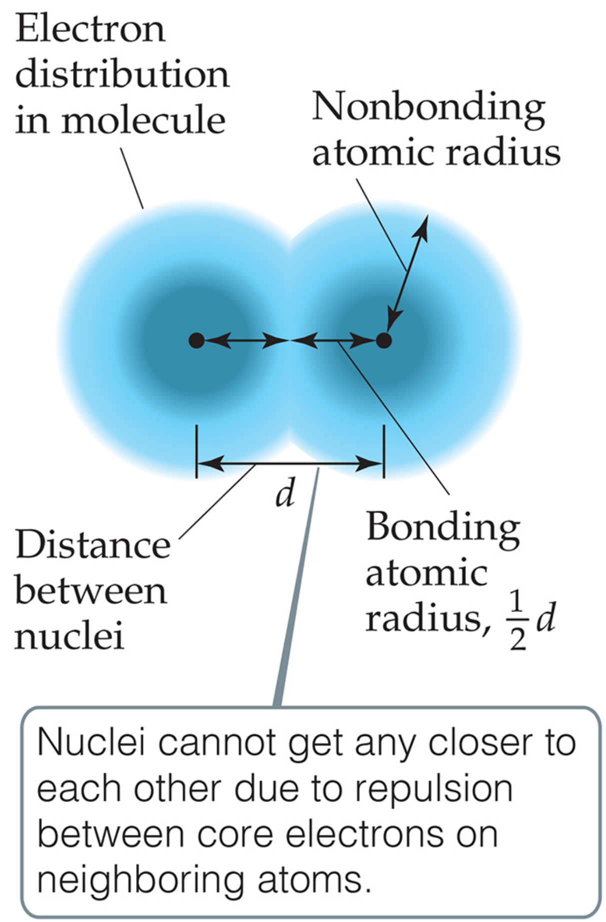


2. Ionization Energy – energy needed to remove an electron from gaseous atom



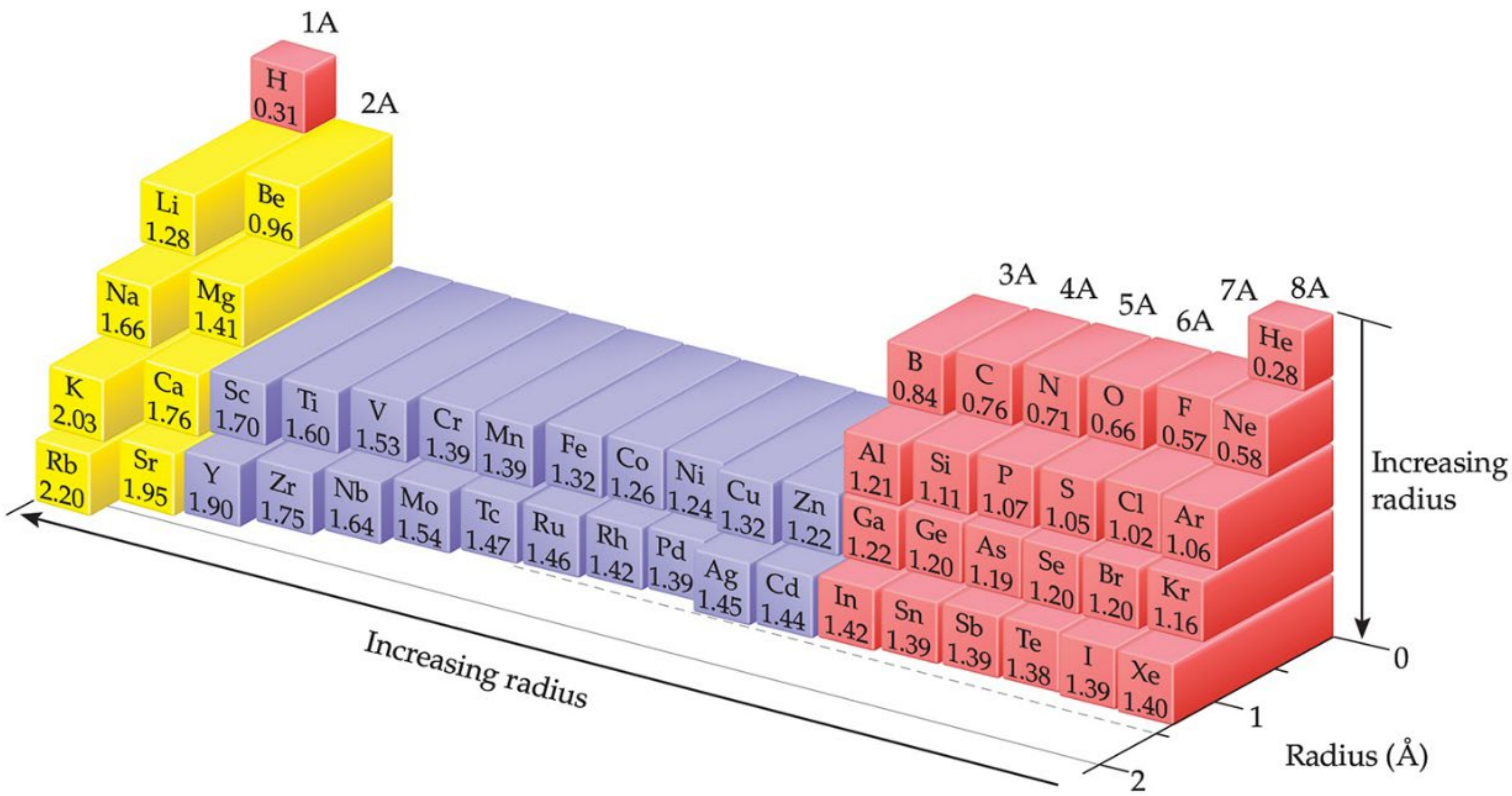
What Is the Size of an Atom?

- The **nonbonding atomic radius,** or **van der Waals radius,** is half of the shortest distance separating two nuclei during a collision of atoms.
- The **bonding atomic radius**, or covalent radius, is half the distance between nuclei in a bond.



