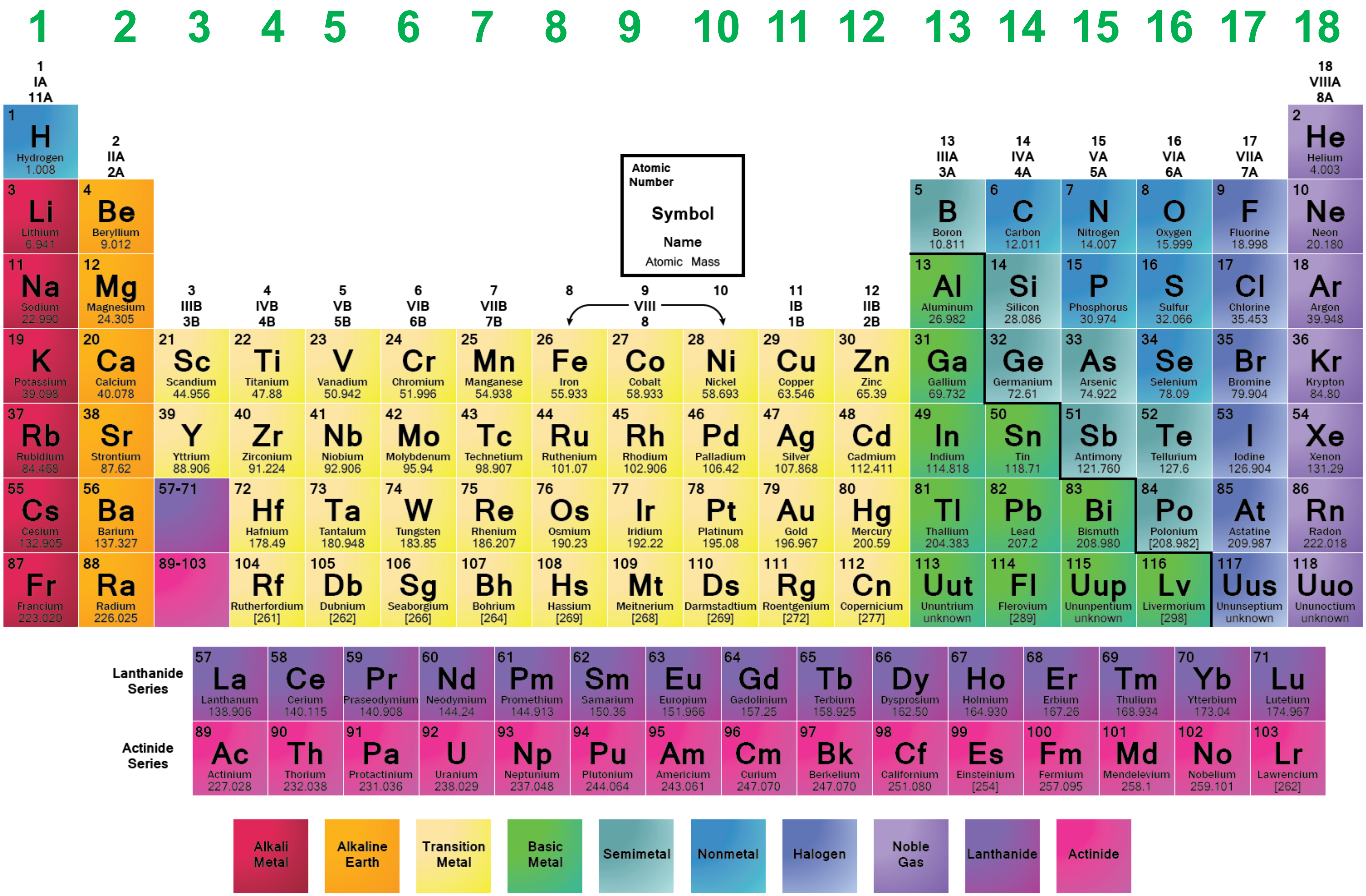
PERIODIC TABLE OF THE ELEMENTS



Atomic Number
Symbol
Name
Atomic Mass

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 IA 11A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

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

Chapters 14 and 23. PROPERTIES OF THE ELEMENTS

First, let's look at Periodic Table and Group numbering.

14.1 Hydrogen. The simplest atom, ~90% of all atoms in the universe. The only element whose isotopes are each given a different symbol and name.

^{1}H (or H, protium) = one proton (p^+), plus one e^- surrounding it.
^{2}H (or D, deuterium) = one p^+ and one neutron (n), plus one e^-
^{3}H (or T, tritium) = one p^+ and two n, plus one e^-.

Deuterium (^{2}H) was produced in the 'Big Bang' — it is too fragile to survive fusion conditions in the stars (which produce the lighter elements) or supernovas (which produce heavier elements).

Hydrogen is the exception in the periodic table — it cannot be satisfactorily classified in any group: it has similarities both to (a) group 1 metals such as Li, Na, etc, in forming H^+ and (b) group 17 non-metals such as F, Cl, etc, in being H_2 (H-H with a single covalent bond) in its stable elemental form (compare F_2, Cl_2, etc) and also forming H^- (hydride ion) analogous to F^-, Cl^-, etc.

Brief Summary of Hydrogen Chemistry

- most commonly forms covalent compounds; ionic compounds are rare.
- high ionization energy (unlike group 1, because e^- close to nucleus without other e's to shield it) and low electronegativity (unlike group 1, because only one proton to attract e^-s).
  ∴ unlike groups 1 and 17 in that H^+ and H^- ions are rare (whereas Na^+, K^+, etc, ions are common, as are F^-, Cl^-, etc ions) because they usually bond covalently to other things *e.g.*, H_3O^+ , OH^-, NH_4^+, etc
  Very rare exceptions are certain ionic salts of H^-, the hydride ion, in compounds such as NaH and CaH_2 (similar to NaCl and $CaCl_2$).

Ionic Hydrides (H^-). With very strong reducing agents (Na(s), Ca(s), Li(s), etc.), hydrogen is reduced to H^- = ionic hydrides.

e.g. $2\ Na\ (s) + H_2\ (g) \rightarrow 2\ NaH\ (s)$

Note that: $H_2\ (g) + 2\ e^- \rightarrow 2\ H^-\ (g)$ $E^\circ = -2.23\ V$ (very negative!)

Hydrides are thus very reactive (strong reducing agents) and will either:

(1) react with a H^+ and go to H_2 (g):

$$NaH\ (s) + H_2O\ (l) \rightarrow Na^+\ (aq) + OH^-\ (aq) + H_2\ (g)$$

or (2) reduce something and go to H_2 (g):

$$TiCl_4\ (l) + 4\ LiH\ (s) \rightarrow Ti\ (s) + 4\ LiCl\ (s) + 2\ H_2\ (g)$$

Covalent Hydrogen Compounds. Very common and stable: CH_4, NH_3, H_2O, HF, etc, etc. These other elements have higher electronegativity than H (H = 2.2, C = 2.5, N = 3.1, O = 3.5 F = 4.1)

$\therefore$ we think of these as containing H^+ oxidation state and C^{4-}, N^{3-}, O^{2-}, F^- oxidation states. e.g. $F_2(g) + H_2(g) \rightarrow 2HF(g)$

H_2 is a very important gas, for many reasons. For example:

