Chapter 22
Chemistry of The NonMetals

- Descriptive chemistry of the elements is consistent with the various principles discussed earlier.
- We will focus on trends in and explanations for the observed behavior of the elements.

22.1 General Concepts: Periodic Trends
- Main–group elements — the valence electrons are filling s and p orbitals
- Three types of main–group elements: metal, metalloid, nonmetal
- Increasing metallic character going down a group and from right to left across a period
- Group Work: List the relative properties of the metals:
  - volatility
  - melting and boiling points
  - density
  - thermal conductance
  - electrical conductance
  - appearance as solids
  - brittleness
  - typical structure
  - bonding
  - tendency to lose or gain electrons
  - acidity/basicity of oxides

Metals
- Metals: nonvolatile, high melting and boiling points, high density and thermal and electrical conductance, characteristic shine or luster as crystalline solids, malleable and ductile, consist of large arrays of atoms with long–range bonding forces (the metallic bond) between free electrons and cations, tend to lose electrons, oxides are alkaline
- Group Work: List the relative properties of the non–metals:
  - volatility
  - melting and boiling points
  - density
  - thermal conductance
  - electrical conductance
  - appearance as solids
  - brittleness
  - typical structure
  - bonding
  - tendency to lose or gain electrons
  - acidity/basicity of oxides
NonMetals

- Nonmetals: volatile, low melting and boiling points, low density, brittle or soft as solids, low thermal and electrical conductance, solids dull in appearance, many are discrete small molecules with atoms joined by strong covalent bonds, intermolecular forces between molecules are weak, chemical properties characterized by their tendency to gain electrons, oxides are usually acidic

- Group Work: Which group of metals is the most reactive?
  - Alkali metals – why?
- Which group of nonmetals is the most reactive?
  - Halogens – why?
- Compare the metalloids to the metals and the non–metals.

Metalloids

- Metalloids: physical properties more like those of metals, but chemical reactivity is more like that of nonmetals; many atomic properties are intermediate between those of metals and of nonmetals

Period 2 Elements are Unique

- Compounds formed between nonmetals tend to be molecular.
- As we move down the periodic table bonding changes.
- The third period onwards has accessible d–orbitals that can participate in bonding.
- Therefore, the octet rule can be broken for the third period onwards.
- The first member of a group can form $\pi$ bonds more readily than subsequent members.
- Si is much larger than C and the 3p orbital is much larger than the 2p orbital, so the overlap between 3p orbitals to form a $\pi_{3p}$ bond is significantly poorer than for a $\pi_{2p}$ bond.
- Since the Si–Si $\pi$ bond is much weaker than the C–C $\pi$ bond, Si tends to form $\sigma$ bonds.
- Example: CO$_2$ is a gas with O=C=O bonds.
  SiO$_2$ is a network solid with Si–O bonds.

Lightest Elements are Unique

- Properties of the first element in each group are usually more distinctive, while the rest of the elements in a group have similar properties
- The unusual properties of the first element in a group can be explained on the basis of its unusually small size, which arises because the valence electrons are not shielded from the nucleus and the electrons are held relatively tightly in the atom

Metals with Covalent Bonds

- Small metal ions such as Be$^{2+}$ are polarizing and pull electrons from nonmetal anions to form partly covalent bonds.
- Small nonmetals (such as N, O, F) are highly electronegative because of the increased attraction of the nucleus for the electrons at short distances and form multiple bonds because p orbitals can overlap.
Diagonal Relationships

- In addition to horizontal and vertical trends, there is a diagonal relationship between elements such as Li and Mg, Be and Al, B and Si, that have an adjacent upper left/lower right relative location in the periodic table.
- These pairs of elements have similar size and electronegativity, resulting in similar properties.

22.2 Hydrogen

Isotopes of Hydrogen

- There are three isotopes of hydrogen: Protium \(^1\)H, deuterium \(^2\)H, and tritium \(^3\)H.
- Deuterium (D) is about 0.0156 % of naturally occurring H.
- Tritium (T) is radioactive with a half-life of 12.3 yr.