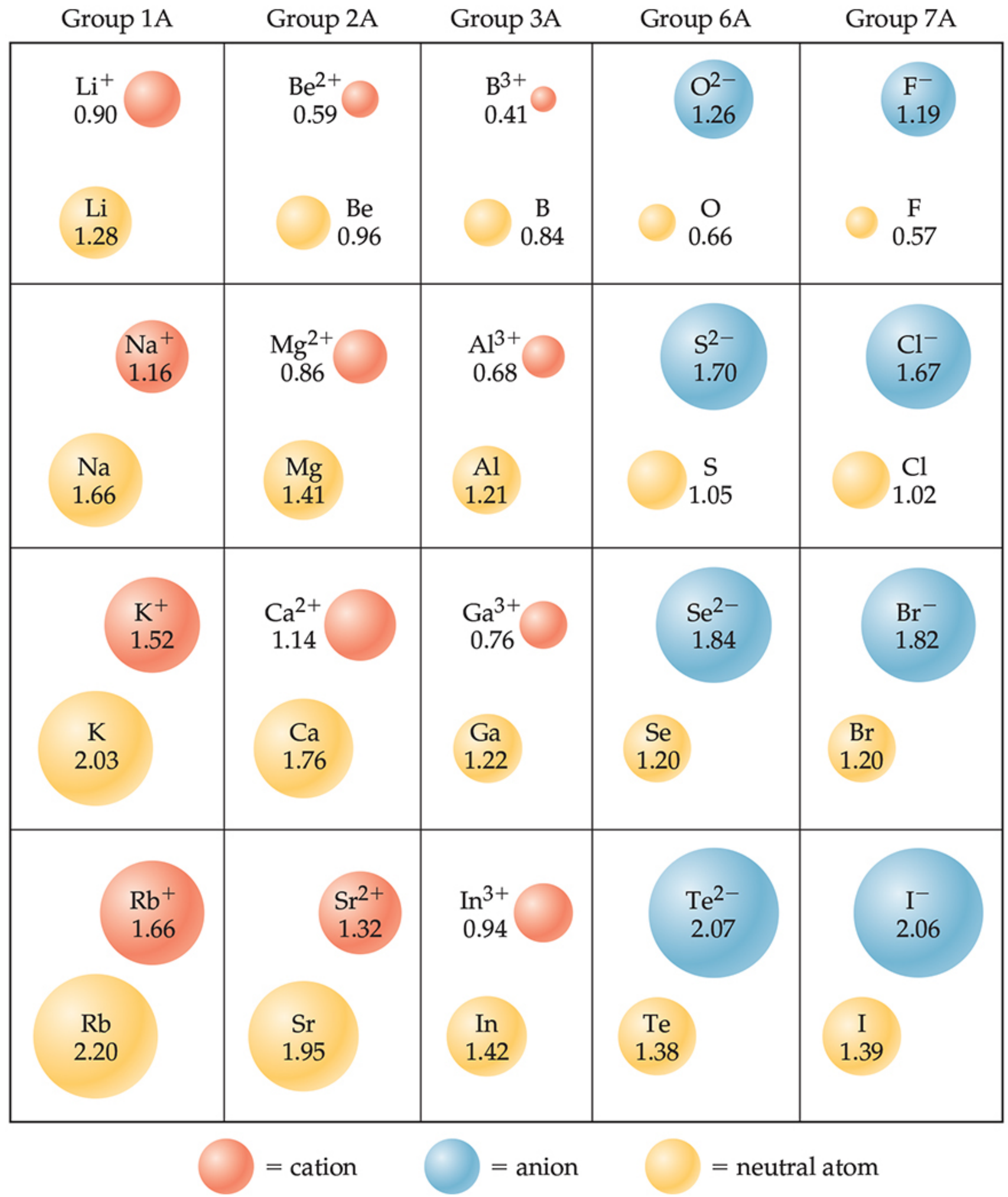
Sizes of Atoms

- This figure shows the trend in bonding atomic radius.
- The bonding atomic radius tends to
  - decrease from left to right across a period (Z_{eff} ↑).
  - increase from top to bottom of a group (n ↑).



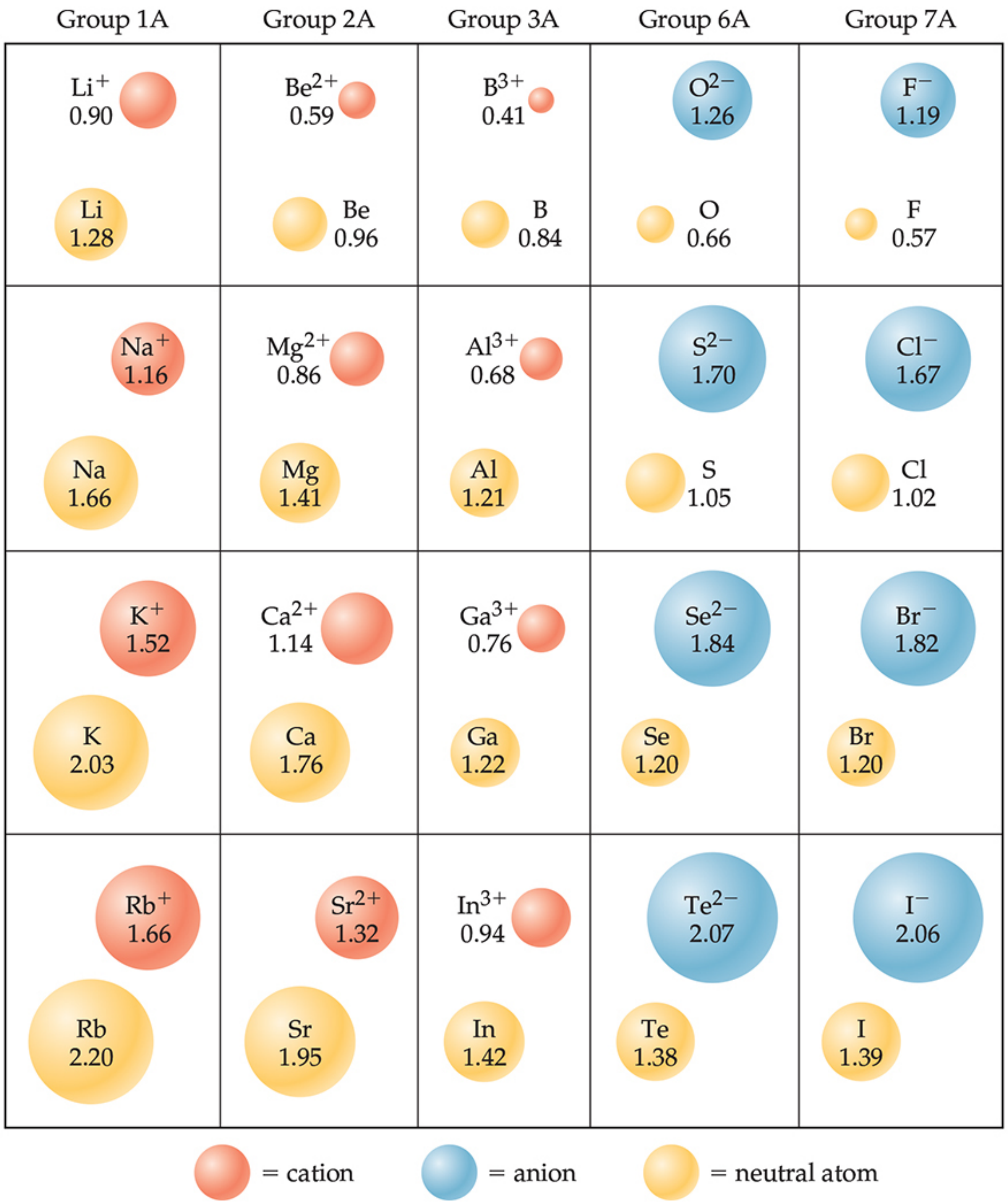
Sizes of Ions

- Determined by interatomic distances in ionic compounds
- Ionic size depends on
  - the nuclear charge.
  - the number of electrons.
  - the orbitals in which electrons reside.



Sizes of Ions

- Cations are smaller than their parent atoms:
  - The outermost electron is removed and repulsions between electrons are reduced.
- Anions are larger than their parent atoms:
  - Electrons are added and repulsions between electrons are increased.



