GENERAL CHEMISTRY I

Chapter 7
Periodic Properties of the Elements

Contents

7-1 Development of the Periodic Table

The discovery of chemical elements has been ongoing since ancient times

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	[113]	Fl	[115]	Lv	[117]	[118]
				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

Ancient Times	Middle Ages–1700	1735–1843	1843–1886	1894–1918	1923–1961
(9 elements)	(6 elements)	(42 elements)	(18 elements)	(11 elements)	(17 elements)

As the number of known elements increased, scientists began classifying them

- 1869, Dimitri Mendeleev
  Lother Meyer

When the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically.

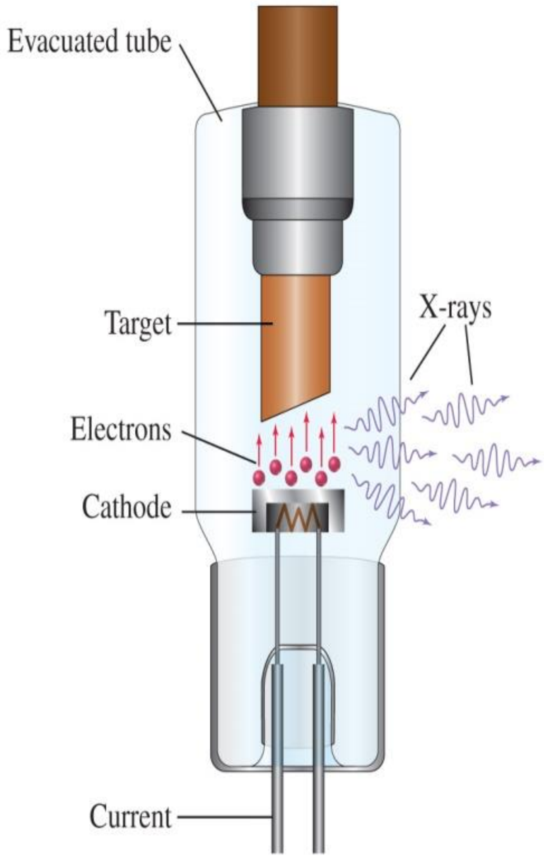
Table 7.1 Comparison of the Properties of Eka-Silicon Predicted by Mendeleev with the Observed Properties of Germanium

Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat (J/g-K)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride (°C)	A little under 100	84

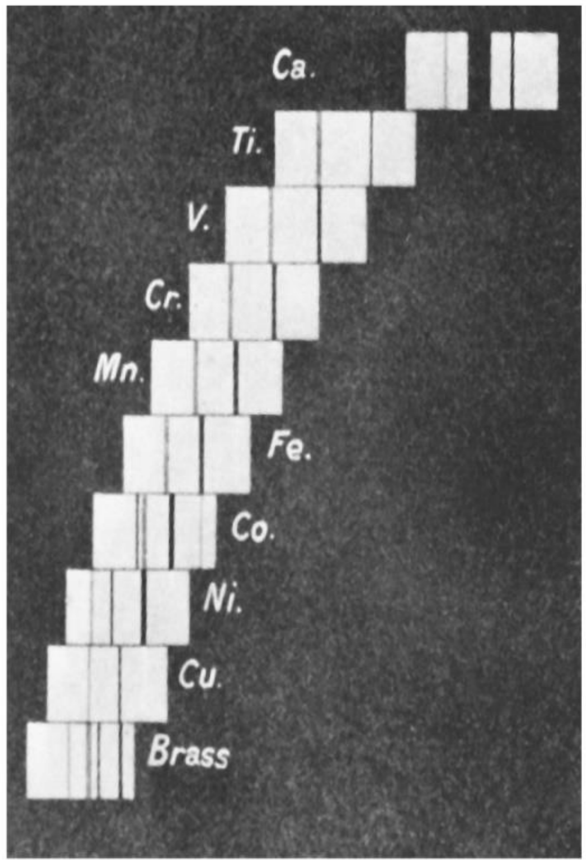
Gallium (Ga) was unknown to Mendeleev. He boldly predicted its existence and properties, referring to it as eka-aluminum eka-silicon ("under" silicon).

When this elements were discovered, it's properties closely matched Mendeleev's prediction