Properties of Hydrogen

- Hydrogen is unique.
- Hydrogen has a 1s\(^1\) electron configuration so it is placed above Li in the periodic table.
- However, H is significantly less reactive than the alkali metals.
- Hydrogen can gain an electron to form H\(^-\), which has a He electron configuration. Therefore, H could be placed above the halogens.
- However, the electron affinity of H is lower than any halogen.
- Elemental hydrogen is a colorless, odorless gas at room temperature.
- Since H\(_2\) is nonpolar and only has two electrons, the intermolecular forces are weak (boiling point –253°C, melting point –259°C).
- The H–H bond enthalpy is high (436 kJ/mol). Therefore, reactions with hydrogen are slow and a catalyst needs to be used.
- When hydrogen reacts with air explosions result (Hindenburg exploded in 1937):
  \[
  2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) \quad \Delta \text{H} = -571.7 \text{ kJ}
  \]

Preparation of Hydrogen

- In the laboratory hydrogen is usually prepared by reduction of an acid.
- Zn is added to an acidic solution and hydrogen bubbles are formed.
- The hydrogen bubbles out of solution and is collected in a flask.
- The collection flask is usually filled with water so the volume of hydrogen collected is the volume of water displaced.
- In larger quantities, hydrogen can be prepared by the reduction of methane in the presence of steam at 1100°C:
  \[
  \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g)
  \]
  \[
  \text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g)
  \]

Uses of Hydrogen

- Hydrogen is used for ammonia production and to hydrogenate vegetable oils to make margarine and shortening.
- Hydrogen is used to manufacture methanol:
  \[
  \text{CO}(g) + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(g)
  \]
Chapter 22

**Binary Hydrogen Compounds**
- There are three types of binary hydrogen compounds formed:
  - Ionic hydrides (e.g., LiH, made between metals and H);
  - Metallic hydrides (e.g., TiH₂, made between transition metals and H); and
  - Molecular hydrides (e.g., CH₄, made between nonmetals and metalloids and H).
- Thermal stability (measured by $\Delta G^\circ_f$) decreases as we go down a group and increases across a period.
- Most stable is HF.
- Metal hydrides, such as CaH₂, react with water to give H₂ and metal hydroxide.

**22.3 The Noble Gases**

**Noble Gas Compounds**
- Noble gases are very unreactive.
- All elements have high ionization energies.
- He is the most important noble gas as liquid helium is used as a coolant.
- The heavier noble gases react more readily than the lighter ones.
- The most common compounds of noble gases are xenon fluorides.
- Xenon fluorides have Xe in the +2 to +8 oxidation states.
- Noble gas compounds violate the octet rule.
- In the presence of water, xenon fluorides form oxyfluorides:
  - $\text{XeF}_6(s) + \text{H}_2\text{O}(l) \rightarrow \text{XeOF}_4(l) + 2\text{HF}$
  - $\text{XeF}_6(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{XeO}_3(aq) + 6\text{HF}$
- The only other noble gas compound known is KrF₂, which decomposes at $-10^\circ C$.
- Xenon fluorides are more stable than the oxides and oxyfluorides.

**22.4 Group 7A: The Halogens**
- F, Cl, Br, I, At
- Most common are chlorine, bromine, and iodine
- Fluorine has properties atypical of the group
- Astatine is radioactive and exists naturally only in very small amounts
- The halogens exist as diatomic molecules
- At room temperature, fluorine is a yellow gas, chlorine is a pale green gas, bromine is a red liquid, and iodine is a purple solid
- The elements have very high ionization energies, typical of nonmetals

**Properties of the Halogens**
- Outer electron configurations: ns²np⁵.
- All halogens have large electron affinities.
- Most common oxidation state is −1, but oxidation states of +1, +3, +5, and +7 are possible.
- Halogens are good oxidizing agents.
- Each halogen is the most electronegative element in its row.
- The properties of the halogens vary regularly with their atomic number.
Fluorine

- The bond enthalpy of F₂ is low. Hence fluorine is very reactive.
- Water is oxidized more readily than fluorine, so F₂ cannot be prepared by electrolysis of a salt solution. F₂ is an extremely reactive gas, which reacts with all the elements, except oxygen and the lighter noble gases, to form stable fluorides, often explosively.
- F₂ is such a strong oxidizing agent that it can convert oxides, including water, to molecular oxygen.
- Write a balanced equation for the reaction of F₂ with H₂O (to form O₂ and ??).

