Chapter 19:

The Representative Elements: Groups 1A Through 4A

19.1 A Survey of the Representative Elements

Reviewing the Periodic Table Regions

- Representative elements: Groups 1A - 8A - filling *s* and *p* orbitals.
- Transition elements: Center of the table - filling *d* orbitals
- Lanthanides, Actinides: listed separately, on the bottom of the table - filling 4*f* and 5*f*
- Metalloids: separate metals from nonmetals

Figure 19.1: The periodic table.

1A	2A											3A	4A	5A	6A	7A	8A
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	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Ha	Unh	Uns	Uno	Une	Uun	Uuu	Uub						

Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 19.2: The atomic radii of some atoms in picometers.

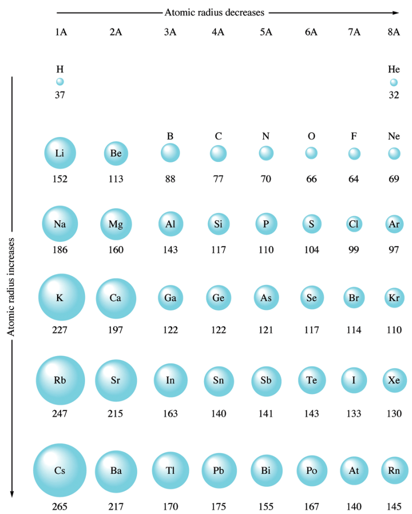


TABLE 19.1 **Distribution (Mass Percent) of the 18 Most Abundant Elements in the Earth's Crust, Oceans, and Atmosphere**

Element	Mass Percent	Element	Mass Percent
Oxygen	49.2	Chlorine	0.19
Silicon	25.7	Phosphorus	0.11
Aluminum	7.50	Manganese	0.09
Iron	4.71	Carbon	0.08
Calcium	3.39	Sulfur	0.06
Sodium	2.63	Barium	0.04
Potassium	2.40	Nitrogen	0.03
Magnesium	1.93	Fluorine	0.03
Hydrogen	0.87	All others	0.49
Titanium	0.58		

Figure 19.3: The structure of quartz, which has the empirical formula SiO_2.

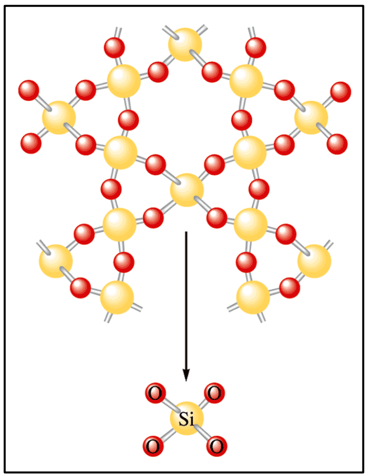


TABLE 19.2 **Abundance of Elements in the Human Body**

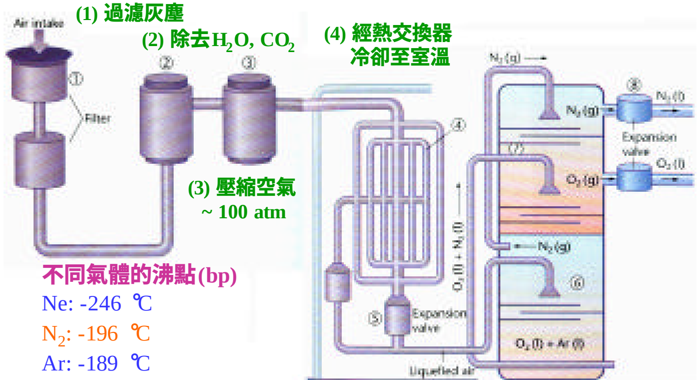
Major Elements	Mass Percent	Trace Elements (in alphabetical order)
Oxygen	65.0	Arsenic
Carbon	18.0	Chromium
Hydrogen	10.0	Cobalt
Nitrogen	3.0	Copper
Calcium	1.4	Fluorine
Phosphorus	1.0	Iodine
Magnesium	0.50	Manganese
Potassium	0.34	Molybdenum
Sulfur	0.26	Nickel
Sodium	0.14	Selenium
Chlorine	0.14	Silicon
Iron	0.004	Vanadium
Zinc	0.003	

Metallurgy

- . . . the process of obtaining a metal from its ore.
- This always involves reduction of the ions to the elemental metal (oxidation state = 0).