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$$

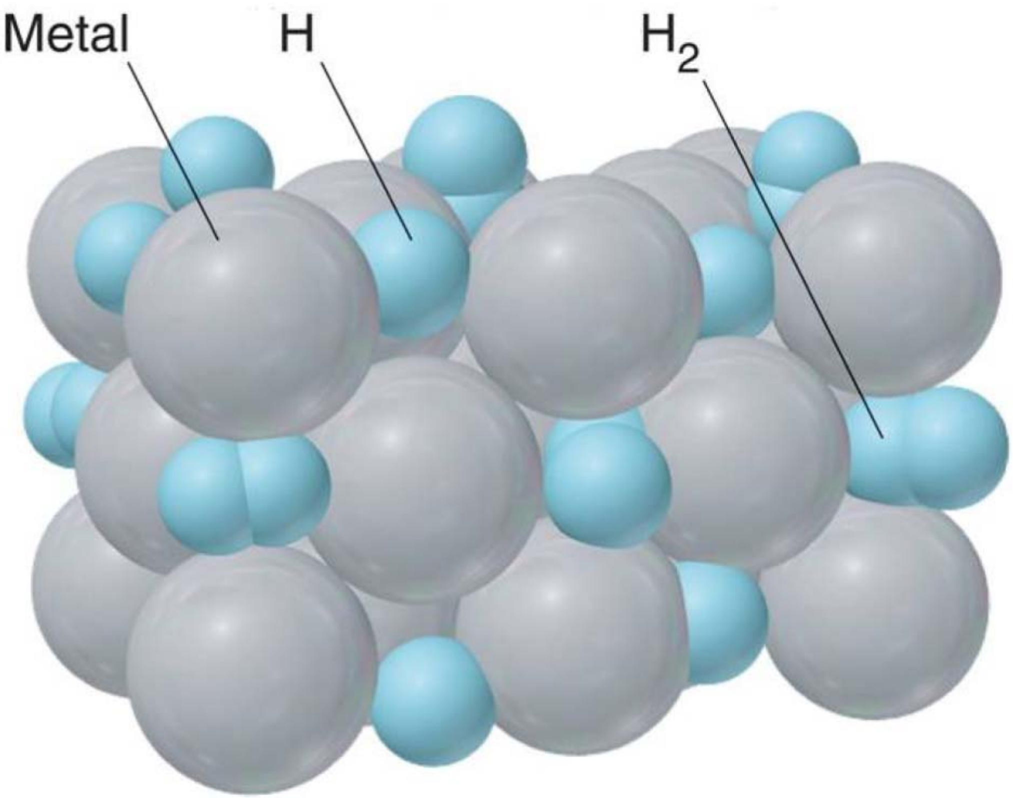
$\Delta G < 0$ (spontaneous) but very slow under normal conditions due to very strong $N\equiv N$ $\therefore$ reaction run in industry at high T (~400 °C) and pressure (250 atm) with an Fe catalyst to speed it up. This is called the **Haber process**, and is the main source of NH_3 for the fertilizer industry.

Metallic (Interstitial) Hydrides. H_2 molecules and H atoms can occupy space in-between the atoms of a metal. In particular, palladium (Pd) has a high affinity and can hold vast amounts (Pd: $\leq$ 935 times its volume = $PdH_{0.5}$). Best thought of as a solution of the gas in the metal! Came to people's attention during Cold Fusion stories of late 1980's.

Formation of Pd/H_2 is used to purify H_2 from gas mixtures.

Figure 14.2 A metallic (interstitial) hydride

Many transition metals form ***metallic (interstitial) hydrides***, in which H_2 molecules and H atoms occupy the holes in the crystal structure of the metal.



PERIODIC TRENDS ACROSS THE PERIODIC TABLE

Increasing:

metallic character	← ↓	non-metallic character	↑ →
ionic oxides	← ↓	covalent oxides	↑ →
basicity of oxides	← ↓	acidity of oxides	↑ →
electropositivity	← ↓	electronegativity	↑ →

ALSO: (i) Trends for a given element are affected by changes in its oxidation state
(ii) For Periods 2 and 3, atom size decreases left-to-right Figure 14.1

Examples: Which is the most metallic element
a) Li or Be b) Be or Mg c) Al or K

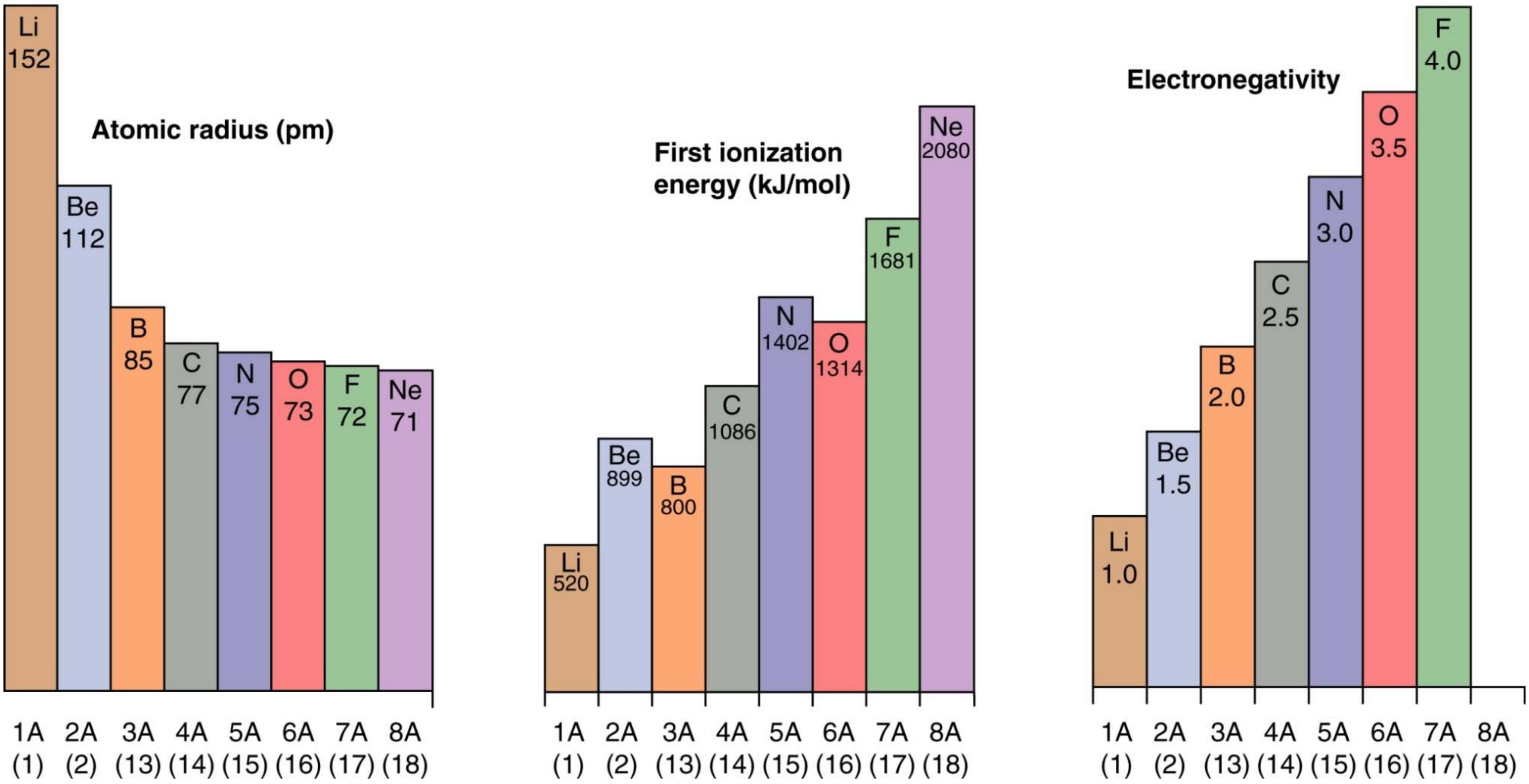
Which is the most acidic oxide? (i.e. dissolve in H_2O to give acidic soln)
a) Na_2O or Cl_2O_7 b) BaO or As_2O_5

Which is the stronger reducing agent?
a) Al or Mg b) Na or K c) Br^- or Cl^-

Which is the stronger oxidizing agent?
a) S or Se b) Br_2 or Cl_2 c) O_2 or F_2

Summary: The more metallic an element, the more basic is its oxide, the more ionic is its oxide, and the more electropositive (less electronegative) it is.

Table 14.1 Trends in Atomic, Physical, and Chemical Properties of the Period 2 Elements.



Trends in atomic radius, ionization energy, and electronegativity across Period 2.

GROUP 1. ALKALI METALS (ns^1)

Found as M^+ in minerals (loss of ns^1 electron). Too reactive (strong reducing agents) to be found as the free metal. Prepared in industry by electrolysis of melted salts.

All well-studied except Francium — radioactive, longest-lived isotope is ^{283}Fr: half-life of only 21.8 min. Estimated only ~25 g on Earth at any one time

Properties. Soft, silvery metals at 20 °C. All react vigorously with water to give H_2 gas: the reactivity increases down group.

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

(video)

half-reactions:

$$M\ (s) \rightarrow M^+\ (aq) + e^-$$

$$H_2O\ (l) + e^- \rightarrow \tfrac{1}{2}H_2\ (g) + OH^-\ (aq)$$

overall: $M\ (s) + H_2O\ (l) \rightarrow \tfrac{1}{2}H_2\ (g) + M^+\ (aq) + OH^-\ (aq)$

All react with O_2 gas <u>but products depend on metal</u>:

Li gives Li_2O (contains O^{2-} i.e. normal oxide ion)
Na gives Na_2O_2 (contains O_2^{2-} = O-O^{2-} i.e. peroxide ion)
K, Rb, Cs give MO_2 (contains O_2^{-} = O-O^{-} i.e. superoxide ion)

All M(s) must therefore be stored under inert oils to prevent reactions with air and water.