Chlorine

- Chlorine exists as chlorides in sea water, salt lakes, and brine deposits.
- Cl₂ gas prepared industrially by the electrolysis of sodium chloride solutions.
- Also a by-product of the preparation of metals by electrolysis of molten salts such as NaCl, MgCl₂, and CaCl₂.
- Most Cl₂ is used as a raw material in the production of other chemicals, in the synthesis of herbicides and insecticides, in the bleaching of textiles and paper, in purifying drinking water, and in the production of plastics such as polyvinyl chloride (PVC).

Bromine

- Bromine exists in small quantities in the form of bromides co-existing with chlorides.
- Prepared by reacting a solution containing bromide ion with chlorine.
- Uses of bromine:
  - as a bleach
  - in the manufacture of bromide compounds
  - ethylene bromide, C₂H₄Br₂, used as an antiknock agent in gasoline.

Iodine

- Iodine exists as iodides in brines and seaweed, and as iodates in deposits of sodium nitrate (NaNO₃, or Chile saltpeter).
- Recovered by oxidation of I⁻ with Cl₂ or by reduction of IO₃⁻ with HSO₃⁻.
- Used as an antiseptic and disinfectant and as a reagent for chemical analysis.

Astatine

- Not much is known about its chemistry.
- It is highly radioactive; all chemical studies have used small quantities added to iodine solutions and measure behavior by determining where the radioactivity ends up.
- The total amount in the Earth’s crust is estimated to be < 30 g at any one time.

Halogens

- In addition to the common −1 and 0 oxidation numbers, the halogens (except for fluorine) exist with each positive oxidation number through +7.
- Halogen oxides are known with oxidation numbers as high as +7; most are very strong oxidizing agents.
**Oxyacids and Oxyanions**

- Fluorine only forms one oxyacid: HOF. Oxygen is in the zero oxidation state.
- All are strong oxidizing agents.
- All are unstable and decompose readily.
- Oxyanions are more stable than oxyacids.
- Acid strength increases as the oxidation state of the halogen increases.

**Periodic Acid**

- Periodic (HIO₄) and paraperiodic (H₅IO₆) acid have iodine in the +7 oxidation state.
- Periodic acid is a strong acid, paraperiodic acid is a weak acid ($K_{a1} = 2.8 \times 10^{-2}$, $K_{a2} = 4.9 \times 10^{-9}$).
- The large iodine atom allows 6 oxygen atoms around it.
- Smaller halogens cannot form this type of compound.

**Halogens**

- Many aqueous halogen species are susceptible to disproportionation:
  - ClO₂
  - HClO₂
  - HOCI
  - Cl₂ (in base)
  - HOBr
  - Br₂ (in base)
  - HOI
  - IO⁻
  - I₂ (in base)
- How do we decide which species will disproportionate?

22.5 **Oxygen**

**Properties of Oxygen**

- Oxygen has two allotropes: O₂ and O₃.
- O₂ is a colorless, odorless gas at room temperature.
- The electron configuration is [He]2s²2p⁴, which means the dominant oxidation state is 2⁻.
- The O=O bond is strong (bond enthalpy 495 kJ/mol).

**Preparation of Oxygen**

- Commercially: obtained by fractional distillation of air. (Normal boiling point of O₂ is −183°C and N₂ −196°C.)
- Laboratory preparation of oxygen is the catalytic decomposition of KClO₃ in the presence of MnO₂:
  \[
  2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g).
  \]
- Atmospheric oxygen is replenished by photosynthesis (process in plants where CO₂ is converted to O₂ in the presence of sunlight).
Chapter 22

*Uses of Oxygen*

- Most widely used as an oxidizing agent. (E.g. in the steel industry to remove impurities.)
- Oxygen is used in medicine.
- It is used with acetylene, C\textsubscript{2}H\textsubscript{2} for oxyacetylene welding:
  \[
  2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})
  \]