$$WO_3(s) + 3H_2(g) \xrightarrow{\text{heat}} W(l) + 3H_2O(g)$$

空氣分餾 (Fractionation of air)



不同氣體的沸點(bp)

Ne: -246 ℃

N_2: -196 ℃

Ar: -189 ℃

O_2: -183 ℃

Kr: -153 ℃

Xe: -108 ℃

19.2 The Group 1A Elements

TABLE 19.3 Sources and Methods of Preparation of the Pure Alkali Metals

Element	Source	Method of Preparation
Lithium	Silicate minerals such as spodumene, $LiAl(Si_2O_6)$	Electrolysis of molten LiCl
Sodium	NaCl	Electrolysis of molten NaCl
Potassium	KCl	Electrolysis of molten KCl
Rubidium	Impurity in lepidolite, $Li_2(F,OH)_2Al_2(SiO_3)_3$	Reduction of RbOH with Mg and H_2
Cesium	Pollucite ($Cs_4Al_4Si_9O_{26} \cdot H_2O$) and an impurity in lepidolite (see Fig. 19.4)	Reduction of CsOH with Mg and H_2

Figure 19.4: Lepidolite is composed mainly of lithium, aluminum, silicon, and oxygen, but it also contains significant amounts of rubidium and cesium.

TABLE 19.4 Selected Physical Properties of the Alkali Metals

Element	Ionization Energy (kJ/mol)	Standard Reduction Potential (V) for $M^+ + e^- \rightarrow M$	Radius of M^+ (pm)	Melting Point (°C)
Lithium	520	−3.05	60	180
Sodium	495	−2.71	95	98
Potassium	419	−2.92	133	63
Rubidium	409	−2.99	148	39
Cesium	382	−3.02	169	29

Group 1A Oxides

In the presence of ample oxygen,

- $4Li + O_2 \rightarrow 2Li_2O$
- $2Na + O_2 \rightarrow Na_2O_2$
- $K + O_2 \rightarrow KO_2$
- $Rb + O_2 \rightarrow RbO_2$
- $Cs + O_2 \rightarrow CsO_2$

TABLE 19.5 Types of Compounds Formed by the Alkali Metals with Oxygen

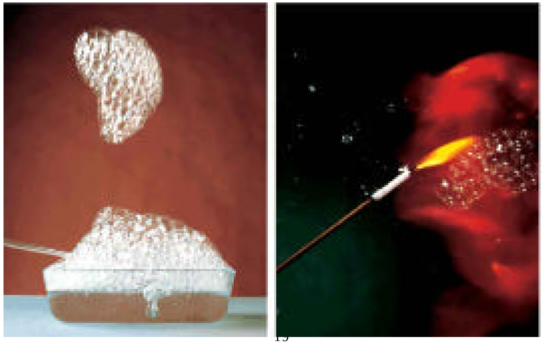
General Formula	Name	Examples
M_2O	Oxide	Li_2O, Na_2O
M_2O_2	Peroxide	Na_2O_2
MO_2	Superoxide	KO_2, RbO_2, CsO_2

TABLE 19.6 Selected Reactions of the Alkali Metals

Reaction	Comment
$2M + X_2 \rightarrow 2MX$	X_2 = any halogen molecule
$4Li + O_2 \rightarrow 2Li_2O$	Excess oxygen
$2Na + O_2 \rightarrow Na_2O_2$	
$M + O_2 \rightarrow MO_2$	M = K, Rb, or Cs
$2M + S \rightarrow M_2S$	
$6Li + N_2 \rightarrow 2Li_3N$	Li only
$12M + P_4 \rightarrow 4M_3P$	
$2M + H_2 \rightarrow 2MH$	
$2M + 2H_2O \rightarrow 2MOH + H_2$	
$2M + 2H^+ \rightarrow 2M^+ + H_2$	Violent reaction!

19.3 Hydrogen

(left) Hydrogen gas being used to blow soap bubbles. (right) As the bubbles float upward, they are lighted using a candle on a long pole. The orange flame is due to the heat from the reaction of hydrogen with the oxygen in the air that excites sodium ions in the soap solution.

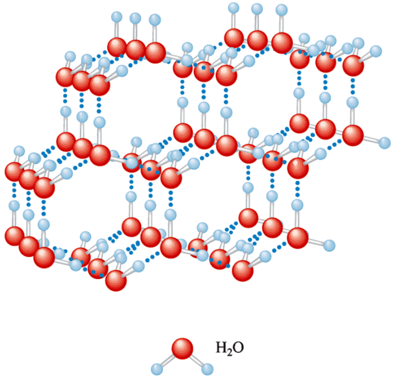


Hydrides

- . . . are binary compounds containing hydrogen.