<u>Note</u>: Burning in air (rather than pure O_2 gas) gives above products, but Li (and only Li) also reacts with N_2 (*g*) to give the nitride, Li_3N, containing Li^+ and N^{3-}.

$$6\ Li\ (s) + N_2\ (g) \rightarrow 2\ Li_3N$$

Important Question – WHY is Li different? The difference between Li and the rest of group 1 (e.g. gives oxide with O_2, reacts with N_2, etc) is due to the small size of Li^+ - leads to high charge-to-size ratio. This also causes Li compounds to have significant covalent character (i.e. LiCl is still fairly ionic but has noticeable covalent character, whereas NaCl is very ionic). Li^+ has too high a charge-to-size ratio ("charge density") to be happy as completely free Li^+ ion, so it shares electrons a bit with anions (i.e. some covalency).

*** For this and other reasons (see later), the top member of every group is significantly different from the rest ***

Note 1: The decreasing charge-to-size ratio down the group (i.e. $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$) explains the products on reaction with O_2. The highest charge density (highest charge-to-size ratio) is Li^+, and this forms the highest charge density O^{2-} salt, whereas down the group the metals form the O_2^{2-} (peroxide) and then the O_2^- (superoxide) salts, i.e. decreasing charge density ions.

i.e., high charge density Li^+ favors forming a salt with high charge density O^{2-}, but down the group progressively lower charge density M^+ favor formation of progressively lower charge density anions.

Note 2: Group 1 metals have very high 2nd Ionization Potential -means M^{2+} not possible to make (in stable form at 25 °C). Of course, in places such as the surface of the sun, all sorts of other ions are possible.

GROUP 2. ALKALINE EARTH METALS (ns^2)

Occur in nature as M^{2+} — too reactive to exist as free metals.
Radium (Ra) radioactive: ^{226}Ra: half-life of 1599 years.

Again, Be slightly different from the rest due to high charge-to-size ratio (cf. Li in group 1): very hard metal and toxic. Others softer and not toxic. Also, Be compounds are mostly covalent, since Be^{2+} has too high a charge density to be happy as the free ion in ionic compounds – therefore it shares electrons with other atoms, decreasing its charge density (i.e. covalent bonding).

Be is unreactive to H_2O; Mg reacts slowly with cold H_2O, but fast with steam; others react vigorously with H_2O.

$$M\ (s) + 2\ H_2O\ (l) \rightarrow M(OH)_2\ (aq) + H_2\ (g)$$

All react with O_2 to give oxides MO except Ba, gives peroxide BaO_2.

Mg reacts with N_2 gas to ionic nitride, like Li. Others only at high T.

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s) \qquad (Mg + CO_2)$$

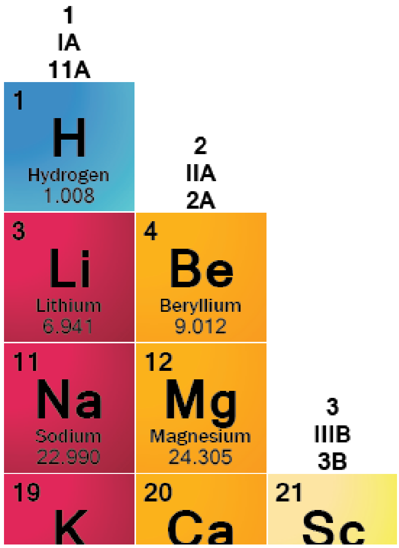
1st and 2nd ionizations are both very easy ∴ M^{2+} (no M^+).
3rd ionization very difficult — no M^{3+}

Diagonal Relationships

- similarities in properties between a period (row) 2 element and period 3 element, one group to the right.

Consider: Li vs Mg

- similar size of Li^+ *vs* Mg^{2+} (0.76 vs 0.72 Å) and similar properties (*e.g.*, both give nitrides with N_2, salts with similar solubilities and thermal stabilities, and significant covalency in their bonds). The origin of these similarities is again the high charge-to-size ratios of Li^+ and Mg^{2+}. Mg is bigger than Li, so Mg^{2+} and Li^+ end up being similar size.



Section 14.5. GROUP 13. (ns^2np^1)

Metallic character decreases moving right, and we find that boron (B) is not a metal = "metalloid" or "semi-metal". Al video

**** Metalloid = element with props between metals and non-metals ****

B_2O_3 is acidic (cf., Li_2O is basic, gives OH^- in water). Down group, metallic character increases - remainder of group 13 are metals but oxides of Al and Ga are amphoteric (see below), while those of In and Tl are basic.

Compare:

B:

$$\underset{\text{acid}}{B_2O_3\,(s)} + \underset{\text{base}}{6\,NaOH\,(aq)} \rightarrow \underset{\text{salt}}{2\,Na_3BO_3\,(aq)} + \underset{\text{water}}{3\,H_2O\,(l)}$$

$$(cf.\quad HCl\,(g) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O(l)\,)$$

in water, forms $B(OH)_3$ (or H_3BO_3), known as boric acid.

$$B(OH)_3 + 2\,H_2O \rightleftharpoons B(OH)_4^- + H_3O^+ \qquad pK_a = 9.25$$

Al, Ga: oxides react with bases as above, but also with acids. They are "amphoteric" (= can behave as both acids or bases)

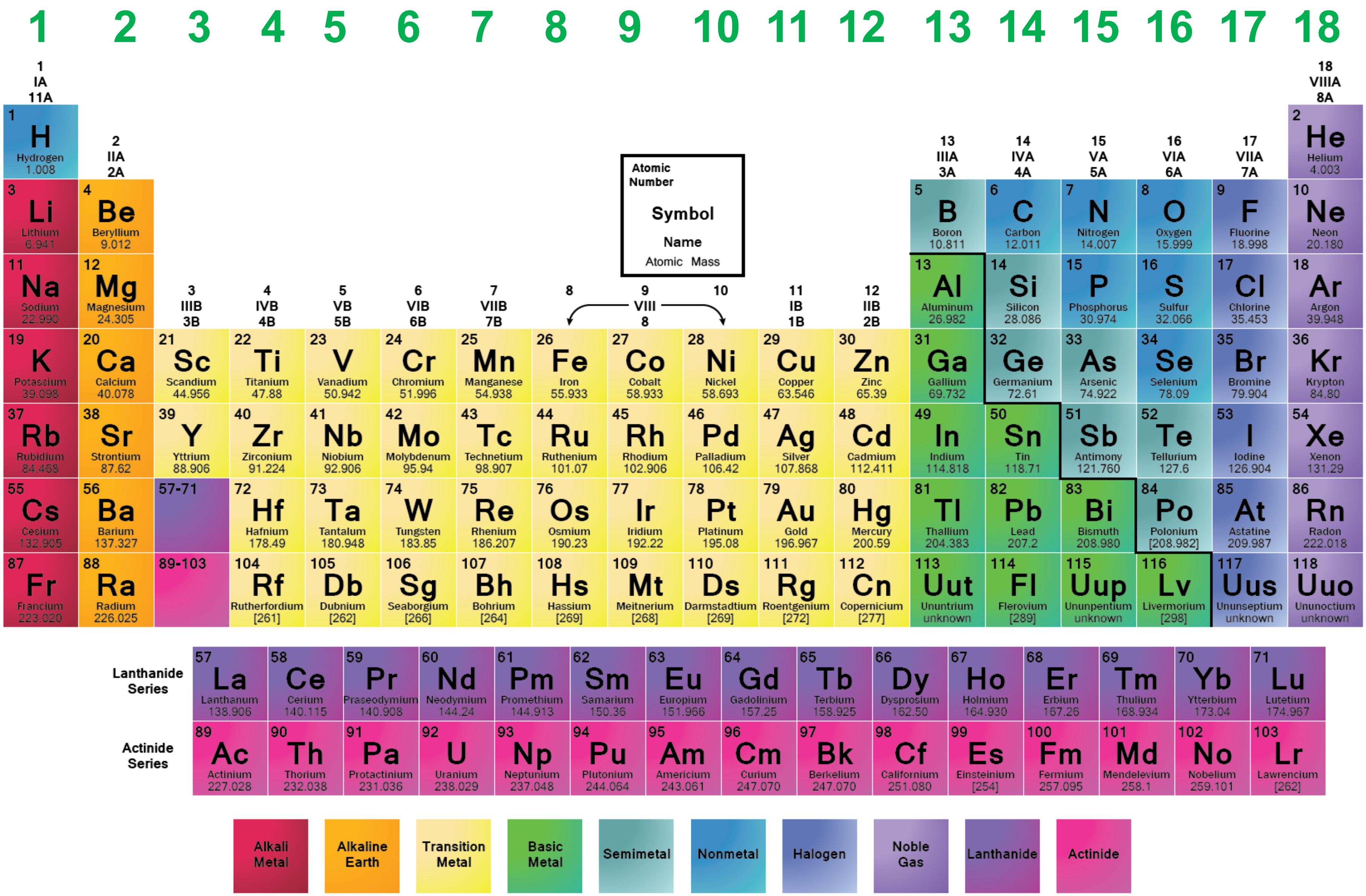
$$\underset{\text{acid}}{Al_2O_3\,(s)} + \underset{\text{base}}{6\,NaOH} \rightarrow \underset{\text{salt}}{2\,Na_3AlO_3\,(aq)} + \underset{\text{water}}{3\,H_2O\,(l)}$$