*Ozone*

- Pale blue, poisonous gas.
- Ozone dissociates to form oxygen:
  \[
  \text{O}_3(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{O}(\text{g}) \quad \Delta H^\circ = 107 \text{ kJ}
  \]
- Ozone is a stronger oxidizing agent than oxygen:
  \[
  \begin{align*}
  \text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- & \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) & E^\circ = 2.07 \text{ V} \\
  \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- & \rightarrow 2\text{H}_2\text{O}(\text{l}) & E^\circ = 1.23 \text{ V}
  \end{align*}
  \]
- Ozone can be made by passing an electric current through dry O\textsubscript{2}:
  \[
  3\text{O}_2(\text{g}) \rightarrow 2\text{O}_3(\text{g})
  \]

*Peroxides and Superoxides*

- Peroxides: have an O–O bond and O in the –1 oxidation state.
- Hydrogen peroxide is unstable and decomposes into water and oxygen:
  \[
  2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \quad \Delta H = -196.0 \text{ kJ}
  \]
- The oxygen produced will kill bacteria.
- Peroxides are important in biochemistry: it is produced when O\textsubscript{2} is metabolized.

*Peroxides*

- Disproportionation occurs when an element is simultaneous oxidized and reduced:
  \[
  \begin{align*}
  2\text{H}^+(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + 2\text{e}^- & \rightarrow 2\text{H}_2\text{O}(\text{l}) & E^\circ = 1.78 \text{ V} \\
  \text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- & \rightarrow \text{H}_2\text{O}_2(\text{aq}) & E^\circ = 0.68 \text{ V}
  \end{align*}
  \]
- Disproportionation:
  \[
  2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \quad E^\circ = 1.10 \text{ V}
  \]

*Superoxides*

- Superoxides: have an O–O bond and O in an oxidation state of –½ (superoxide ion is O\textsubscript{2}–).
- Usually form with active metals (KO\textsubscript{2}, RbO\textsubscript{2} and CsO\textsubscript{2}).
- Potassium superoxide reacts with water vapor from the breath to form oxygen gas.
  \[
  4\text{KO}_2 + 2\text{H}_2\text{O} \rightarrow 3\text{O}_2 + 4\text{KOH}
  \]

22.6 *The Other Group 6A Elements: S, Se, Te, and Po (Chalcogens)*

- Trend that affects other properties is the increase in metallic character down the group, indicated by the decreases in ionization energy and electronegativity

*Group 6A*

- Nonmetallic character dominates in this group
- Nonmetallic O exists as diatomic molecules

22–7
• Nonmetallic S exists as various covalently bonded polyatomic forms
• Metalloids Se and Te are more metallic than S, but bear some resemblance to S
• Po is even more metallic, but its behavior is not well known since it is a rare, radioactive element
• Oxygen dominated by oxidation number −2
• The other elements have oxidation numbers from −2 through +6, the higher ones being quite common, especially in combination with oxygen

**Sulfur**
• S found in earth's crust as sulfide and sulfate minerals and as the free element
• Also a small but critical constituent of plant and animal tissue
• Occurs as sulfur dioxide and sulfur trioxide in the atmosphere
• Elemental sulfur is a tasteless, odorless, combustible yellow solid existing in a variety of allotropes with different molecular structures
• Rhombic and monoclinic forms consist of S₈ rings
• Major use of sulfur is the preparation of sulfuric acid, which is used primarily to make phosphate fertilizers and impure phosphoric acid from phosphate rock
• Sulfur forms binary compounds with all the elements except iodine and the noble gases
• Hydrogen sulfide (H₂S):
  • usually prepared by reaction of a metal sulfide with an acid
  • gas well known for its "rotten–egg" odor
  • extremely poisonous
  • largest source of sulfur in the atmosphere
• Sulfur reacts with oxygen to form two oxides, sulfur dioxide and sulfur trioxide, which form oxoanions (SO₃²⁻ and SO₄²⁻) and oxoacids (H₂SO₃ and H₂SO₄) by reaction with metal oxides or water
• Sulfuric acid is a powerful dehydrating agent, strong acid and moderate oxidizer.
• Sulfuric acid removes H₂O from the sugar leaving a black mass of C. Steam is produced because the reaction is very exothermic.