Size of Ions—Isoelectronic Series

- In an **isoelectronic series**, ions have the same number of electrons.
- Ionic size decreases with an increasing nuclear charge.
  - **An isoelectronic series (10 electrons)**
- Note increasing nuclear charge with decreasing ionic radius as atomic number increases

Increasing nuclear charge →

8 protons	9 protons	11 protons	12 protons	13 protons
10 electrons	10 electrons	10 electrons	10 electrons	10 electrons
O^{2-}	F^{-}	Na^{+}	Mg^{2+}	Al^{3+}
1.26 Å	1.19 Å	1.16 Å	0.86 Å	0.68 Å

Decreasing ionic radius →

Ionization Energy (*IE*)

- The **ionization energy** is the minimum energy required to remove an electron from the ground state of a gaseous atom or ion.
  - **The first ionization energy is that energy required to remove the first electron.**
  - **The second ionization energy is that energy required to remove the second electron.**

- Note: The higher the ionization energy, the more difficult it is to remove an electron!

Ionization Energy

- It requires more energy to remove each successive electron.
- When all valence electrons have been removed, it takes a great deal more energy to remove the next electron (a core electron).

Table 7.2 Successive Values of Ionization Energies, *IE*, for the Elements Sodium through Argon (kJ/mol)

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4562					
Mg	738	1451	7733		(inner-shell electrons)		
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

Periodic Trends in First Ionization Energy (IE_1)

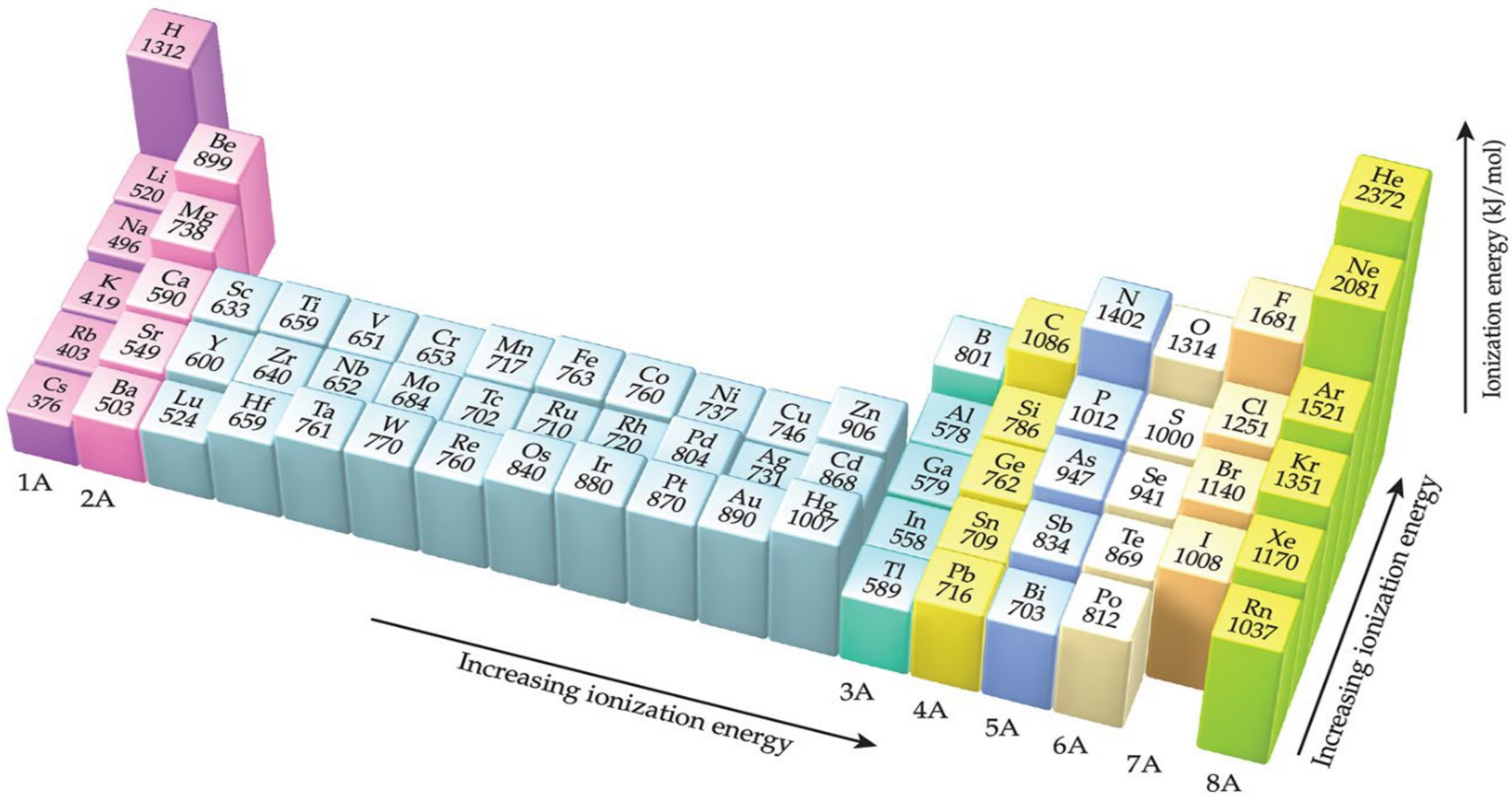
1) IE_1 generally increases across a period.

2) IE_1 generally decreases down a group.

3) The *s*- and *p*-block elements show a larger range of values for IE_1. (The *d*-block generally increases slowly across the period; the *f*-block elements show only small variations.)

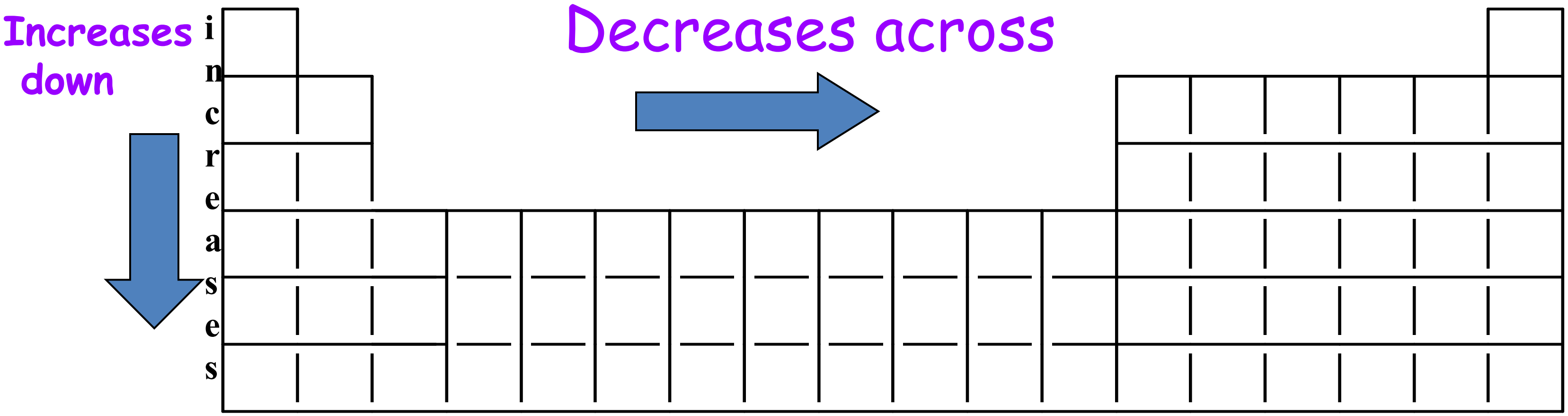
Factors That Influence Ionization Energy

- Smaller atoms have higher *IE* values.
- *IE* values depend on effective nuclear charge and average distance of the electron from the nucleus.