X-Ray Spectra



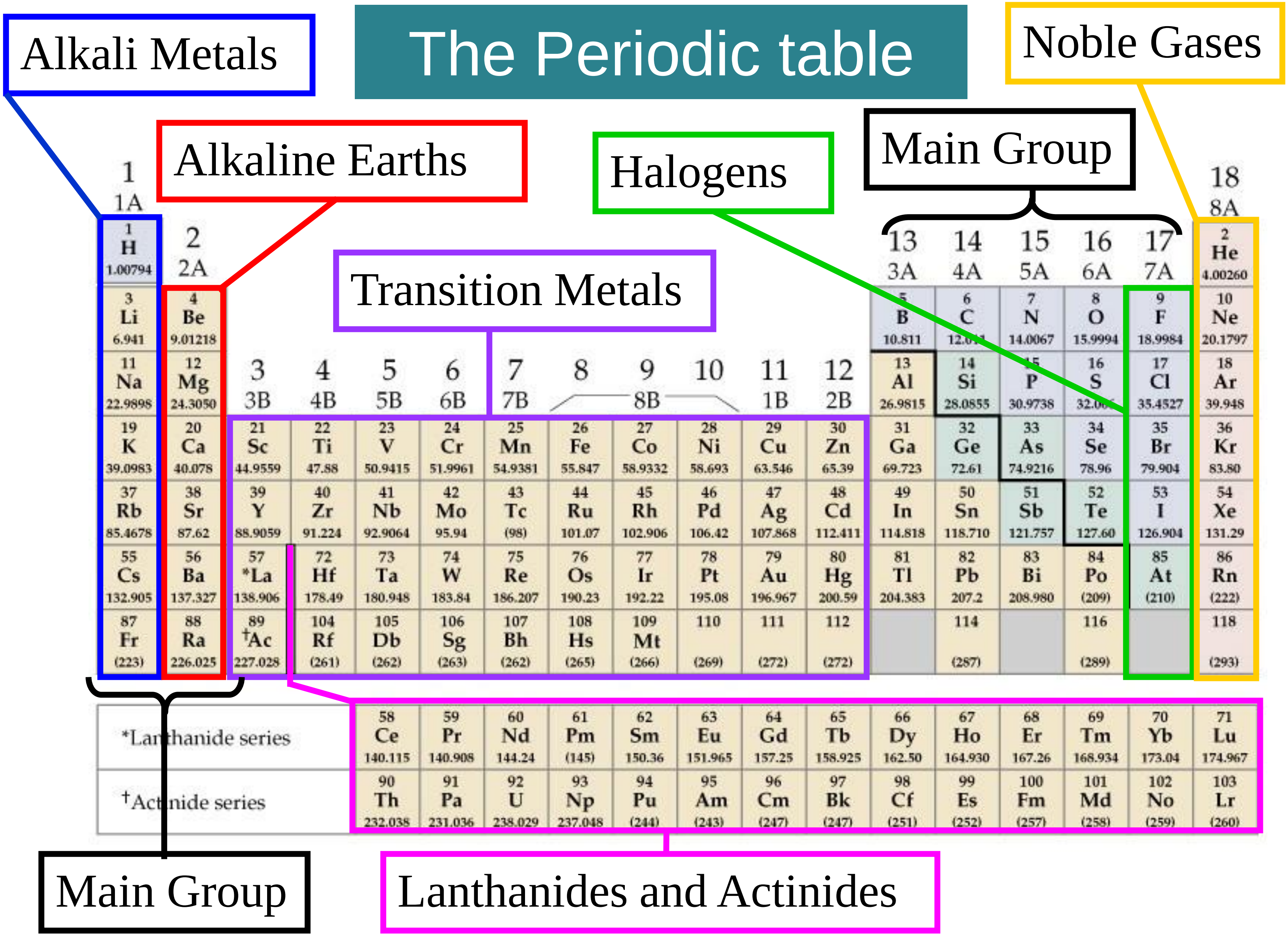
(a)



(b)

- Moseley 1913
  - X-ray emission is explained in terms of transitions in which e^- drop into orbits close to the atomic nucleus.
  - Correlated frequencies to nuclear charges.
- $\nu = A\,(Z - b)^2$
  - Used to predict new elements (43, 61, 75) later discovered.

The Periodic table



7-2 Effective Nuclear Charge

When looking at any particular electron within an atom it experiences two major forces.

- An **attractive** force from the nucleus,
- A **repulsive** force from the surrounding electrons.

➔ The electron can become ***shielded from the full force*** of the nucleus because of the other surrounding electrons.

➔ Effective Nuclear Charge (Z_{eff}) measures the force exerted onto an electron by the nucleus, and can be calculated using Slater's Rules.

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

Z = Nuclear Charge

S = Shielding Constant

the value of S is usually close to the number of core electrons

Slater's rules

1. The atom's electronic configuration is grouped as follows, in terms of increasing *n* and *l* quantum numbers:

(1s) (2s,2p) (3s,3p) (3d) (4s,4p) (4d) (4f) (5s,5p) (5d) etc.

2. Electrons in groups to the right of a given electron do not shield electrons to the left.

3. The shielding constant S for electrons in certain groups.

For ns and np valence electrons:

a) Each electron in the same group contributes 0.35 except the 1s, where 0.30 works better.

b) Each electron in n – 1 group contributes 0.85

c) Each electron in n – 2 or lower groups contributes 1.00.

For nd and nf valence electrons:

a) Each electron in the same group contributes 0.35.

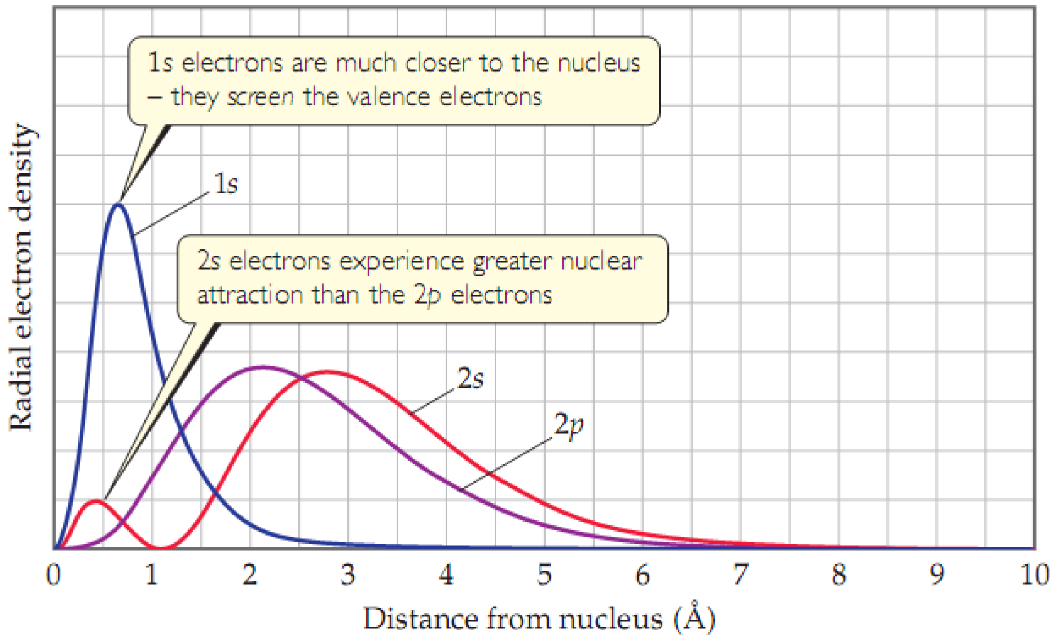
b) Each electron in groups to the left contributes 1.00

EXAMPLE

Calculate Z_{eff} of a valence electron of fluorine.