**Group Work**

• What are the structures of:
  • SO₂
  • SO₃
  • SO₃²⁻
  • SO₄²⁻
  • H₂SO₃
  • H₂SO₄

22.7 Nitrogen
• Electronic configuration of the Group VA (15) elements is ns²np³
• Little resemblance between the chemistry of nitrogen and the other elements in this group
Nitrogen

- Nitrogen as an element is the colorless, odorless, diatomic molecule $N_2$, the major constituent of air
- An essential component of all living matter in protein and amino acids
- Nitrogen compounds are important components of chemical fertilizers
- Most uses of nitrogen involve its compounds, such as ammonia and nitrogen oxides.

**Group Work**

- List the formulas for all the oxides that you expect nitrogen to form.

**Preparation of Nitrogen**

- $N_2$ is produced by fractional distillation of air.
- Nitrogen is fixed by forming $NH_3$ (Haber Process).
- $NH_3$ is converted into other useful chemicals ($NO, NO_2, nitrites and nitrates$).

**Nitrogen**

- Positive oxidation numbers of nitrogen occur in the oxides, including $N_2O, NO, N_2O_3, NO_2, N_2O_4, and N_2O_5$.
- Aqueous $N_2O_3$ is converted to nitrous acid ($HNO_2$), and $N_2O_5$ to nitric acid ($HNO_3$).
- Nitrous oxide, $N_2O$, occurs naturally in the atmosphere, as a result of the natural degradation of proteins.
- $N_2O$ can be formed by thermal decomposition of $NH_4NO_3$.
- $N_2O$ is used as an anesthetic (in laughing gas).
- Nitric oxide, $NO$, is formed by reaction of Cu metal with dilute aqueous nitric acid or in high temperature combustion processes and in the oxidation of ammonia gas commercially.
- NO reacts rapidly with $O_2$ to form reddish–brown $NO_2$.
- Dinitrogen trioxide results from reaction between $NO$ and $NO_2$.
- $N_2O_3$ is blue as a liquid.
- Gaseous $N_2O_3$ reacts with water to form the weak acid, nitrous acid, $HNO_2$.

**Group Work**

- Write an equation for the preparation of nitrogen dioxide from common laboratory chemicals.

**Nitrogen**

- Nitrogen dioxide, $NO_2$, is a poisonous, reddish–brown gas with an irritating odor, which exists in equilibrium with colorless $N_2O_4$.
- Dinitrogen pentoxide, $N_2O_5$, is a volatile low–melting white solid; dissolved in water, it forms $HNO_3$, nitric acid.

22.8 The Other Group 5A Elements: P, As, Sb, and Bi (Pnictogens)

- Although nitrogen is found in nature primarily as unreactive $N_2$, the other elements are found only in compounds.
- Metallic nature increases down the group.
**Group Work**

- Predict the following properties for phosphorus:
  - metallic character
  - type of bonding
  - acid/base character of oxides
  - formulas of oxides

**Phosphorus**

- Phosphorus is essentially nonmetallic, forms covalent bonds and has acidic oxides

**Group Work**

- Predict the acid/base character of the oxides of As, Sb, and Bi, relative to those of P. How can we explain the predicted trend?

**Group 5A**

- Arsenic has properties between those of a nonmetal and a metalloid, with amphoteric (though more acidic than basic) oxides
- Antimony is mostly metallic, but with some properties of a metalloid, and amphoteric (more basic than acidic) oxides
- Bismuth, is metallic, with basic oxides
- These trends are consistent with dramatic decreases in ionization energy down the group
- Trends in oxidation number:
  - N and P range from –3 to +5
  - As primarily +3 and +5
  - Sb mostly +3, occasionally +5
  - Bi almost exclusively +3, rarely as +5
- The lower, more metallic elements in the group have fewer stable oxidation numbers than N

**Phosphorus**

- Phosphorus found as phosphates in 190 different minerals, most importantly apatite, Ca₅(PO₄)₃OH
- Phosphates are an important constituent of all bone tissue
- Mainly occurs in phosphorus minerals (e.g. phosphate rock, Ca₃(PO₄)₂).
- Elemental P₄ produced by reduction
  \[ 2 \text{Ca}_3(\text{PO}_4)_2(s) + 6\text{SiO}_2(s) + 10\text{C}(s) \rightarrow \text{P}_4(g) + 6\text{CaSiO}_3(l) + 10\text{CO}(g) \]
- Phosphoric acid, made from phosphate rock, is one of the ingredients in Coca–Cola.
- Phosphorus occurs as 19 allotropes, the principal ones being white (tetrahedral P₄), red, and black phosphorus
- White phosphorus is a soft solid, with molecules held together by weak intermolecular forces.
- White phosphorus is poisonous and causes painful skin burns.
- White phosphorus is quite reactive and ignites spontaneously in air
- Red phosphorus is an amorphous solid formed by heating white phosphorus
Chapter 22