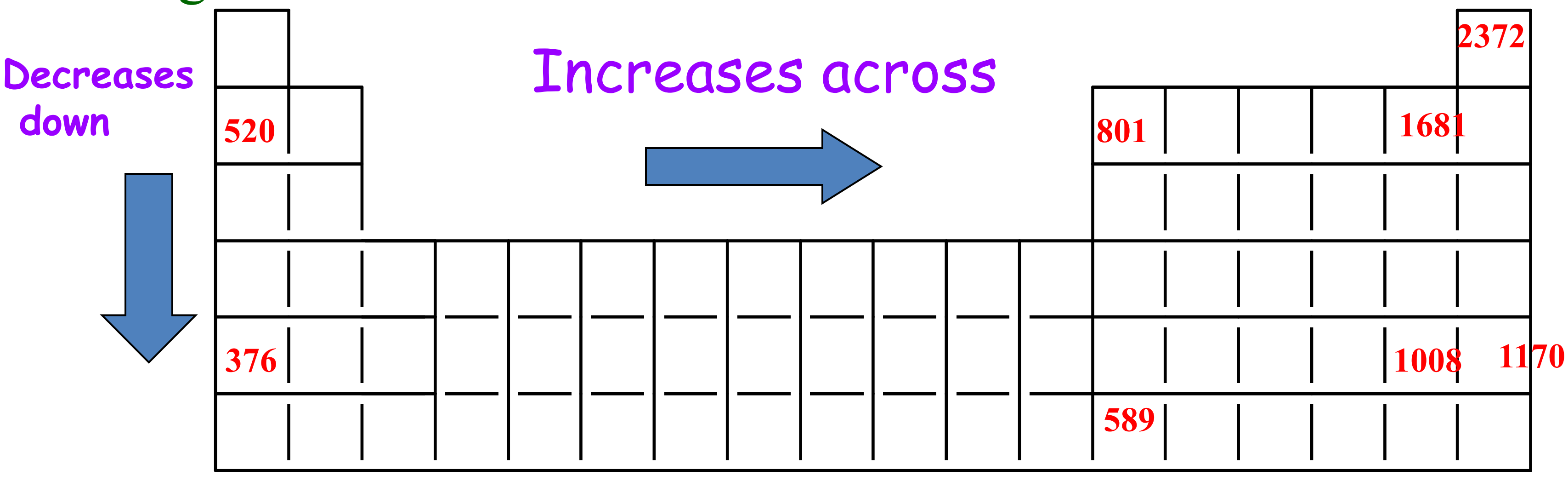


Periodic Trends

1. Atomic Radius



2. Ionization Energy – energy needed to remove an electron from gaseous atom



LECTURE QUIZ #16A on periodic trends

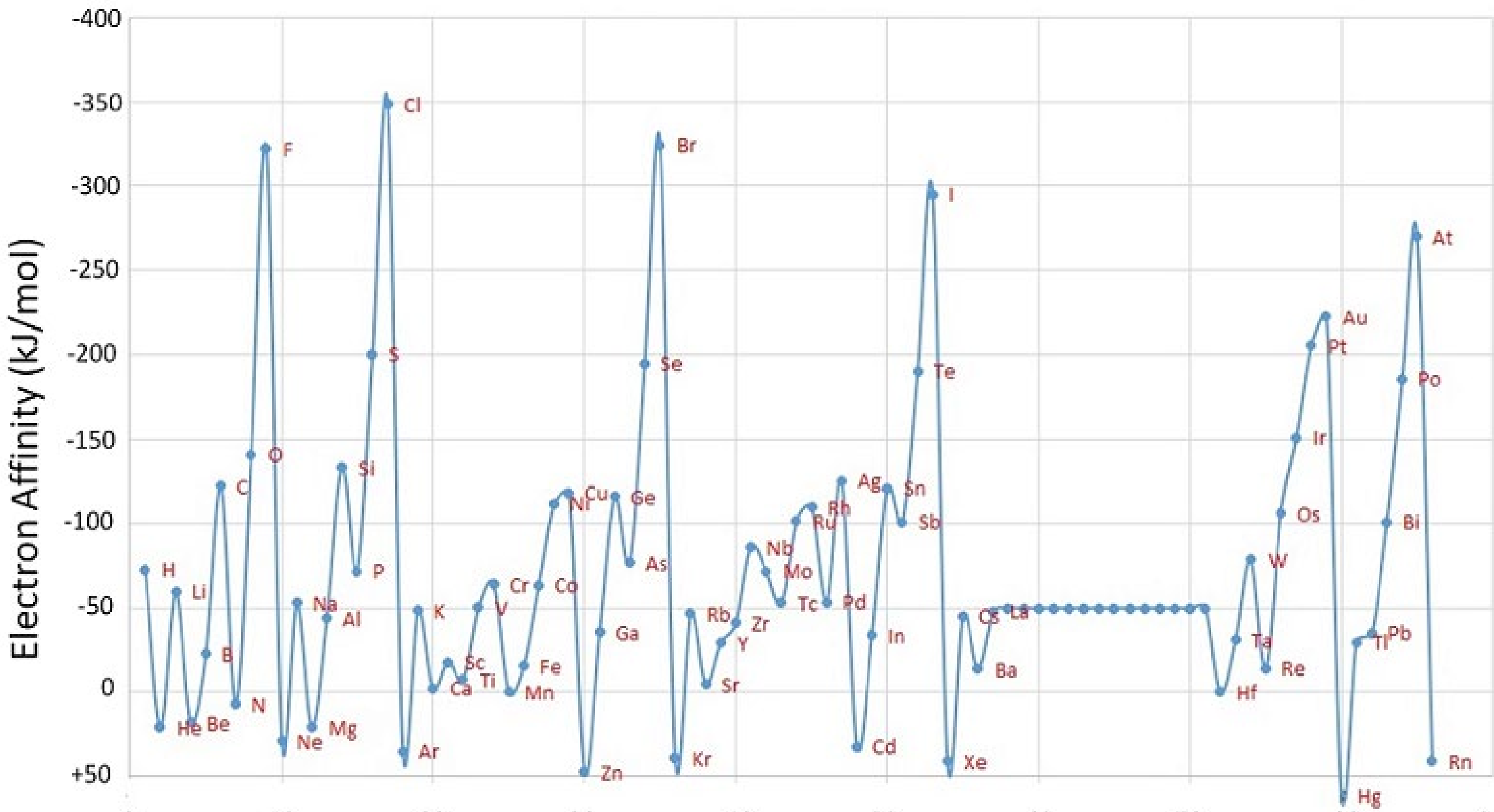
1. Arrange the following in terms of DECREASING atomic radius & then first ionization energy :