- ionic hydrides: hydrogen + the most active metals (eg; LiH, CaH_2)
- covalent hydrides: hydrogen + other nonmetals (eg; H_2O, CH_4, NH_3)
- metallic (interstitial) hydrides: transition metal crystals treated with H_2 gas.

Figure 19.5: The structure of ice, showing the hydrogen bonding.



Ice

19.4 The Group 2A Elements

TABLE 19.7 Selected Physical Properties, Sources, and Methods of Preparation for the Group 2A Elements

Element	Radius of M^{2+} (pm)	Ionization Energy (kJ/mol) First	Ionization Energy (kJ/mol) Second	$\mathcal{E}°$(V) for $M^{2+} + 2e^- \rightarrow M$	Source	Method of Preparation
Beryllium	~30	900	1760	−1.70	Beryl ($Be_3Al_2Si_6O_{18}$)	Electrolysis of molten $BeCl_2$
Magnesium	65	738	1450	−2.37	Magnesite ($MgCO_3$), dolomite ($MgCO_3 \cdot CaCO_3$), carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$)	Electrolysis of molten $MgCl_2$
Calcium	99	590	1146	−2.76	Various minerals containing $CaCO_3$	Electrolysis of molten $CaCl_2$
Strontium	113	549	1064	−2.89	Celestite ($SrSO_4$), strontianite ($SrCO_3$)	Electrolysis of molten $SrCl_2$
Barium	135	503	965	−2.90	Baryte ($BaSO_4$), witherite ($BaCO_3$)	Electrolysis of molten $BaCl_2$
Radium	140	509	979	−2.92	Pitchblende (1 g of Ra/7 tons of ore)	Electrolysis of molten $RaCl_2$

Calcium metal reacting with water to form bubbles of hydrogen gas.

Figure 19.6: (a) Solid $BeCl_2$ can be visualized as being formed from many $BeCl_2$ molecules, where lone pairs on the chlorine atoms are used to bond to the beryllium atoms in adjacent $BeCl_2$ molecules. (b) The extended structure of solid $BeCl_2$. (c) The ball-and-stick model of the extended structure.

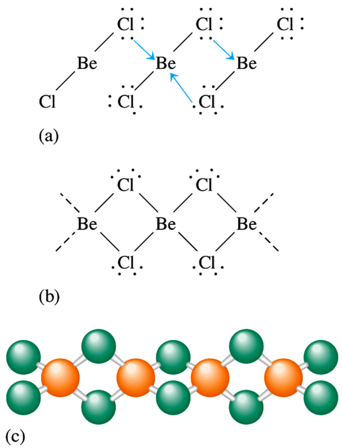


TABLE 19.8 Selected Reactions of the Group 2A Elements

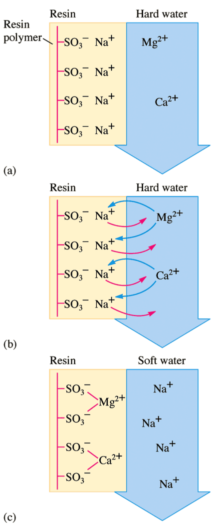
Reaction	Comment
$M + X_2 \rightarrow MX_2$	X_2 = any halogen molecule
$2M + O_2 \rightarrow 2MO$	Ba gives BaO_2 as well
$M + S \rightarrow MS$	
$3M + N_2 \rightarrow M_3N_2$	High temperatures
$6M + P_4 \rightarrow 2M_3P_2$	High temperatures
$M + H_2 \rightarrow MH_2$	M = Ca, Sr, or Ba; high temperatures; Mg at high pressure
$M + 2H_2O \rightarrow M(OH)_2 + H_2$	M = Ca, Sr, or Ba
$M + 2H^+ \rightarrow M^{2+} + H_2$	
$Be + 2OH^- + 2H_2O \rightarrow Be(OH)_4^{2-} + H_2$	

Ion Exchange

Ca^{2+} and Mg^{2+} are often removed during ion exchange, releasing Na^+ into solution.

- Ion exchange resin: large molecules that have many ionic sites.