$$\underset{\text{base}}{Al_2O_3\,(s)} + \underset{\text{acid}}{3\,H_2SO_4\,(l)} \rightarrow \underset{\text{salt}}{Al_2(SO_4)_3\,(s)} + \underset{\text{water}}{3\,H_2O\,(l)}$$

In, Tl: oxides are basic and react only with acids.

$$\underset{\text{Base}}{In_2O_3\,(s)} + \underset{\text{acid}}{3\,H_2SO_4\,(l)} \rightarrow \underset{\text{salt}}{In_2(SO_4)_3\,(s)} + \underset{\text{water}}{3\,H_2O\,(l)}$$

PERIODIC TABLE OF THE ELEMENTS



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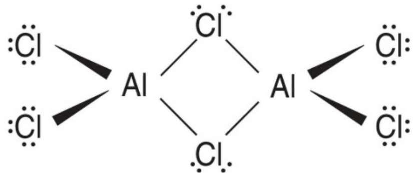
Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide

Bonding: Also varies - ionic character increases down the group (because metallic character is increasing). B compounds are all covalent, Al are sometimes ionic and sometimes covalent (e.g. $AlCl_3$); the rest mainly ionic (but also affected by oxidation state).



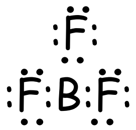
$AlCl_3$ is covalent!

Oxidation States

All form +3, but Tl also can be +1. ** In general, when two oxidation states are possible, lower one becomes more important down the group, and its properties are more metal-like **

Again, B (period 2) more different from the rest of group. For example, B forms many electron-deficient compounds – these are stable but nevertheless react with Lewis bases ⇨ attain an octet.

e.g., BF_3



B has only 6 e^- in its outer (valence) shell

∴ strong Lewis acid ∴ will accept electron pair from Lewis base

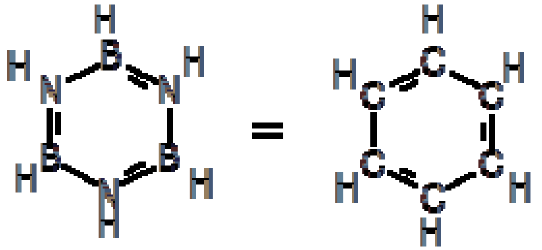
e.g., $F_3B + {:}NH_3 \rightarrow F_3B{-}NH_3$

this is source of acidity of $B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+$

Uses: Plentiful. B_2O_3 used in production of borosilicate glass. $B(OH)_3$ (boric acid) used as disinfectant, eyewash, insecticide. $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ used in washing powders.

Boron hydrides B_xH_y very important class of compounds. Figure 14.8

Aluminum sulfate used in water purification, dye industry, antiperspirants, etc.
Al_2O_3 used as a support for industrial catalysts, chromatography supports, etc.



BN compounds similar to analogous C compounds.
e.g. borazene, like benzene.

Borazon $(BN)_\infty$ has a similar structure to diamond and thus also <u>very</u> hard.

Diagonal Relationships: Be with Al (and B with Si)

Be and Al have similar properties
e.g., similar covalency in their compounds.

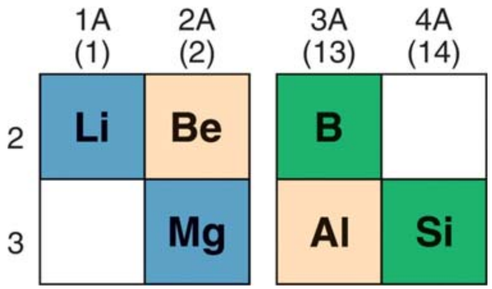
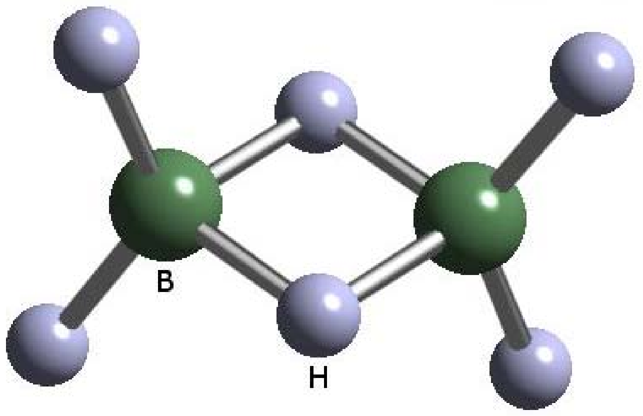
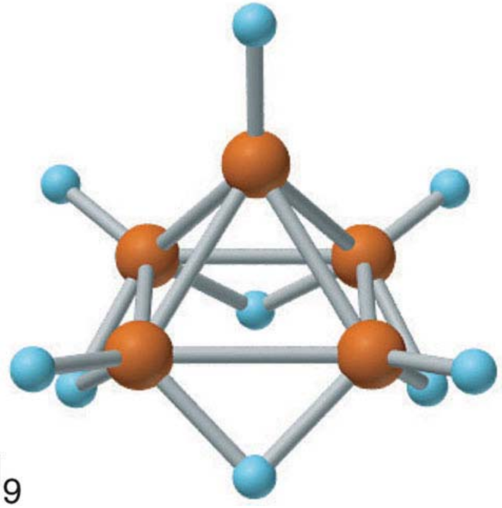


Figure 14.8 Some boron hydride structures (“boranes”)

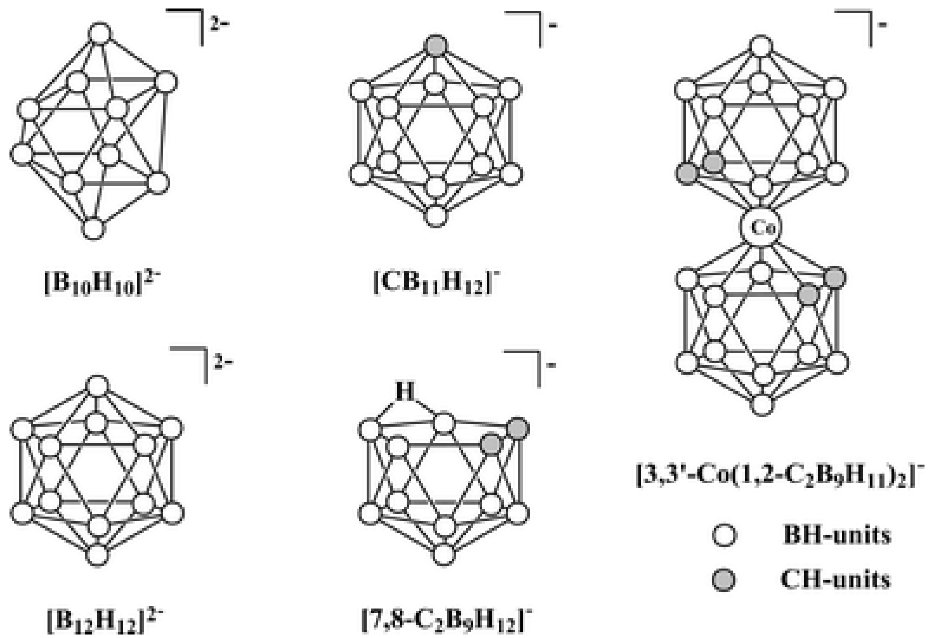
Borane is BH_3



Diborane



B_5H_9



Section 14.6. GROUP 14. (ns^2np^2)