Be, B, C, N, O, F, Ne

Electron Affinity

- **Electron affinity** is the energy change accompanying the addition of an electron to a gaseous atom:

$$Cl + e^{-} \rightarrow Cl^{-}$$

- 

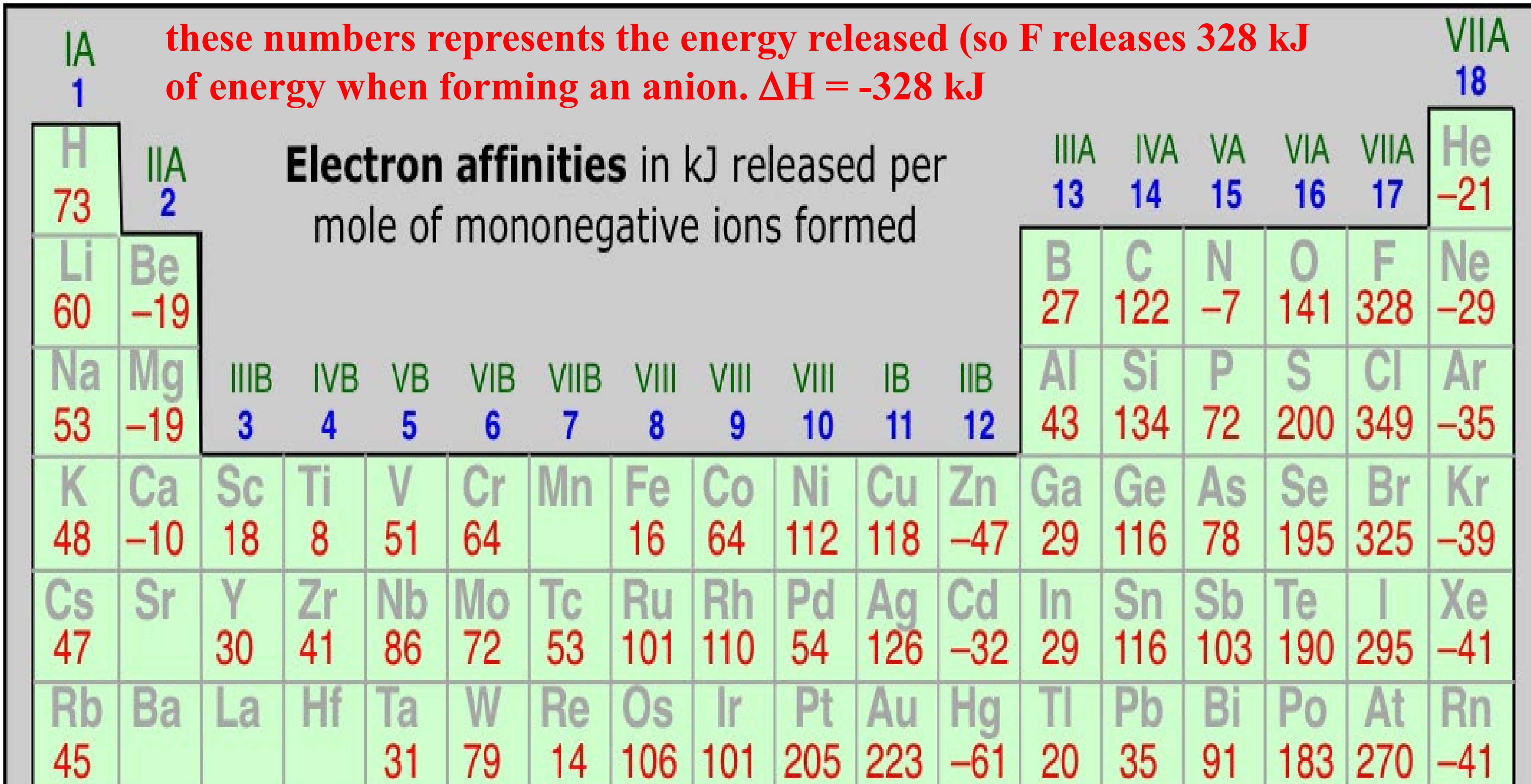
General Trend in Electron Affinity

- Not much changes in a group.
- Across a period, it generally increases. **Three** notable exceptions include the following:
  1) Group 2A: *s* sublevel is full!
  2) Group 5A: *p* sublevel is half-full!
  3) Group 8A: *p* sublevel is full!

1A	2A	3A	4A	5A	6A	7A	8A
H −73							**He** > 0
Li −60	**Be** > 0	**B** −27	**C** −122	**N** > 0	**O** −141	**F** −328	**Ne** > 0
Na −53	**Mg** > 0	**Al** −43	**Si** −134	**P** −72	**S** −200	**Cl** −349	**Ar** > 0
K −48	**Ca** −2	**Ga** −30	**Ge** −119	**As** −78	**Se** −195	**Br** −325	**Kr** > 0
Rb −7	**Sr** −5	**In** −30	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** > 0

*Note: The electron affinity for many of these elements is **positive** (X^- is unstable).

3. Electron Affinity – energy released when an electron is added to gaseous atom - make an anion!



these numbers represents the energy released (so F releases 328 kJ of energy when forming an anion. $\Delta H = -328$ kJ

Electron affinities in kJ released per mole of mononegative ions formed

IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIII 8	VIII 9	VIII 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIA 18
H 73																	He −21
Li 60	Be −19											B 27	C 122	N −7	O 141	F 328	Ne −29
Na 53	Mg −19											Al 43	Si 134	P 72	S 200	Cl 349	Ar −35
K 48	Ca −10	Sc 18	Ti 8	V 51	Cr 64	Mn	Fe 16	Co 64	Ni 112	Cu 118	Zn −47	Ga 29	Ge 116	As 78	Se 195	Br 325	Kr −39
Cs 47	Sr	Y 30	Zr 41	Nb 86	Mo 72	Tc 53	Ru 101	Rh 110	Pd 54	Ag 126	Cd −32	In 29	Sn 116	Sb 103	Te 190	I 295	Xe −41
Rb 45	Ba	La	Hf	Ta 31	W 79	Re 14	Os 106	Ir 101	Pt 205	Au 223	Hg −61	Tl 20	Pb 35	Bi 91	Po 183	At 270	Rn −41