Electronic configuration $1s^2\mathbf{2s^22p^5}$

0.85 0.35



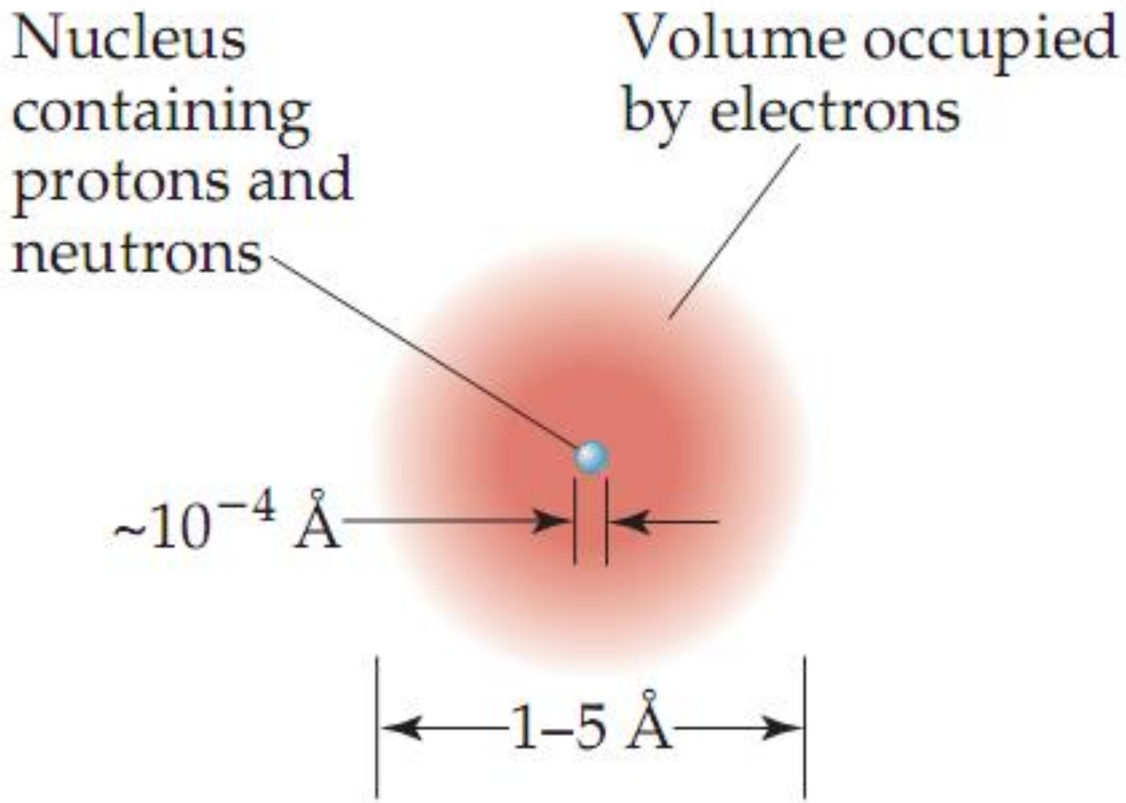
Apply the Slater's rules

S = (0.35 x 6) + (0.85 * 2) = 3.8.

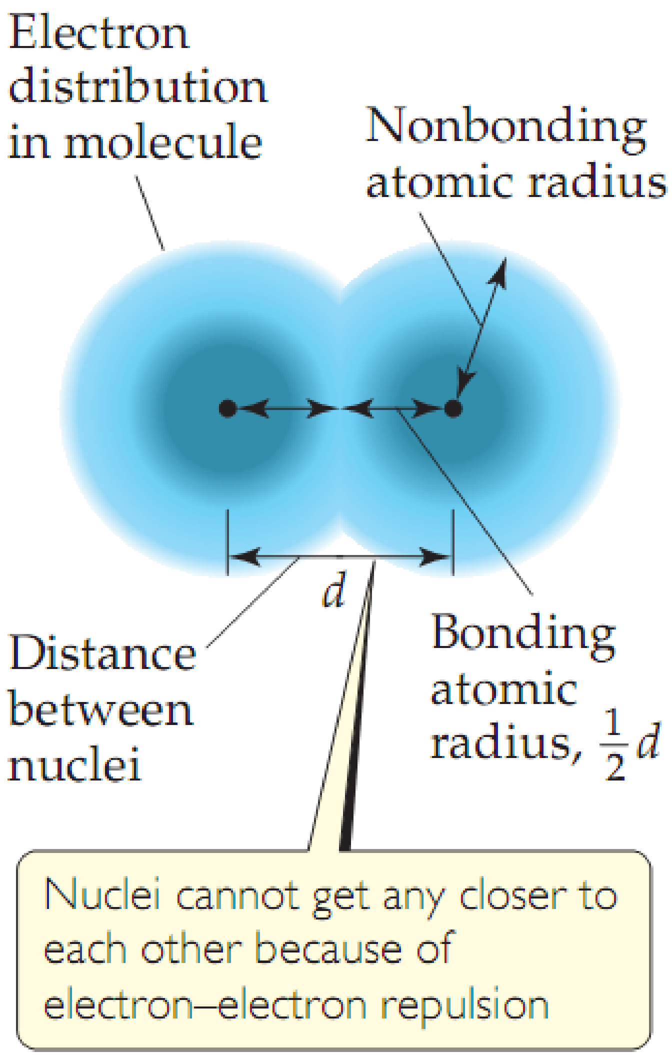
Slater's rules ignore the contribution of an electron to itself in screening; therefore, we consider only six n = 2 electrons, not all seven.