- first group to show complete range of properties, from non-metal (C) to metal (Sn and Pb) – shows up in properties such as melting points and ΔH_{fus} - non-metals give strong covalent bonding $\therefore$ higher melting points (Table 14.2)

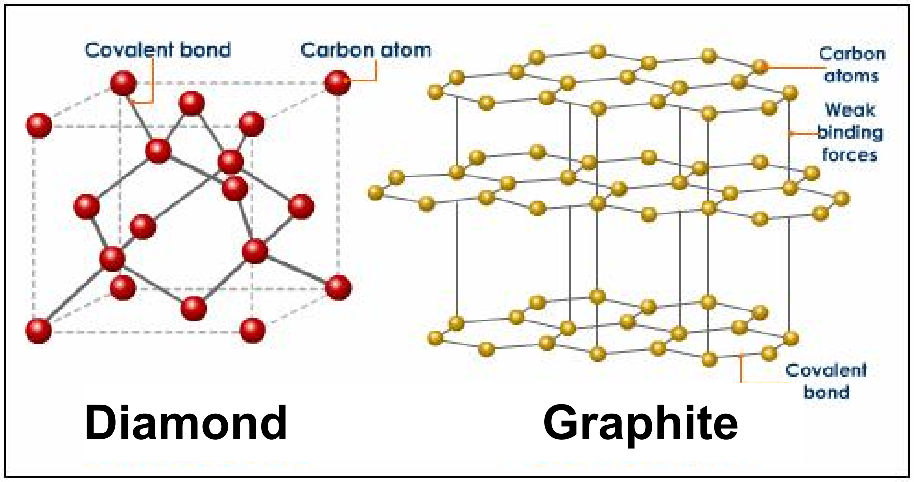
Elements: show important allotropes for the first time in C chemistry: graphite (2D sheets), diamond (3-D network), C_n (molecular fullerenes, *e.g.*, C_{60}, C_{70}, …), graphene (single sheet of graphite). C_{60} looks like a soccer ball. Figure 14.10

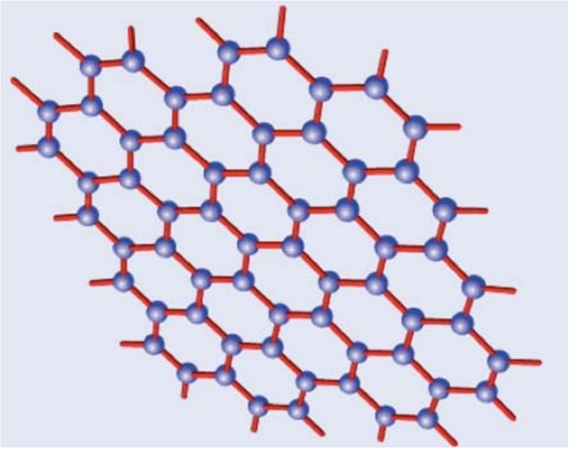
e.g.,

diamond	**graphite**
very hard	soft and greasy (used as lubricant)
colorless	black
3D	2D sheets
insulator	conductor

Graphite is the standard state of C at 298 K and 1 atm. Diamond formed at high T and P and interconverts to graphite at 298 K (1 atm, but very slowly).

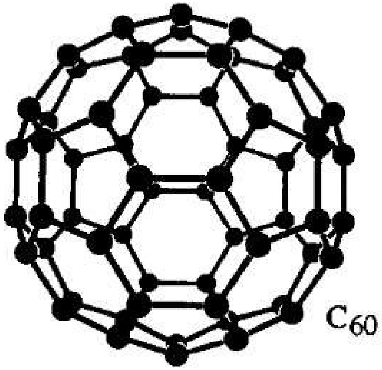
Allotropes of Carbon



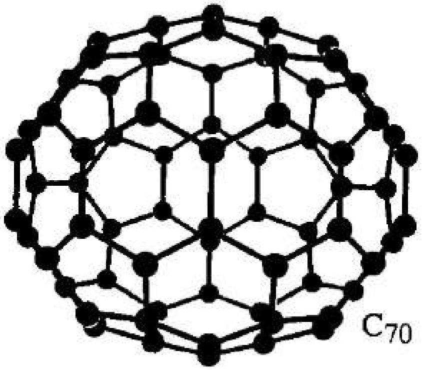


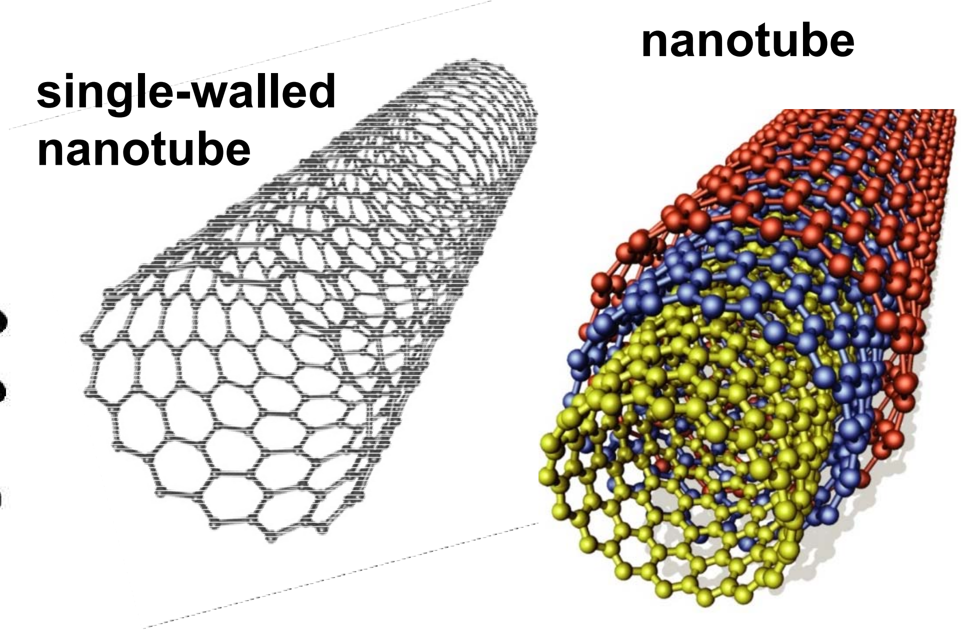
graphene – single sheet of graphite

C_{60}



C_{70}





single-walled nanotube

multi-walled nanotube

Oxidation states: **** multiple ones now more common! ****

C: non-metal: compounds all covalent except C^{4-} (carbide) ion e.g. Ca_2C. Oxide (CO_2) acidic: almost all oxid. states from -4 to +4 (*e.g.*, CH_4 to CO_2) known.

Si, Ge: metalloids – essentially all compounds are +4 ox. state, but a few are +2.