Periodic Table of the Elements

Electronegativity

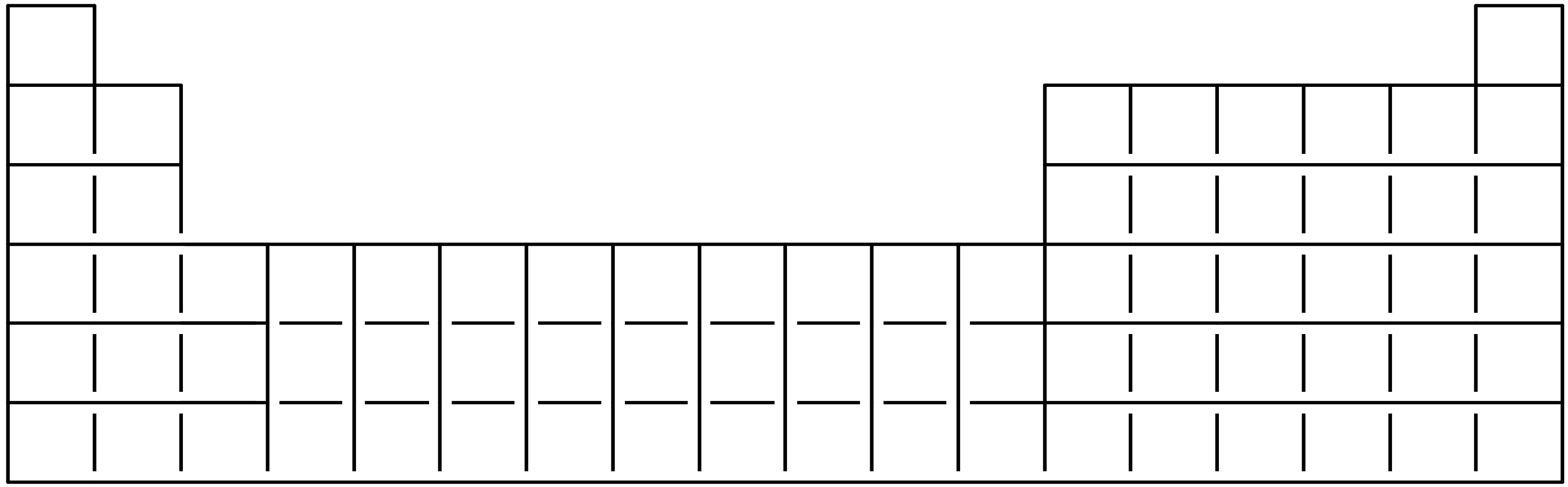
H 2.1																	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.4	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
Cs 0.7	Ba 0.9	La - Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9	Ac - Lr 1.1-1.7															

ELECTRONEGATIVY

Draw the trends:

3. Electron Affinity – energy released when an electron is added to gaseous atom

4. Electronegativity – the electron pulling power of an atom when it is part of a molecule (denoted with the Greek letter χ)



5. Metallic Character

LECTURE QUIZ #16B on periodic trends

2A. Why is the first ionization energy of aluminum slightly lower than the first ionization energy for magnesium?

2B. Give a reason why the electronegativity for F is so much greater than the electronegativity for Fr.

Group 6A—Increasing in Metallic Character down the Group

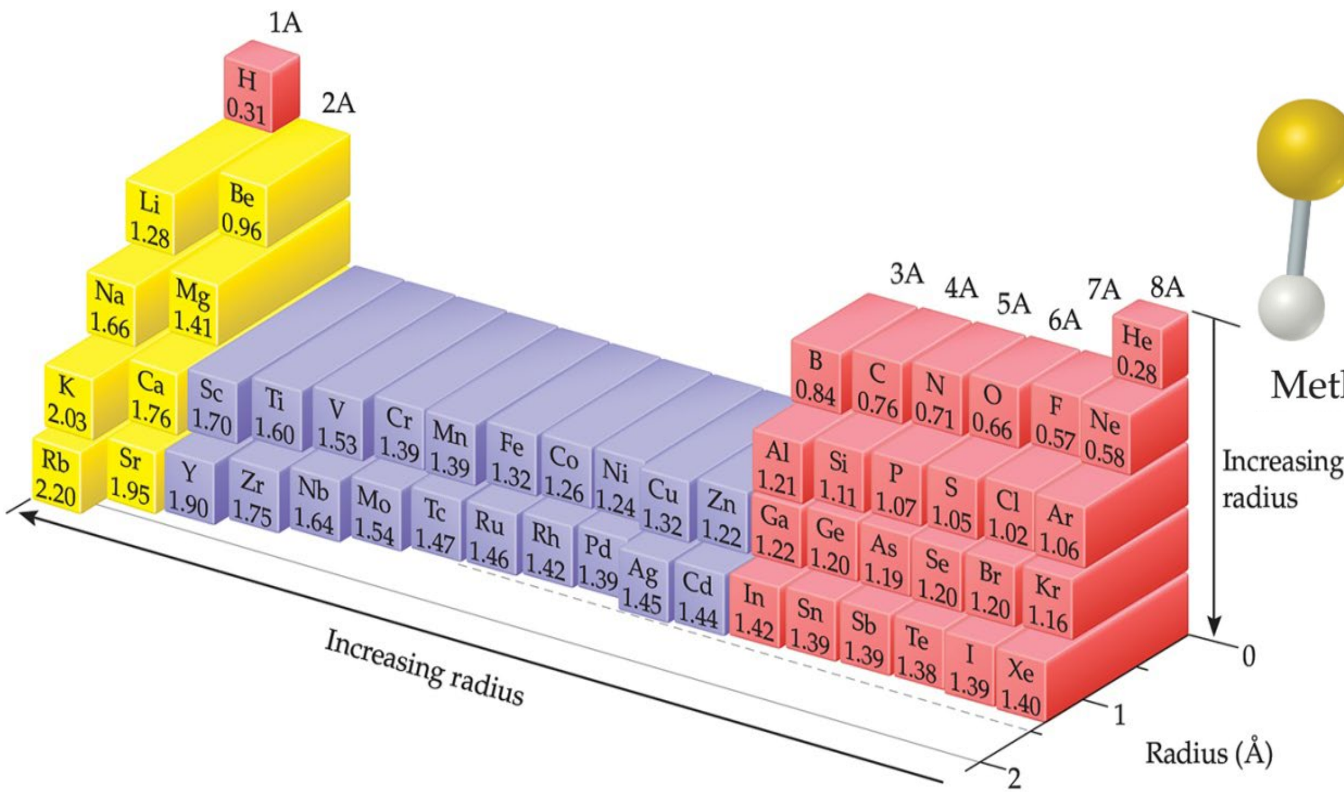
Table 7.6 Some Properties of the Group 6A Elements

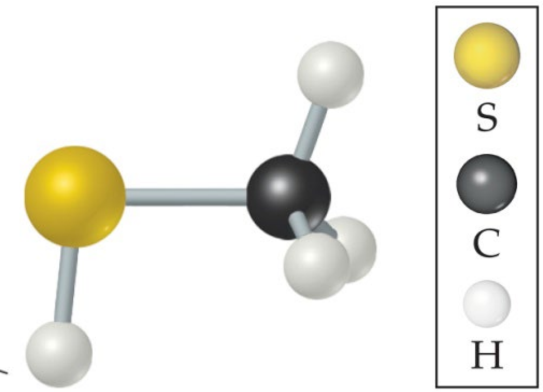
Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ /mol)
Oxygen	$[He]2s^2 2p^4$	-218	1.43g/L	0.66	1314
Sulfur	$[Ne]3s^2 3p^4$	115	$1.96 g/cm^3$	1.05	1000
Selenium	$[Ar]3d^{10} 4s^2 4p^4$	211	$4.82 g/cm^3$	1.20	941
Tellurium	$[Kr]4d^{10} 5s^2 5p^4$	450	$6.24 g/cm^3$	1.38	869
Polonium	$[xe]4f^{14} 5d^{10} 6s^2 6p^4$	254	$9.20 g/cm^3$	1.40	812

- Oxygen, sulfur, and selenium are nonmetals.
- Tellurium is a metalloid.
- The radioactive polonium is a metal.
- Trend: Oxygen is more likely to form –2 anion; polonium is most likely to have a positive charge.