Thus, Z_{eff} = Z - S = 9 - 3.8 = 5.2+

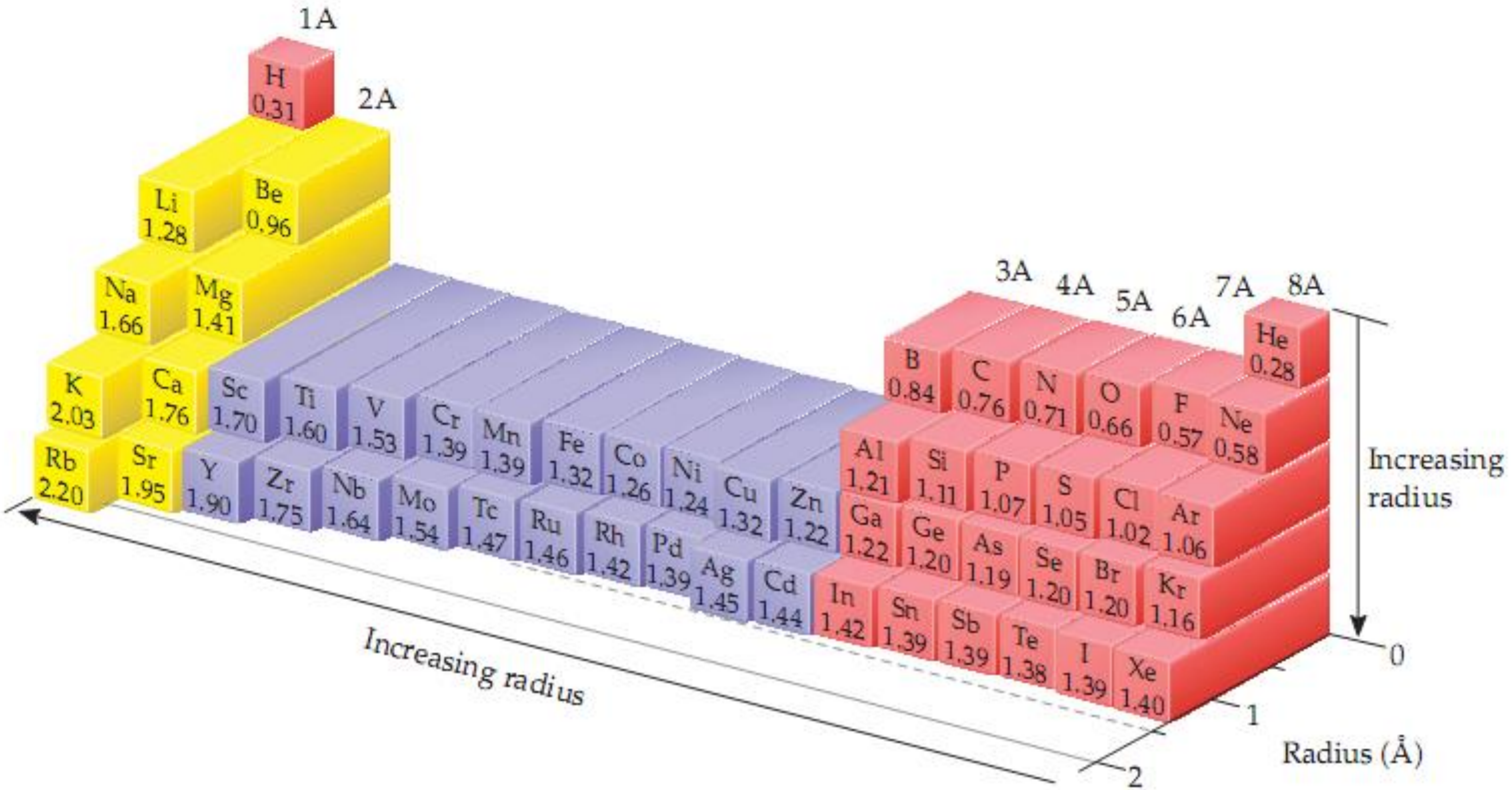
7-3 Sizes of Atoms and Ions



The shortest distance separating the two nuclei during collisions is twice the radii of the atoms. We call this radius the *nonbonding atomic radius* or the *Van der Waals radius*



Periodic Trends in Atomic Radii



- Within each group, bonding atomic radius tends to increase from top to bottom.
- Within each period, bonding atomic radius tends to decrease from left to right

EXAMPLE

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. Predict the lengths of the C-S, C-H, and S-H bonds in this molecule. Bonding atomic radius of C, S and H is 0.76 Å, 1.05Å, and 0.31Å, respectively.