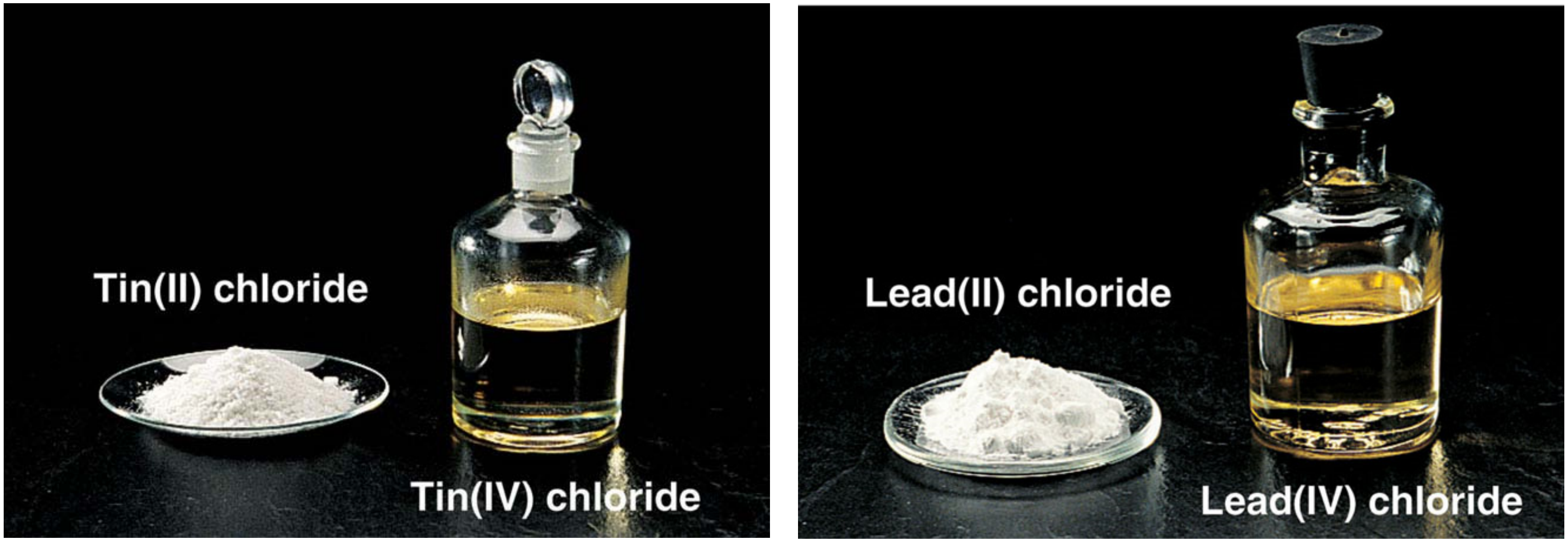
Sn, Pb: metals +4 (covalent) *e.g.*, MO_2
+2 (ionic usually) *e.g.*, MO

Figure 14.11

C usually four-coordinate (exception C≡O). Other elements show more exceptions (*e.g.*, SiF_6^{2-}, $GeCl_6^{2-}$, $Sn(OH)_6^{2-}$, $Pb(OH)_6^{2-}$) but still usually four-coordinate.

Note difference: C has $2s^22p^2$ outer configuration with no available d orbitals. Remainder of elements have d orbitals they can use in bonding ∴ can form six bonds (sp^3d^2 hybrids).

Figure 14.11 Salt-like M^{2+} chlorides and oily M^{4+} chlorides show greater metallic character of tin and lead in the lower oxidation state.



M^{2+} – ionic bonding, typical of metals

M^{4+} – covalent bonding, typical of non-metals

Again: big difference between C and rest of group. Main ones:

(i) ability to form lowest (-4) and highest (+4) oxidation states

(ii) forms multiple bonds to itself or other light elements (N, O) e.g. CO_2 (i.e. O=C=O), acetone (i.e. $(CH_3)_2C=O$)

(iii) forms stable/common single bonds to itself ("catenation" = chain formation). e.g. n-butane is $H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_3$ containing a C-C-C-C chain.

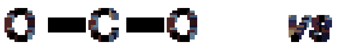
Include O, N, S, etc. and you have organic and biochemistry, and Life!

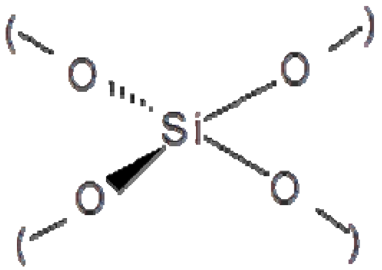
π-bonding: C is small, forms strong enough π bonds to give stable compounds.

Elements further down the group: π-bonding is much weaker and usually prefers to form extra sigma (σ) bonds.

Compare CO_2 vs SiO_2 both are oxidation state = +4

but





3D polymer

strong C-O π bond

∴ C=O is 1 sigma, 1 pi

∴ each C has 2 sigma, 2 pi

weak Si-O π bond, therefore each Si forms four Si-O bonds

C can even form further π bonding i.e., $C\equiv O$ (1 sigma, 2 pi bonds)

$$CO_2\,(g) + C\,(s) \rightleftharpoons 2\,CO\,(g) \qquad \Delta H > 0,\ \Delta S > 0$$

Non-spontaneous ($\Delta G > 0$) at R.T but spontaneous ($\Delta G < 0$) at high T. In fact, favored at >700 °C unless excess O_2 present ∴ CO is a major pollutant from combustion processes at high T and/or in O_2-starved conditions when $2\,C + O_2 \rightarrow 2\,CO$

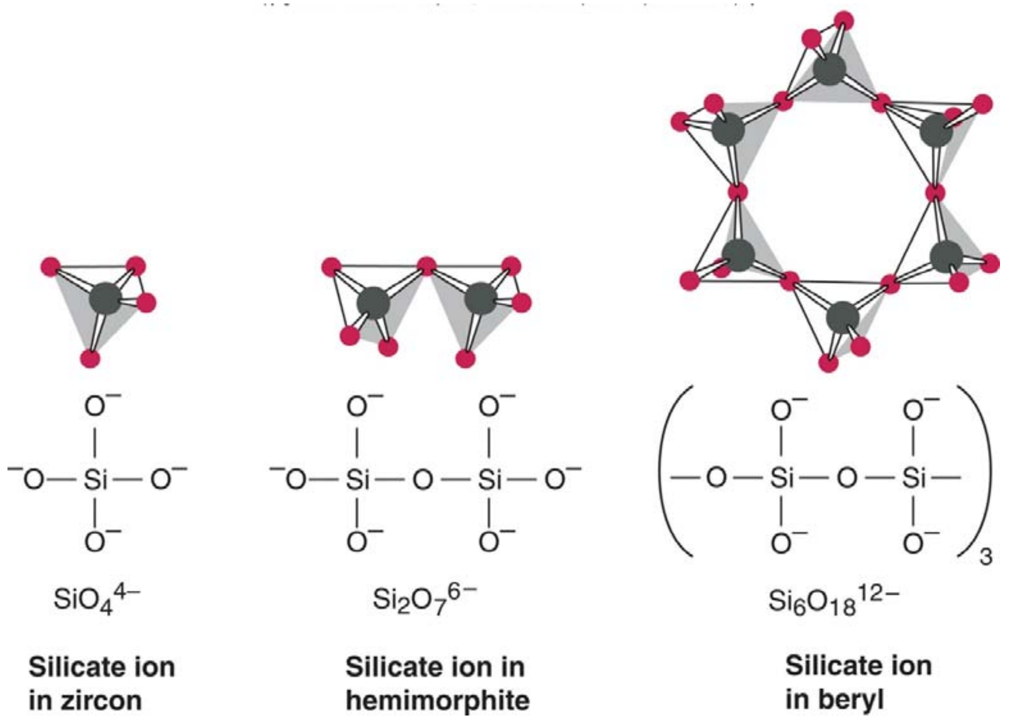
Note: CO_2 is acidic, CO is not

$$\therefore\ CO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \qquad \text{carbonic acid}$$

<u>but</u> $CO\,(g) + H_2O\,(l)$ no reaction !

CO (g) <u>very</u> poisonous – binds to hemoglobin <u>ir</u>reversibly.

$(SiO_4)_n$ tetrahedra form many structures by condensation:



SiO_4^{4-}

Silicate ion in zircon

$Si_2O_7^{6-}$

Silicate ion in hemimorphite

$Si_6O_{18}^{12-}$

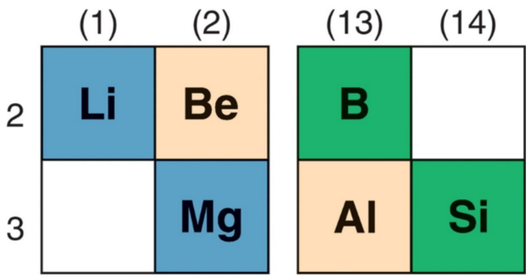
Silicate ion in beryl

1D polymers include asbestos.

3D polymers (SiO_2), include quartz, mica, feldspar, sand, clay, zeolites, gems, etc.