Example: Bond Lengths in a Molecule from atomic radius

Natural gas used in home heating and cooking is odorless. Because natural gas leaks pose the danger of explosion or suffocation, various smelly substances are added to the gas to allow detection of a leak. One such substance is methyl mercaptan, CH_3SH. Use the Figure to predict the lengths of the C—S, C—H, and S—H bonds in this molecule.





Methyl mercaptan

Example: Bond Lengths in a Molecule from atomic radius

Solution

Analyze and Plan: We are given three bonds and told to use the figure for bonding atomic radii. We will assume that each bond length is the sum of the bonding atomic radii of the two atoms involved.

$$
\begin{aligned}
\text{C—S bond length} &= \text{bonding atomic radius of C} \\
&\quad + \text{bonding atomic radius of S} \\
&= 0.76\ \text{Å} + 1.05\ \text{Å} = 1.81\ \text{Å} \\
\text{C—H bond length} &= 0.76\ \text{Å} + 0.31\ \text{Å} = 1.07\ \text{Å} \\
\text{S—H bond length} &= 1.05\ \text{Å} + 0.31\ \text{Å} = 1.36\ \text{Å}
\end{aligned}
$$

Check: The experimentally determined bond lengths are C—S = 1.82 Å, C—H = 1.10 Å, and S—H = 1.33 Å. (In general, the lengths of bonds involving hydrogen show larger deviations from the values predicted from bonding atomic radii than do bonds involving larger atoms.)

Comment: Notice that our estimated bond lengths are close but not exact matches to the measured bond lengths. Bonding atomic radii must be used with some caution in estimating bond lengths.

Example: Bond Lengths in a Molecule from atomic radius

Practice Exercise 1

Hypothetical elements X and Y form a molecule XY_2, in which both Y atoms are bonded to atom X (and not to one another). The X—X distance in the elemental form of X is 2.04 Å, and the Y—Y distance in elemental Y is 1.68 Å. What would you predict for the X—Y distance in the XY_2 molecule?

(a) 0.84 Å **(b)** 1.02 Å **(c)** 1.86 Å **(d)** 2.70 Å **(e)** 3.72 Å

The radius is d/2 so (2.04/2)+(1.68/2) = **1.86**

Practice Exercise 2

Using the Figure, predict which is longer, the P—Br bond in PBr_3 or the As—Cl bond in $AsCl_3$.

P-Br = 1.07 + 1.20 = 2.27 Å As-Cl = 1.19+1.02 = 2.21 Å

Integrative Exercise **Putting Concepts Together**

The element bismuth (Bi, atomic number 83) is the heaviest member of group 5A. A salt of the element, bismuth subsalicylate, is the active ingredient in Pepto-Bismol®, an over-the-counter medication for gastric distress.

Periodic table

(a) Based on values presented in the Figure and the TABLES, what might you expect for the bonding atomic radius of bismuth?

(a) Bismuth is directly below antimony, Sb. *Based on the observation that atomic radii increase as we go down a column, we would expect the radius of Bi to be greater than that of* **Sb=1.39 Å.** *We also know that atomic radii generally decrease as we proceed from left to right in a period.*

Using the tables, Bi is near Ba and Po. We would therefore expect that the radius of Bi is smaller than that of **Ba (2.15 Å)** and larger than that of **Po (1.40 Å).** We also see that in other periods, the difference in radius between the neighboring group 5A and group 6A elements is relatively small. *We might therefore expect that the radius of Bi is slightly larger than that of Po—much closer to the radius of Po than to the radius of Ba.*

The tabulated value for the atomic radius on **Bi is 1.48 Å**

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	3A	4A	5A	6A	7A	18
1 H Hydrogen 1.01																	2 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 51.99	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.38	31 Ga Gallium 69.72	32 Ge Germanium 72.63	33 As Arsenic 74.92	34 Se Selenium 78.97	35 Br Bromine 79.90	36 Kr Krypton 84.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.95	43 Tc Technetium 98.91	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.6	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 Po Polonium [208.98]	85 At Astatine 209.98	86 Rn Radon 222.02
87 Fr Francium 223.02	88 Ra Radium 226.03	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]

57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 144.91	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.06	71 Lu Lutetium 174.97
89 Ac Actinium 227.03	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.05	94 Pu Plutonium 244.06	95 Am Americium 243.06	96 Cm Curium 247.07	97 Bk Berkelium 247.07	98 Cf Californium 251.08	99 Es Einsteinium [254]	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Metalloid | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide

A B
C D
E F

Integrative Exercise Putting Concepts Together

Table 7.5 Some Properties of the Alkaline Earth Metals

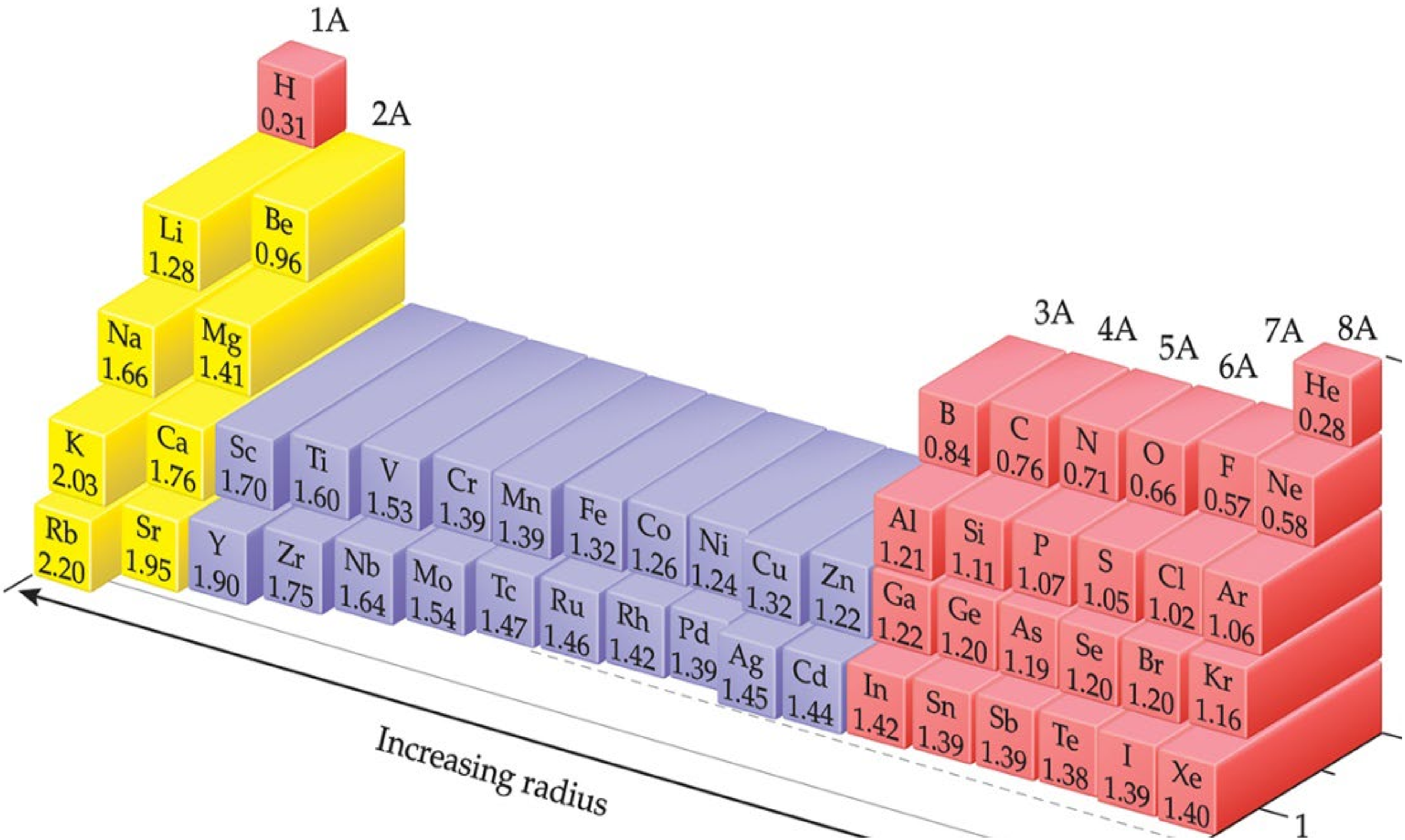
Element	Electron Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius (Å)	I_1 (kJ/mol)
Beryllium	$[He]2s^2$	1287	1.85	0.96	899
Magnesium	$[Ne]3s^2$	650	1.74	1.41	738
Calcium	$[Ar]4s^2$	842	1.55	1.76	590
Strontium	$[Kr]5s^2$	777	2.63	1.95	549
Barium	$[Xe]6s^2$	727	3.51	2.15	503