- Red phosphorus involves $P_4$ tetrahedral molecules bonded to one another in long chains
- Black phosphorus is still less reactive
- Black phosphorus may be amorphous or have a graphite–like structure; it is metallic in appearance and an electrical conductor

**Group Work**

- What acids are formed when the oxides, $P_4O_6$ and $P_4O_{10}$, are reacted with excess water?

**Phosphorus**

- Two oxides of phosphorus, $P_4O_6$ and $P_4O_{10}$, formed by burning phosphorus
- React with water to form phosphorous acid, $H_3PO_3$ and phosphoric acid, $H_3PO_4$
- $P_4O_{10}$ is used as a drying agent because of its affinity for water.

22.9 **Carbon**

- Carbon constitutes about 0.027 % of the earth’s crust.
- Carbon is the main constituent of living matter.
- Study of carbon compounds is called organic chemistry.
- Carbon forms more compounds than all other elements except hydrogen; typical compounds are the hydrocarbons and their derivatives
- Exists as diamond, graphite, and an amorphous form, as well as the recently discovered allotrope $C_{60}$, called buckminsterfullerene
- Diamond: clear crystalline form of carbon, one of the hardest substances known, can be synthesized from graphite with high temperature and pressure and a metal catalyst

**Group Work**

- Why is diamond so hard, while graphite is soft and slippery, even though both are pure carbon?

**Carbon**

- Graphite:
  - slippery gray–black solid
  - strong covalent bonds hold atoms together in each layer, but the layers are bonded only by weak van der Waals forces, so the layers slide across one another readily
  - found widely distributed in the earth's crust and synthesized from amorphous carbon
- Uses of graphite:
  - crucibles
  - lubricants
  - pencils
  - nuclear reactors (to slow down fast neutrons)
  - electrodes for electrolysis reactions
- Amorphous carbon:
  - carbon blacks
- charcoal
- activated carbon
- soot
- coke
- Essentially microcrystalline forms of graphite with no layering
- Formed by thermal decomposition or partial decomposition of coal, petroleum, natural gas, and wood with an insufficient supply of oxygen
- burning oil gives lampblack
- heating coal in the absence of air produces coke
- heating wood in the absence of air gives charcoal
- Carbon black used as a filler in rubber tires to increase toughness and prevent brittleness
- Lampblack used in inks, paints, coating on carbon paper
- Charcoal used:
  - in filters to adsorb odors
  - in gas masks to adsorb poisonous gases
  - in the decolorizing of sugar
  - in water treatment
  - in the reclamation of dry-cleaning solvents
- Coke used in the extraction of metals from their oxide ores
- Buckminsterfullerene consists of molecules of C\textsubscript{60} formed by laser or high-temperature carbon arc vaporization of graphite
- One member of a class of new forms of carbon called fullerenes, which consist of clusters of carbon atoms containing even numbers from 44 to 84
- C\textsubscript{60} exists as a truncated icosahedron, which contains 12 pentagonal faces and 20 hexagonal faces
- Remarkable physical stability, but chemically reactive
- Now being prepared as tubes, into which metals can be inserted. These are the thinnest capillary tubes known.
- Elemental carbon is relatively unreactive at room temperature
- Insoluble in water, dilute acids and bases, and organic solvents
- At high temperatures, carbon becomes highly reactive and combines directly with many elements, including oxygen
- Carbon at high temperatures also reduces water, metal oxides, oxoanions (e.g., phosphate in phosphate rock), hydrogen