Solution:

C-S bond length = bonding atomic radius of C + bonding atomic radius of S

= 0.76 Å+ 1.05 Å= 1.81 Å

C-H bond length = 0.76 Å+ 0.31 Å= 1.07 Å

S-H bond length = 1.05 Å+ 0.31 Å= 1.36 Å

Periodic Trends in Ionic Radii

- The size of an ion depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the valence electrons reside

- When a cation is formed from a neutral atom,
  - electrons are removed from the occupied atomic orbitals that are the most spatially extended from the nucleus
  - the number of electron–electron repulsions is reduced

➔ ***Cations are smaller than their parent atoms, and anions are larger than their parent atoms***

➔ ***For ions carrying the same charge, ionic radius increases as we move down a column in the periodic table***

EXAMPLE

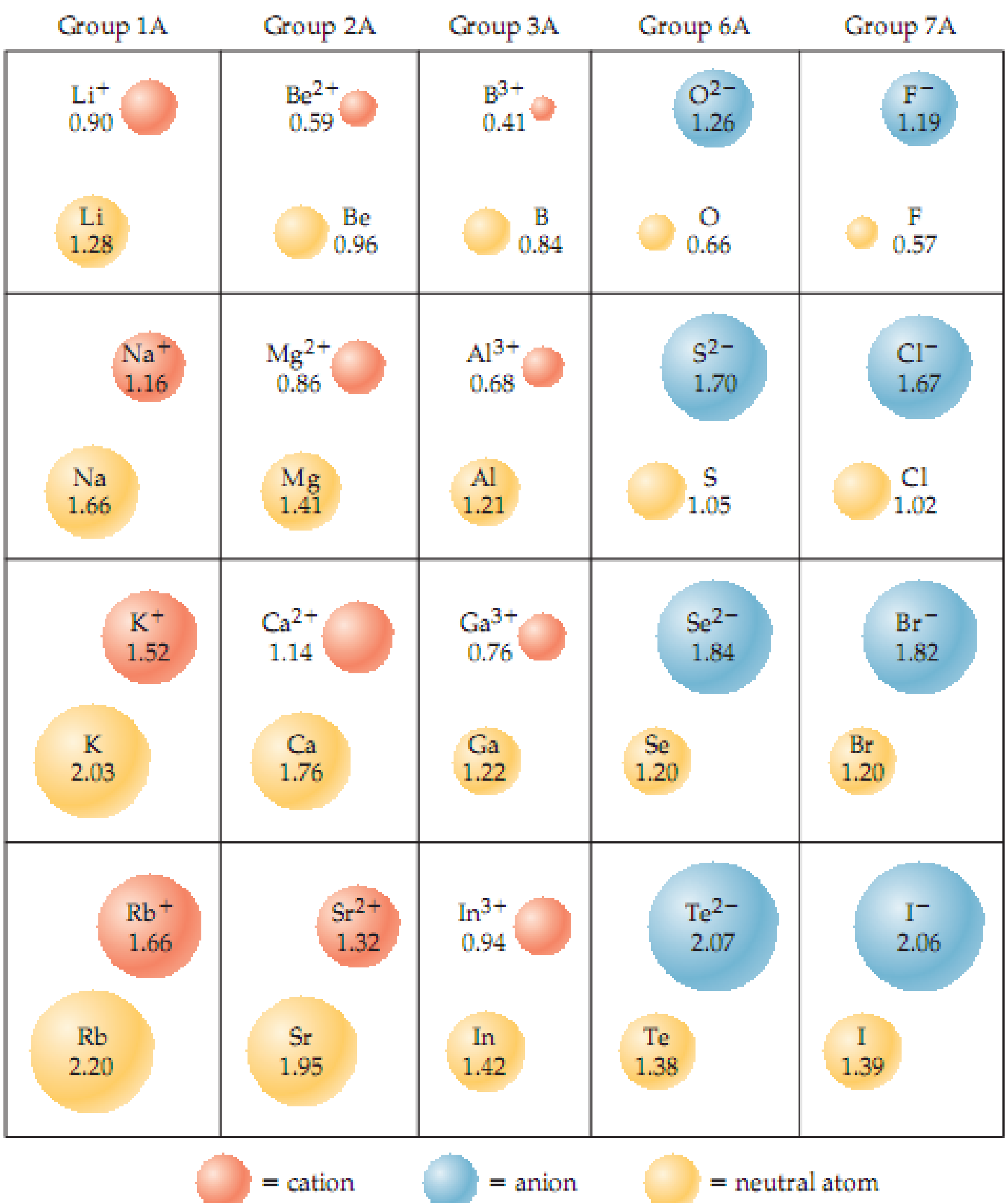
Arrange Mg^{2+}, Ca^{2+}, and Ca in order of decreasing radius.

Solution:

Cations are smaller than their parent atoms: $Ca^{2+} < Ca$.

Ca is below Mg in group 2A, $Ca^{2+} > Mg^{2+}$.

Consequently, ***Ca >Ca²⁺ > Mg²⁺.***



Group 1A
Group 2A
Group 3A
Group 6A
Group 7A
Li+ 0.90
Be2+ 0.59
B3+ 0.41
O2− 1.26
F− 1.19
Li 1.28
Be 0.96
B 0.84
O 0.66
F 0.57
Na+ 1.16
Mg2+ 0.86
Al3+ 0.68
S2− 1.70
Cl− 1.67
Na 1.66
Mg 1.41
Al 1.21
S 1.05
Cl 1.02
K+ 1.52
Ca2+ 1.14
Ga3+ 0.76
Se2− 1.84
Br− 1.82
K 2.03
Ca 1.76
Ga 1.22
Se 1.20
Br 1.20
Rb+ 1.66
Sr2+ 1.32
In3+ 0.94
Te2− 2.07
I− 2.06
Rb 2.20
Sr 1.95
In 1.42
Te 1.38
I 1.39
= cation
= anion
= neutral atom

7-4 Ionization Energy

$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$ $I_1 = 738$ kJ

$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$ $I_2 = 1451$ kJ

The first ionization energy, I_1, is the energy needed to remove the first electron from a neutral atom.