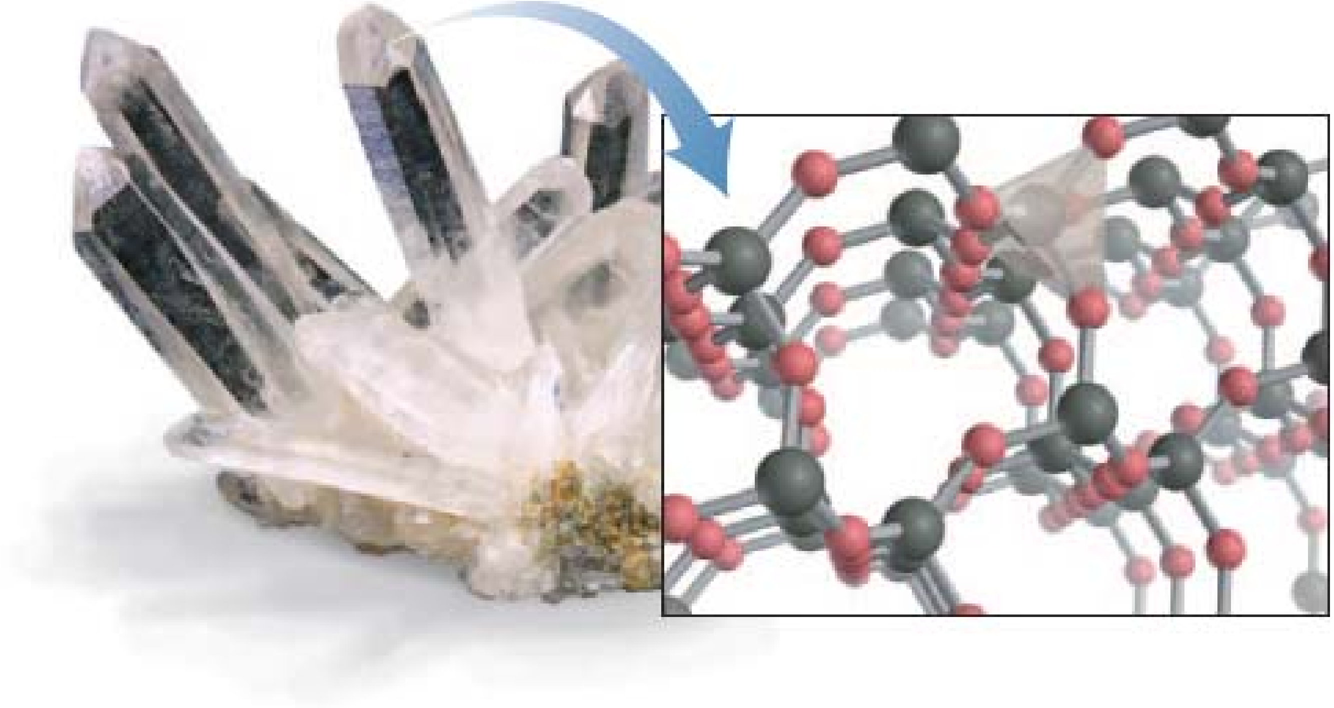
Fig 14.15

Diagonal Relationship: B with Si



	(1)	(2)	(13)	(14)
2	Li	Be	B	
3		Mg	Al	Si

Figure 14.15 Quartz is a three-dimensional framework silicate.



Section 14.7. GROUP 15. (ns^2np^3)

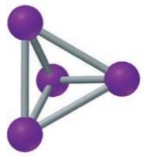
N, P = non-metals; As, Sb = metalloids; Bi = metal

N again different from the rest of the group.

All show +5 ox. state; +3 becomes more important down group

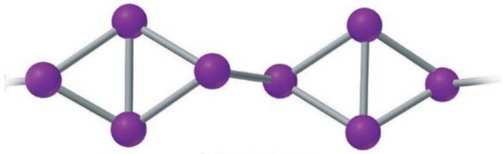
N_2 gas (N≡N) *vs.* solid P_4

1σ, 2π bonds (3σ)



(white P)

or



(red P)

Oxidation States

N	all from +5 to -3 common
P, As, Sb	+5 and +3 common, others rare
Bi	only +3 is common, others very rare

Lowest ox. state (-3) reacts with H_2O to give EH_3 - toxic except NH_3.

$$Ca_3As_2\ (s) + 6\ H_2O\ (l) \rightarrow 2\ AsH_3\ (g) + 3\ Ca(OH)_2\ (aq)$$

N, P oxides acidic; As, Sb, amphoteric; Bi basic

Acidity of oxides increases with higher oxidation states

The oxides of N – many are known and important

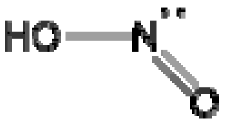
N_2O	NO	N_2O_3	NO_2	N_2O_4	N_2O_5
+1	+2	+3	+4	+4	+5
nitrous oxide	nitric oxide	dinitrogen trioxide	nitrogen dioxide	dinitrogen tetraoxide	dinitrogen pentoxide

(N_2O is an anesthetic and 'laughing gas')

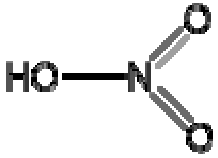
In contrast, only two N-containing oxo-acids are known:

(must learn the –ous vs –ic and –ite vs –ate naming rules!!)

HNO_2 is nitrous acid (N is +3 oxid state) (NO_2^- = nitrite ion)



HNO_3 is nitric acid (N is +5 oxid state) (NO_3^- = nitrate ion)



HNO_3 is a strong acid, HNO_2 is weak ($K_a = 7.1 \times 10^{-4}$, pKa = 3.15)

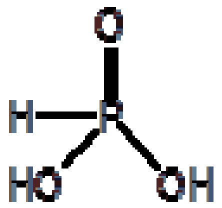
Similarly for P (the element is spelled phosphorus - not phosphorous!)

$P_4\ (s) + 3\ O_2\ (g) \rightarrow P_4O_6\ (s)$ oxid. st. +3

$P_4\ (s) + 5\ O_2\ (g) \rightarrow P_4O_{10}\ (s)$ oxid. st. +5

1) $P_4O_6 + H_2O \rightarrow H_3PO_3$ (phosphorous acid)

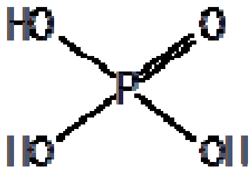
diprotic acid



$\rightarrow [H_2PO_3]^- \rightarrow HPO_3^{2-}$ (no PO_3^{3-})
(H bound to P cannot dissociate)

2) $P_4O_{10} + H_2O \rightarrow H_3PO_4$ (phosphoric acid)

triprotic acid



$\rightarrow H_2PO_4^- \rightarrow HPO_4^{2-} \rightarrow PO_4^{3-}$

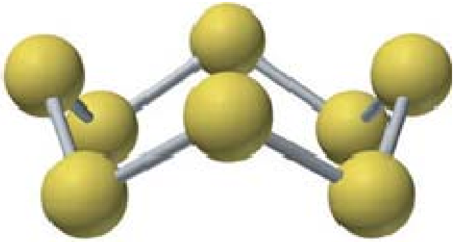
Section 14.8 GROUP 16. (ns^2np^4)

O, S, Se non-metals   Te metalloid   Po metal (radioactive)

O is too electronegative to show maximum oxidation state + 6. S does, then lower oxidation states again become more important. Main oxidation state: O(-2), S(+6), Se(+4), Te(-2).

O found everywhere, e.g., as O_2 and H_2O. S also found as element, S_8, others as minerals.

O_2 is O=O (1 σ, 1 π) gas. S occurs as yellow S_8 solid (only σ) and other S_n. Similarly for Se_n.

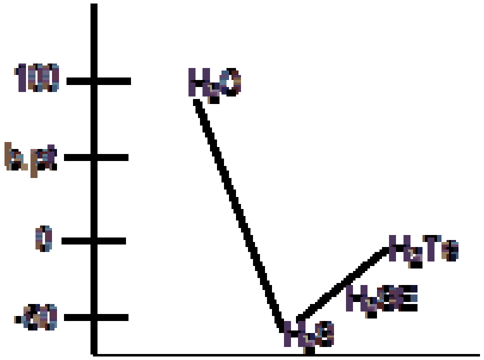


Oxides	SO_2	and	SO_3	give	H_2SO_3	and	H_2SO_4 in water
	(+4)		(+6)		(sulfurous acid)		(sulfuric acid)
	SeO_2	and	SeO_3	give	H_2SeO_3	and	H_2SeO_4
	(+4)		(+6)		(selenous acid)		(selenic acid)

Hydrogen compounds

H_2O, H_2S, H_2Se, H_2Te are all -2 oxidation state

Note: usually b.pts of compounds increase down a group but due to strong O-H···O hydrogen-bonding, b.pt. of liquid H_2O is very high. S-H···S etc. are much weaker.