\textit{Oxides of Carbon}

- Carbon forms CO and CO\textsubscript{2}.
- CO is very toxic (binds irreversibly to Fe in hemoglobin, causing respiratory arrest).
- CO also has a lone pair on C, which is unusual.
- CO is a good Lewis base
  Ni(CO)\textsubscript{4} forms when Ni is warmed in CO
- CO can be used as a fuel
  \[ 2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) \quad \Delta H = -566 \text{ kJ} \]
• CO is a good reducing agent
  \[ \text{Fe}_3\text{O}_4(\text{s}) + 4\text{CO}(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 4\text{CO}_2(\text{g}) \]
• CO2 is produced when organic compounds are burned in oxygen:
  \[ \text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \]
  \[ \text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \]
• CO2 is produced by treating carbonates with acid.
• Fermentation of sugar to produce alcohol also produces CO2:
  \[ \text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{aq}) + 2\text{CO}_2(\text{g}) \]
• At atmospheric pressure, CO2 condenses to form CO2(s) or dry ice.
• CO2 is used as dry ice (refrigeration), carbonation of beverages, washing soda (Na2CO3.10H2O) and baking soda (NaHCO3.10H2O).

**Carbonic Acid and Carbonates**

• When CO2 dissolves in water (moderately soluble) carbonic acid forms:
  \[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \]
• Carbonic acid is responsible for giving carbonated beverages a sharp acidic taste.
• Partial neutralization of H2CO3 gives hydrogen carbonates (bicarbonates) and full neutralization gives carbonates.
• Many minerals contain CO3^2-.
• At elevated temperatures CaCO3 decomposes:
  \[ \text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + 2\text{CO}_2(\text{g}) \]
• This reaction is the commercial source of lime, CaO.
• CaO reacts with water and CO2 to form CaCO3 which binds the sand in mortar:
  \[ \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \]
  \[ \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) + \text{CO}_2(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \]

**Carbides**

• Carbon combines with elements with a lower electronegativity to form carbides, which exist in three classes
• Salt–like carbides form with the most electropositive metals and are ionic, so they are hydrolyzed by water or dilute acid to give hydrocarbons
• Interstitial carbides are formed with transition metals, are very hard and have very high melting points, high metallic conductivity, and metallic luster; they consist of a metal with carbon atoms located in some of the interstitial sites (or holes) in the metal structure
• Covalent carbides include those of silicon and boron, which are close in size and electronegativity to carbon; they are completely covalent and form infinite network structures, are exceptionally hard materials widely used as abrasives

**22.10 The Other Group 4A Elements: Si, Ge, Sn, and Pb**

**General Characteristics of Group 4A Elements**

• The electronegativities are low.
• The dominant oxidation state for Ge, Sn and Pb is +2.
• Carbon has a coordination number of 4, the other members have higher coordination
numbers.
• C–C bonds are very strong, so C tends to form long chains.
• Because the Si–O bond is stronger than the Si–Si bond, Si tends to form oxides (silicates).

Group Work
• Compare the following properties on going down Group 4A:
  • Metallic character
  • Ionization energies
  • Melting points
  • Acid/base nature of oxides

Group 4A
• Si is nonmetallic/metalloid with only some of its chemistry similar to carbon
• Ge is a metalloid
• Sn and Pb are metallic
• Ionization energies and melting points decrease down the group, reflecting the change from nonmetal to metal
• Carbon bonds readily to itself
• This tendency diminishes on going down the group because the bond strength decreases considerably as the elements get larger
• Oxidation number +4 dominates near the top of the group, +2 becomes more stable down the group

Silicon
• Silicon exists in the earth's crust as silicon dioxide and over 800 silicate minerals
• Elemental silicon obtained by reduction of SiO₂ with C or CaC₂ at high temperature, purified by zone refining
  \[ \text{SiO}_2(\text{l}) + 2\text{C}(\text{s}) \rightarrow \text{Si}(\text{l}) + 2\text{CO}(\text{g}) \]
• Silicon:
  • brittle gray–black metallic–looking solid
  • quite hard
  • high melting point
  • diamond–like tetrahedral network structure
  • inert at room temperature but reactive at high temperatures
• Used in semiconductor devices
• Silicon hydrides or silanes arise from reaction of Mg₂Si with acids, giving a mixture of SiH₄, Si₂H₆, Si₃H₈, Si₄H₁₀, Si₅H₁₂, and Si₆H₁₄

Group Work
• What is the structure and bonding for Si₂H₆?