The second ionization energy, I_2, is the energy needed to remove the second electron

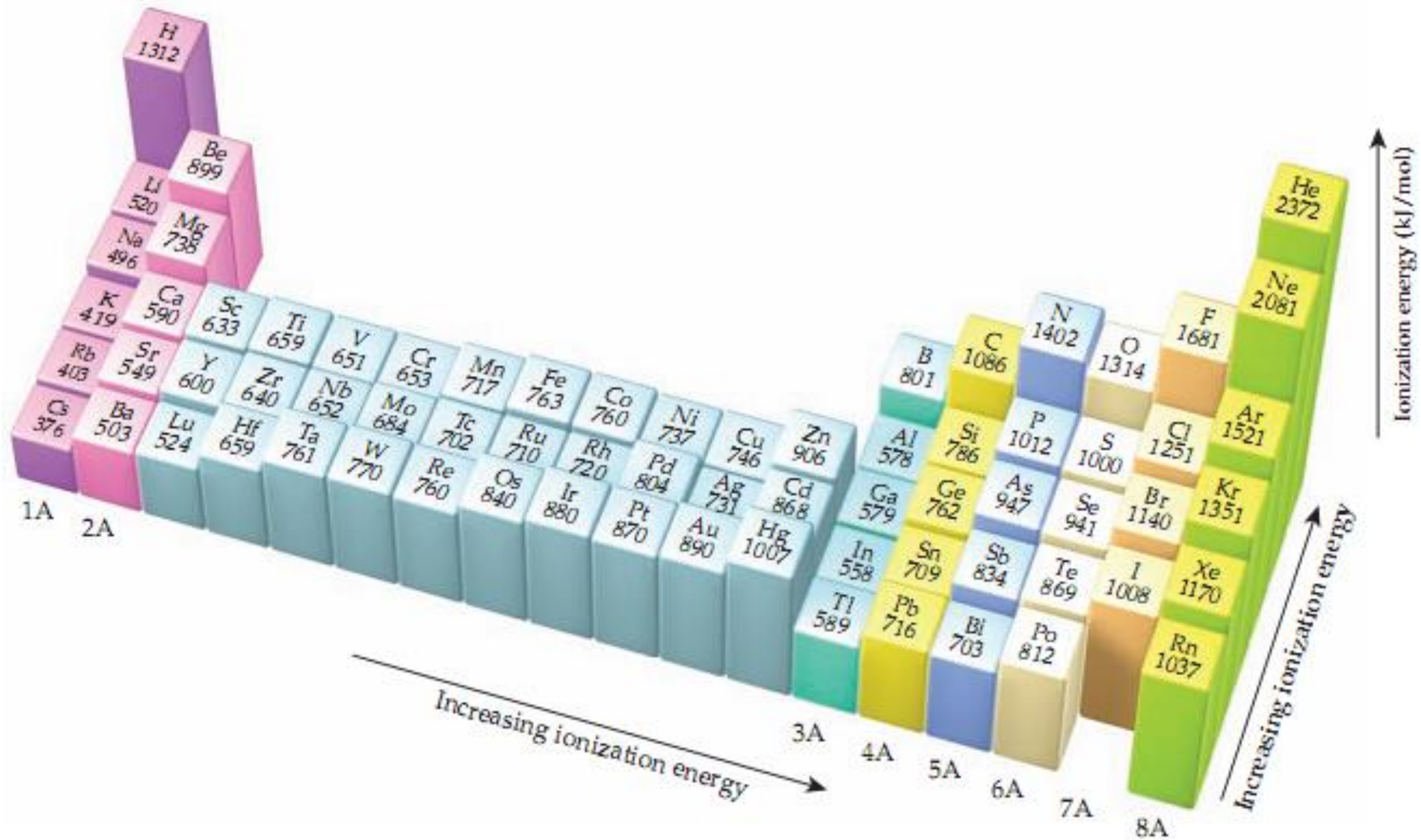
$I_1 < I_2$

Variations in Successive Ionization Energies

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4562			(inner-shell electrons)		
Mg	738	1451	7733				
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

$$I_1 < I_2 < I_3$$

Periodic Trends in First Ionization Energies



1. I_1 generally increases as we move across a period.
2. I_1 generally increases as we move up any column in the periodic table.
3. The s- and p-block elements show a larger range of I1 values than do the transitionmetal elements.

EXAMPLE

Referring to the periodic table, arrange the atoms Ne, Na, P, Ar, K in order of increasing first ionization energy.

Solution

Ionization energy increases as we move left to right across a period, thus $I_{1,Na} < I_{1,P} < I_{1,Ar}$

Ionization increases as we move up a group, thus

$I_{1,Ar} < I_{1,Ne}$

$I_{1,K} < I_{1,Na}$

Therefore, $I_{1,K} < I_{1,Na} < I_{1,P} < I_{1,Ar} < I_{1,Ne}$

Electron Configurations of Ions

- When electrons are removed from an atom to form a cation, they are always removed first from the occupied orbitals having the largest principal quantum number, *n*

$$Li(1s^2 2s^1) \rightarrow Li^+(1s^2) + e^-$$

$$Fe([Ar]\ 4s^2 3d^6) \rightarrow Fe^{2+}([Ar]\ 3d^6) + 2e^-$$

$$Fe^{2+}([Ar]\ 3d^6) \rightarrow Fe^{3+}([Ar]\ 3d^5) + e^-$$

- If there is more than one occupied subshell for a given value of *n*, the electrons are first removed from the orbital with the highest value of *l*.

$$Sn([Kr]\ 5s^2 4d^{10} 5p^2) \rightarrow Sn([Kr]\ 5s^2 4d^{10}) + 2e^- \rightarrow Sn([Kr]\ 4d^{10}) + 4e^-$$

- Electrons added to an atom to form an anion are added to the empty or partially filled orbital having the lowest value of *n*.

$$F(1s^2 2s^2 2p^5) + e^- \rightarrow F(1s^2 2s^2 2p^6)$$

7-5 Electron Affinity

- Ionization energy (IE) is the energy (in kJ) ***absorbed*** to remove an electron from a gaseous atom or ion.