Table 7.6 Some Properties of the Group 6A Elements

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ/mol)
Oxygen	$[He]2s^2 2p^4$	−218	1.43 g/L	0.66	1314
Sulfur	$[Ne]3s^2 3p^4$	115	1.96 g/cm^3	1.05	1000
Selenium	$[Ar]3d^{10} 4s^2 4p^4$	221	4.82 g/cm^3	1.20	941
Tellurium	$[Kr]4d^{10} 5s^2 5p^4$	450	6.24 g/cm^3	1.38	869
Polonium	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$	254	9.20 g/cm^3	1.40	812

A

Integrative Exercise Putting Concepts Together



Integrative Exercise **Putting Concepts Together**

The element bismuth (Bi, atomic number 83) is the heaviest member of group 5A. A salt of the element, bismuth subsalicylate, is the active ingredient in Pepto-Bismol®, an over-the-counter medication for gastric distress.

Periodic table

(b) What accounts for the general increase in atomic radius going down the group 5A elements?

(b) The general increase in radius with increasing atomic number in the group 5A elements occurs because additional shells of electrons are being added, with corresponding increases in nuclear charge. The core electrons in each case largely screen the outermost electrons from the nucleus, so the *effective nuclear charge* does not vary greatly as we go to higher atomic numbers. However, the *principal quantum number, n*, of the outermost electrons steadily increases, with a corresponding increase in orbital radius.

Integrative Exercise **Putting Concepts Together**

The element bismuth (Bi, atomic number 83) is the heaviest member of group 5A. A salt of the element, bismuth subsalicylate, is the active ingredient in Pepto-Bismol®, an over-the-counter medication for gastric distress.

Periodic table

(c) Another major use of bismuth has been as an ingredient in low-melting metal alloys, such as those used in fire sprinkler systems and in typesetting. The element itself is a brittle white crystalline solid. How do these characteristics fit with the fact that bismuth is in the same periodic group with such nonmetallic elements as nitrogen and phosphorus?

(c) The contrast between the properties of bismuth and those of nitrogen and phosphorus illustrates the general rule that there is a trend toward increased metallic character as we move down in a given group.

Bismuth, in fact, is a metal. The increased metallic character occurs because the outermost electrons are more readily lost in bonding, a trend that is consistent with its lower ionization energy.

Integrative Exercise **Putting Concepts Together**

(d) Bi_2O_3 is a basic oxide. Write a balanced chemical equation for its reaction with dilute nitric acid. If 6.77 g of Bi_2O_3 is dissolved in dilute acidic solution to make 0.500 L of solution, what is the molarity of the solution of Bi^{3+} ion?

Periodic table

(d) ***Molecular equation*:**

$$\mathbf{Bi_2O_3(s) + 6\ HNO_3(aq) \rightarrow 2\ Bi(NO_3)_3(aq) + 3\ H_2O(l)}$$

***Net ionic equation*:**

$$\mathbf{Bi_2O_3(s) + 6\ H^+(aq) \rightarrow 2\ Bi^3 + (aq) + 3\ H_2O(l)}$$

In the net ionic equation, nitric acid is a strong acid and $Bi(NO_3)_3$ is a soluble salt, so we need to show only the reaction of the solid with the hydrogen ion forming the $Bi^{3+}(aq)$ ion and water. To calculate the concentration of the solution, we proceed as follows:

$$\frac{6.77\ \cancel{\text{g Bi}_2\text{O}_3}}{0.500\ \text{L soln}} \times \frac{1\ \cancel{\text{mol Bi}_2\text{O}_3}}{466.0\ \cancel{\text{g Bi}_2\text{O}_3}} \times \frac{2\ \text{mol Bi}^{3+}}{1\ \cancel{\text{mol Bi}_2\text{O}_3}}$$

$$= \frac{0.0581\ \text{mol Bi}^{3+}}{\text{L soln}} = 0.0581\ M$$

Integrative Exercise Putting Concepts Together

The element bismuth (Bi, atomic number 83) is the heaviest member of group 5A. A salt of the element, bismuth subsalicylate, is the active ingredient in Pepto-Bismol®, an over-the-counter medication for gastric distress.

(e) ^{209}Bi is the heaviest stable isotope of any element. How many protons and neutrons are present in this nucleus?

Periodic table

(e) Recall that the atomic number of any element is the number of protons and electrons in a neutral atom of the element. (Section 2.3)

Bismuth is element 83;

therefore 83 protons in the nucleus.

Because the atomic mass number is 209, there are 209 – 83 = 126 neutrons in the nucleus.

Integrative Exercise Putting Concepts Together

(f) The density of Bi at 25 °C is 9.808 g/cm^3. How many Bi atoms are present in a cube of the element that is 5.00 cm on each edge? How many moles of the element are present?

Periodic table

(f) We can use the density and the atomic weight to determine the number of moles of Bi, and then use Avogadro's number to convert the result to the number of atoms. (Sections 1.4 & 3.4)

The volume of the cube is $\ell^3 = (5.00)^3\ \text{cm}^3 = 125\ \text{cm}^3$.

$(5.00)^3\ \text{cm}^3 = 125\ \text{cm}^3$. Then we have

$$125\ \cancel{\text{cm}^3}\ \text{Bi} \times \frac{9.808\ \cancel{\text{g Bi}}}{1\ \cancel{\text{cm}^3}} \times \frac{1\ \text{mol Bi}}{209.0\ \cancel{\text{g Bi}}} = 5.87\ \text{mol Bi}$$

$$5.87\ \cancel{\text{mol Bi}} \times \frac{6.022 \times 10^{23}\ \text{atom Bi}}{\cancel{1\ \text{mol Bi}}} = 3.53 \times 10^{24}\ \text{atoms Bi}$$