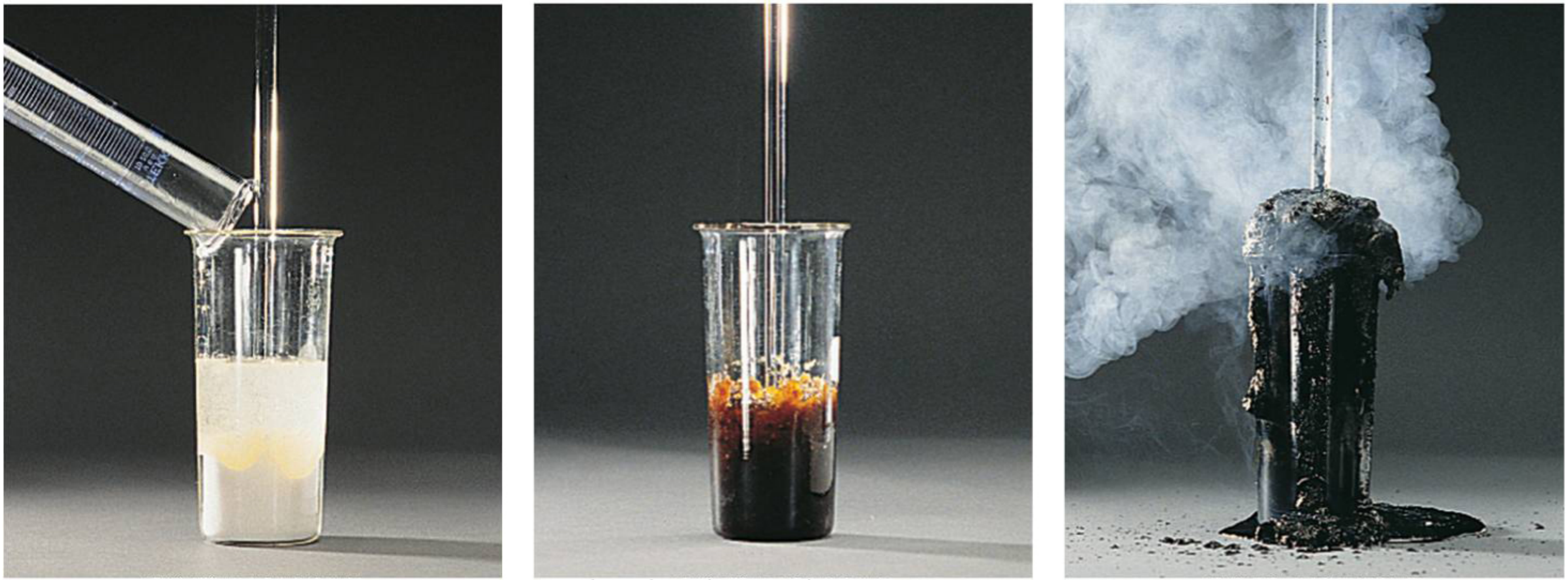


(Similarly for Group 15 hydrogen compounds (NH_3, PH_3, etc, but there they are all gases).

The high b.pt. of water (100°C at 1 atm) is the reason that life on this planet is the way it is. Liquid water allowed a solvent for life's chemistry to develop in.

Note: H_2S, H_2Se, H_2Te very toxic. H_2O obviously is not.

Figure 14.21 The dehydration of sugar by sulfuric acid.



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Section 14.9. GROUP 17. The Halogens (ns^2np^5)

F = the most electronegative element ∴ only -1 oxidation state. F_2 is incredibly reactive – powerful oxidizing agent. Others show range from maximum (+7) to minimum (-1), with –1 the most important.

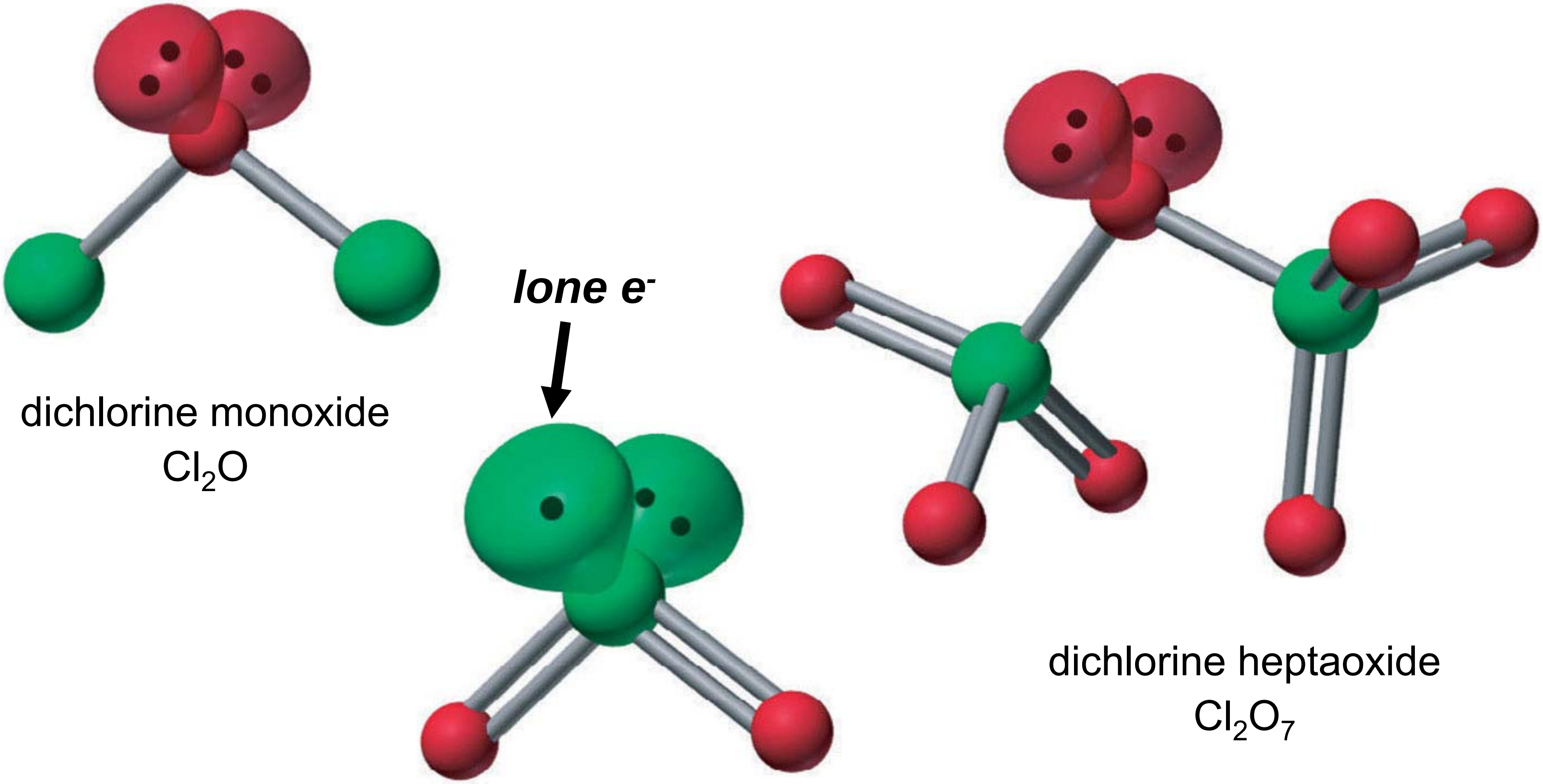
All are non-metals ∴ acidic oxides, dissolve in water to give acids

Oxides: (+1) Cl_2O (rare +4) $ClO_2^{\cdot}$ (+7) Cl_2O_7 Fig 14.25

Oxyacids	**acid**	**anion**	**ox. st.**
$HClO_4$	perchloric acid	perchlorate	+7
$HClO_3$	chloric acid	chlorate	+5
$HClO_2$	chlorous acid	chlorite	+3
$HClO$	hypochlorous acid	hypochlorite	+1
HCl	hydrochloric acid	chloride	-1
$HBrO_4$	perbromic acid	perbromate	+7
$HBrO_3$	bromic acid	bromate	+5
$HBrO_2$	bromous acid	bromite	+3
$HBrO$	hypobromous acid	hypobromite	+1
HBr	hydrobromic acid	bromide	-1

Similarly for I

Figure 14.25 Chlorine oxides.



dichlorine monoxide
Cl_2O

chlorine dioxide
ClO_2

dichlorine heptaoxide
Cl_2O_7

Figure 14.26 Crystals of xenon tetrafluoride (XeF_4).