$Cl\ (g) \rightarrow Cl^{+}\ (g) + e^{-}$ $\Delta E = 1251$ kJ/mol

$[Ne]3s^{2}3p^{5}$ $[Ne]3s^{2}3p^{5}$

- Electron affinity is the energy (in kJ) ***released*** to in-take an electron from a gaseous atom or ion.

$Cl\ (g) + e^{-} \rightarrow Cl^{-}\ (g)$ $\Delta E = -349$ kJ/mol

$[Ne]3s^{2}3p^{5}$ $[Ne]3s^{2}3p^{56}$

- The greater the attraction between an atom and an added electron, the more negative the atom's electron affinity
- For noble gases, the electron affinity has a positive value, meaning that the anion is higher in energy than are the separated atom and electron

$Ar\ (g) + e^{-} \rightarrow Ar^{-}\ (g)$ $\Delta E = >0$

First Electron Affinity

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

Generally, it increases going from left to right across a period and decreases going down a group

7-6 Metals, Nonmetals, and Metalloids

Metal	Nonmetal
Have a shiny luster; various colors, although most are silvery	Do not have a luster; various colors
Solids are malleable and ductile	Solids are usually brittle; some are hard, and some are soft
Good conductors of heat and electricity	Poor conductors of heat and electricity
Most metal oxides are ionic solids that are basic	Most nonmetal oxides are molecular substances that form acidic solutions
Tend to form cations in aqueous solution	Tend to form anions or oxyanions in aqueous solution

Metals

- *Metals tend to have **low ionization energies** and therefore tend to **form cations** relatively easily.*
- *Compounds made up of a metal and a nonmetal tend to be **ionic substances***

$$2\ Ni\ (s) + O_2\ (g) \rightarrow 2\ NiO\ (s)$$

- *Most metal oxides are basic.*
  - *Those that dissolve in water react to form metal hydroxides*

metal oxide + water → metal hydroxide

$$Na_2O\ (s) + H_2O\ (l) \rightarrow 2NaOH\ (aq)$$

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

  - *Even metal oxides that are insoluble in water demonstrate their basicity by reacting with acids to form a salt plus water*

metal oxide + acid → salt + water

$$NiO\ (s) + 2\ HNO_3\ (aq) \rightarrow Ni(NO_3)_2\ (aq) + H_2O$$

EXAMPLE

a) Would you expect scandium oxide to be a solid, liquid, or gas at room temperature?

(b) Write the balanced chemical equation for the reaction of scandium oxide with nitric acid.

Solution

(a) Because scandium oxide is the oxide of a metal, we expect it to be an ionic solid.

(b) In compounds, scandium has a 3+ charge, Sc^{3+}, and the oxide ion is O^{2-}. Consequently, the formula of scandium oxide is Sc_2O_3.

Metal oxides tend to be basic and, therefore, to react with acids to form a salt plus water. In this case the salt is scandium nitrate, $Sc(NO_3)_3$

$$Sc_2O_3(s) + 6\ HNO_3(aq) \rightarrow 2\ Sc(NO_3)_3\,(aq) + 3H_2O\ (l)$$

Nonmetals

- *Because of their relatively large, negative electron affinities, nonmetals* ***tend to gain electrons*** *when they react with metals..*
- *Compounds composed entirely of nonmetals are typically* ***molecular substances*** *that tend to be gases, liquids, or low-melting solids at room temperature*

$$2\ Al\ (s) + 3\ Br_2\ (l) \rightarrow 2\ AlBr_3\ (s)$$

- *Most nonmetal oxides are acidic.*
  - *Those that dissolve in water react to form acid*

nonmetal oxide + water → acid

$$CO_2\ (g) + H_2O\ (l) \rightarrow H_2CO_3\ (aq)$$

$$P_4O_{10} + 6\ H_2O\ (l) \rightarrow 4\ H_3PO_4\ (aq)$$

  - *Most nonmetal oxides dissolve in basic solutions to form a salt plus water*

nonmetal oxide + base → salt + water

$$CO_2\ (g) + 2\ NaOH\ (aq) \rightarrow Na_2CO_3\ (aq) + H_2O\ (l)$$

Metalloids

- Metalloids have properties ***intermediate*** between those of metals and those of nonmetals
  - They may have some characteristic metallic properties but lack others.

    For example, the metalloid silicon looks like a metal, but it is brittle rather than malleable and does not conduct heat or electricity nearly as well as metals do.