Silicon
• Silanes are quite reactive:
  • The first two are stable.
The others decompose to give SiH₄, Si₂H₆, and H₂.

Much more reactive than the corresponding alkanes because of the availability of empty 3d orbitals that can be used to form bonds with another reactant.

They are spontaneously flammable in air.

**Group Work**

SiO₂, found as quartz, is quite hard. What feature of its structure gives rise to this hardness?

**Silicon**

SiO₂ exists as polymeric (SiO₂)n, which has silicon covalently bonded to four bridging oxygen atoms.

Extended covalent bonding network

Hard, high-melting solid

Glass is formed by heating together silicon dioxide, alkali metal and alkaline earth metal oxides, and sometimes other oxides, the particular mixture controlling the properties of the glass.

Silicate structure is somewhat random in contrast to crystalline silicates

Some bonds are under more strain than others, so the glass melts over a range of temperatures and can be softened without melting.

90% of the earth’s crust is composed of compounds of Si and O.

Silicates are compounds where Si has four O atoms surrounding it in a tetrahedral arrangement.

The oxidation state of Si is +4.

The silicate tetrahedra are building blocks for more complicated structures.

Many silicates naturally with the basic structural unit being the SiO₄ tetrahedron occurring in several varieties:

- singly
- small groups sharing oxygen atoms
- small cyclic groups
- infinite chains
- double-stranded chains (or bands)
- infinite sheets

These few structures form many hundreds of minerals by combination of silicate anions with metal cations.

**Silicon**

The silicate structure is reflected in the physical structure of minerals such as mica and asbestos.

**22.11 Boron**

Black crystalline element, extremely hard and brittle, low density, high melting point and boiling point, low electrical conductivity (so classified as a semiconductor), used in semiconductor electronics and added to steel to increase strength and to copper to increase electrical conductivity.

Similarities of some properties to those of carbon, of others to those of silicon (due to
the diagonal relationship leading to similar size and electronegativity)

- Carbon, silicon, and boron all form covalently–bonded extended network solids and covalent halides
- Occurs in deposits of borax, Na₂B₄O₇·10H₂O
- Borax used as an additive to laundry detergents to soften the water.
- Which U.S. president was associated with Twenty Mule Team Borax?
- Resembles metals in its physical properties but is more like nonmetals chemically
- Chemical behavior is complex and unusual: ionization energy is unusually high, so formation of a cation is difficult, high electronegativity (comparable to nonmetals)
- All its compounds are covalent

Group Work

- What is the valence electron configuration of boron? How many covalent bonds will it normally form?

Boron

- Valence electron configuration 2s²2p¹, so forms only three normal covalent bonds, but electron deficiency makes it a good Lewis acid
- Oxidation number +3 common, but others found in boranes
- B³⁺ does not exist in aqueous solution. Why not?
- Reacts with F₂ and Cl₂ to give trihalides
- Great affinity for O₂, which is used to remove oxygen from metal oxides to purify molten metals
- B reacts with N₂ at high temperature to give solid BN.
- BN is very stable due to its graphite–like structure, which arises from the presence of only 3 valence electrons and the tendency to use sp² hybrid orbitals.
- BN is also known in a diamond–like structure, which is formed by application of high temperature and pressure, and is extremely hard and is used as an abrasive.
- Large number of hydrides have been prepared
- BH₃ is known but very unstable (reactive)
- Simplest stable one is diborane, B₂H₆, which decomposes to other boranes, e.g. B₅H₉, when heated
- Unusual structure and bonding in the boranes, in which hydrogens act as bridges between boron and the B–H–B arrangement shares two electrons between three atoms (called three center bonding)
- Because of their electron deficiencies, boranes are highly reactive
- Diborane is very reactive:
  \[ \text{B}_2\text{H}_6(g) + 3\text{O}_2(g) \rightarrow \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g) \quad \Delta H = -2030 \text{ kJ} \]
- Some boranes are reactive (B₂H₆) while some are stable in air at room temperature (B₁₀H₁₄).
- B₂O₃ is the only important boron oxide.
- Boric acid, H₃BO₃ or B(OH)₃ is a weak acid \( K_a = 5.8 \times 10^{-10} \).
- Boric acid is used as an eye wash.