Figure 19.7: (a) A schematic representation of a typical cation-exchange resin. (b) and (c) When hard water is passed over the cation-exchange resin, the Ca^{2+} and Mg^{2+} bind to the resin.



19.5 The Group 3A Elements

TABLE 19.9 Selected Physical Properties, Sources, and Methods of Preparation for the Group 3A Elements

Element	Radius of M^{3+} (pm)	Ionization Energy (kJ/mol)	$\mathscr{E}°$(V) for $M^{3+} + 3e^- \rightarrow M$	Sources	Method of Preparation
Boron	20	798	—	Kernite, a form of borax ($Na_2B_4O_7 \cdot 4H_2O$)	Reduction by Mg or H_2
Aluminum	51	581	−1.71	Bauxite (Al_2O_3)	Electrolysis of Al_2O_3 in molten Na_3AlF_6
Gallium	62	577	−0.53	Traces in various minerals	Reduction with H_2 or electrolysis
Indium	81	556	−0.34	Traces in various minerals	Reduction with H_2 or electrolysis
Thallium	95	589	0.72	Traces in various minerals	Electrolysis

Gallium metal has such a low melting point (30ºC) that it melts from the heat of a hand.

Figure 19.8: (a) The structure of B_2H_6 with its two three-center B—H—B bridging bonds and four "normal" B—H bonds. (b) The structure of B_5H_9. There are five "normal" B—H bonds to terminal hydrogens and four three-center bridging bonds around the base.

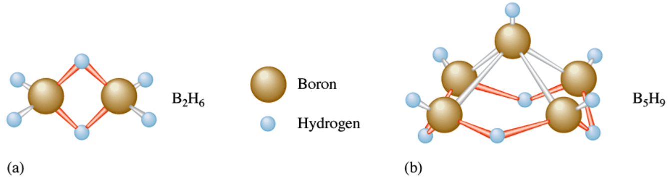


TABLE 19.10 Selected Reactions of the Group 3A Elements

Reaction	Comment
$2M + 3X_2 \rightarrow 2MX_3$	X_2 = any halogen molecule; Tl gives TlX as well, but no TlI_3
$4M + 3O_2 \rightarrow 2M_2O_3$	High temperatures; Tl gives Tl_2O as well
$2M + 3S \rightarrow M_2S_3$	High temperatures; Tl gives Tl_2S as well
$2M + N_2 \rightarrow 2MN$	M = Al only
$2M + 6H^+ \rightarrow 2M^{3+} + 3H_2$	M = Al, Ga, or In; Tl gives Tl^+
$2M + 2OH^- + 6H_2O \rightarrow 2M(OH)_4^- + 3H_2$	M = Al or Ga

19.6 The Group 4A Elements

TABLE 19.11 Selected Physical Properties, Sources, and Methods of Preparation for the Group 4A Elements

Element	Electronegativity	Melting Point (°C)	Boiling Point (°C)	Sources	Method of Preparation
Carbon	2.5	3727 (sublimes)	—	Graphite, diamond, petroleum, coal	—
Silicon	1.8	1410	2355	Silicate minerals, silica	Reduction of K_2SiF_6 with Al, or reduction of SiO_2 with Mg
Germanium	1.8	937	2830	Germanite (mixture of copper, iron, and germanium sulfides)	Reduction of GeO_2 with H_2 or C
Tin	1.8	232	2270	Cassiterite (SnO_2)	Reduction of SnO_2 with C
Lead	1.9	327	1740	Galena (PbS)	Roasting of PbS with O_2 to form PbO_2 and then reduction with C

TABLE 19.12 Strengths of C—C, Si—Si, and Si—O Bonds

Bond	Bond Energy (kJ/mol)
C—C	347
Si—Si	340
Si—O	452

Lead (II) oxide, known as *litharge*.

TABLE 19.13 Selected Reactions of the Group 4A Elements

Reaction	Comment
$M + 2X_2 \rightarrow MX_4$	X_2 = any halogen molecule; M = Ge or Sn; Pb gives PbX_2
$M + O_2 \rightarrow MO_2$	M = Ge or Sn; high temperatures; Pb gives PbO or Pb_3O_4
$M + 2H^+ \rightarrow M^{2+} + H_2$	M = Sn or Pb

Inert Pair Effect

The tendency for the heavier elements of Groups 3A and 4A to exhibit lower oxidation states as well as their expected oxidation states.

- Group 3A   +1 and +3 oxidation states
- Group 4A   +2 and +4 oxidation states