  - Several metalloids, most notably silicon, are electrical semiconductors and are the principal elements used in integrated circuits and computer chips

7-7 Trends for Group 1A and Group 2A Metals

Group 1A: The Alkali Metals

- Alkali metals are ***soft metallic solids***
- Alkali metals have ***low densities and melting points***, and these properties vary in a fairly regular way with increasing atomic number
- The alkali metal of any given period has the ***lowest I_1 value in the period***
- Alkali metals ***react vigorously with water***, producing hydrogen gas and a solution of an alkali metal hydroxide

$$M\ (s) + H_2O\ (l) \rightarrow M(OH)_2\ (aq) + H_2\ (g)$$

- Alkali metals exist in nature only ***as compounds***

$$2\ M(s) + H_2\ (g) \rightarrow 2\ MH\ (s)$$

$$2\ M(s) + S\ (g) \rightarrow M_2S\ (s)$$

Table 7.4 Some Properties of the Alkali Metals

Element	Electron Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius (Å)	I_1 (kJ/mol)
Lithium	$[He]2s^1$	181	0.53	1.28	520
Sodium	$[Ne]3s^1$	98	0.97	1.66	496
Potassium	$[Ar]4s^1$	63	0.86	2.03	419
Rubidium	$[Kr]5s^1$	39	1.53	2.20	403
Cesium	$[Xe]6s^1$	28	1.88	2.44	376

Li

Na

K

The lower the ionization energies, the more violent the reaction of alkali with water

Reactions of Alkali with Oxigen

Li

Na

K

$$4\,Li(s) + O_2(g) \longrightarrow 2\,Li_2O(s)$$

lithium oxide

$$2\,Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

sodium peroxide

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

potassium superoxide

Group 2A: The Alkaline Earth Metals

- The first ionization energies of the alkaline earth metals are low but not as low as those of the alkali metals. Consequently, the alkaline earth metals are less reactive than their alkali metal neighbors.

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

Beryllium and magnesium, the lightest alkaline earth metals, are the least reactive

Reactions of Alkali Earth with Water

- Beryllium does not react with either water or steam, even when heated red-hot
- Magnesium reacts slowly with liquid water and more readily with steam

$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

- Calcium and the elements below it react readily with water at room temperature

$$Ca(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

7-8 Trends for Selected Nonmetals

- Hydrogen
- Group 6A: The Oxygen Group
- Group 7A: The Halogens
- Group 8A: The Noble Gases

Hydrogen

- The $1s^1$ electron configuration of hydrogen suggests that its chemistry should have ***some resemblance to that of the alkali metals***.
- The ionization energy of hydrogen is more than double that of any of the alkali metals ➔ chemistry of hydrogen is ***much richer and more complex*** than that of the alkali metals
- Hydrogen reacts with most nonmetals to form ***molecular compounds***
-

$$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \underset{\text{ionic}}{\mathrm{NaCl}(s)} \qquad \Delta H^\circ = -410.9\ \mathrm{kJ}$$

$$\tfrac{1}{2}\mathrm{H}_2(g) + \tfrac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \underset{\text{molecular}}{\mathrm{HCl}(g)} \qquad \Delta H^\circ = -92.3\ \mathrm{kJ}$$

- Hydrogen has the ability to gain an electron from a metal with a low ionization energy

$$2\,\mathrm{M}(s) + \mathrm{H}_2(g) \longrightarrow 2\,\mathrm{MH}(s)$$

Group 6A: The Oxygen 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	$[He]2s^22p^4$	−218	1.43 g/L	0.66	1314
Sulfur	$[Ne]3s^23p^4$	115	1.96 g/cm^3	1.05	1000
Selenium	$[Ar]3d^{10}4s^24p^4$	221	4.82 g/cm^3	1.20	941
Tellurium	$[Kr]4d^{10}5s^25p^4$	450	6.24 g/cm^3	1.38	869
Polonium	$[Xe]4f^{14}5d^{10}6s^26p^4$	254	9.20 g/cm^3	1.40	812

Oxygen, sulfur, and selenium are typical nonmetals.

Tellurium is a metalloid

Polonium is a metal that is radioactive and quite rare

Group 7A: The Halogens

Table 7.7 Some Properties of the Halogens

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ/mol)
Fluorine	$[He]2s^2 2p^5$	−220	1.69 g/L	0.57	1681
Chlorine	$[Ne]3s^2 3p^5$	−102	3.12 g/L	1.02	1251
Bromine	$[Ar]4s^2 3d^{10} 4p^5$	−7.3	3.12 g/cm^3	1.20	1140
Iodine	$[Kr]5s^2 4d^{10} 5p^5$	114	4.94 g/cm^3	1.39	1008

- All the halogens are typical nonmetals.
- Their melting and boiling points increase with increasing atomic number.
    - Fluorine and chlorine are gases at room temperature,
    - Bromine is a liquid
    - Iodine is a solid.
- Each element consists of diatomic molecules: F_2, Cl_2, Br_2, and I_2

Group 8A: The Noble Gases

Table 7.8 Some Properties of the Noble Gases

Element	Electron Configuration	Boiling Point (K)	Density (g/L)	Atomic Radius* (Å)	I_1 (kJ/mol)
Helium	$1s^2$	4.2	0.18	0.28	2372
Neon	$[He]2s^22p^6$	27.1	0.90	0.58	2081
Argon	$[Ne]3s^23p^6$	87.3	1.78	1.06	1521
Krypton	$[Ar]4s^23d^{10}4p^6$	120	3.75	1.16	1351
Xenon	$[Kr]5s^24d^{10}5p^6$	165	5.90	1.40	1170
Radon	$[Xe]6s^24f^{14}5d^{10}6p^6$	211	9.73	1.50	1037

- Noble gases, are all nonmetals that are gases at room temperature.
- The noble gases have completely filled s and p subshells
- They are all monatomic

Homeworks

Integrative Excercises:

7.110

7.113

Chemistry

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You will have a 15 minute quizz next week

What can you use for assistance?

- A pen
- A calculator
- A periodic table
- An A4-sized sheet of hand written notes

No other devices are allowed!