

Chapter 22. Chemistry of the Nonmetals

Common Student Misconceptions:

- Students often find detailed discussions of descriptive chemistry to be difficult to digest.
- Students often think that all nonmetals are gaseous.

Teaching Tips:

- Videos and similar visual aids are useful in helping students learn the descriptive chemistry in this chapter.
- Students need to be encouraged to look for periodic trends in everything.
- Students should explore connections between the causes (e.g. electron configurations) and effects (e.g. properties, types of compounds formed) of these main group elements.
- Parts of this chapter could be incorporated into lectures on chapters 2, 4, 7, 8, and 9 as illustrations of the concepts discussed in these chapters.

Lecture Outline

22.1 Periodic Trends and Chemical Reactions^{1,2,3}

- We divide the periodic table into metals, nonmetals, and metalloids.
- Nonmetals occupy the upper right portion of the periodic table.
 - H is a special case.
- Electronegativity is important when determining whether an element is a metal.
- Nonmetals tend to have higher electronegativities than metals.
 - Thus, reactions of metals and nonmetals often yield ionic compounds.
 - Compounds formed between nonmetals tend to be molecular.
- As we move down a group, the type of bonding changes.
 - Elements in the third period and below have accessible *d* orbitals that can participate in bonding.
 - Therefore, the octet rule can be broken for elements in the third period and below.
 - The first member of a group can form π bonds more readily than subsequent members.
 - This is due in part to the difference in atomic size.
 - Compare the elemental forms of carbon and silicon
 - Carbon has 5 major crystalline allotropes: diamond, graphite, buckminsterfullerene, graphene, and carbon nanotubes).
 - Diamond is a covalent-network solid with C-C sigma bonds but not pi bonds.
 - Graphite, buckminsterfullerene, graphene and carbon nanotubes have pi bonds from sideways overlap of orbitals
 - Elemental silicon exists only as a diamond-like covalent-network solid with sigma bonds.
 - It exhibits no form that is analogous to the other carbon allotropes.
 - We see significant differences in the dioxides of carbon and silicon.
 - Si is much larger than C, and the *3p* orbitals are much larger than the *2p* orbitals, so the overlap between *3p* orbitals to form a π_{3p} bond is less effective than for a π_{2p} bond.
 - Since the Si-Si π bond is much weaker than the C-C π bond, Si tends to form σ bonds.
 - Example: at room temperature, CO₂ is a molecular gas with O=C=O bonds.
 - At room temperature, SiO₂ is a network solid with Si-O bonds.

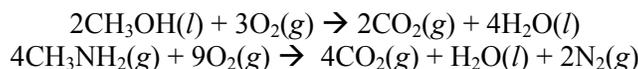
¹ Figure 22.1 from Transparency Pack

² “Carbon-Silicon Orbital Overlap” Activity from Instructor’s Resource CD/DVD

³ “Carbon Dioxide” 3-D Model from Instructor’s Resource CD/DVD

Chemical Reactions

- In this chapter we focus on reactions involving O₂ (oxidation or combustion) and H₂O (especially proton transfer).
- Combustion reactions with O₂ usually form H₂O (with H-containing compounds), CO or CO₂ (with C-containing compounds), and N₂ or NO (with N-containing compounds).
- Water, nitrogen, and CO₂ are thermodynamically stable because of the large bond energies for the H–O, N≡N, and C=O bonds.
- Examples:



- In proton-transfer reactions, the weaker the Brønsted-Lowry acid is, the stronger the conjugate base.

FORWARD REFERENCES

- Corresponding physical properties of metals will be discussed in Chapter 23 (section 23.1).

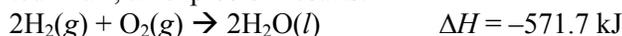
22.2 Hydrogen

Isotopes of Hydrogen

- There are three isotopes of hydrogen: **protium** (${}^1_1\text{H}$), **deuterium** (${}^2_1\text{H}$), and **tritium** (${}^3_1\text{H}$).
 - Protium is the most abundant of these isotopes.
 - Deuterium (D) is about 0.0156% of naturally occurring H.
 - D₂O is also known as *heavy water*.
 - Deuteration (replacement of H for D) results in changes in the kinetics of reactions.
 - This phenomenon is called the *kinetic isotope effect*.
 - Tritium (T) is radioactive with a half-life of 12.3 yr.
 - Deuterium and tritium are substituted for H in compounds in order to provide a molecular marker. Such compounds are said to be "labeled" (e.g., D₂O).

Properties of Hydrogen

- Hydrogen is unique.
- Hydrogen has a 1s¹ 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 the *hydride ion* (H[−]), which has a He electron configuration.
 - Therefore, H could be placed above the halogens.
 - However, the electron affinity of H is lower than that of any halogen.
- Elemental hydrogen is a colorless, odorless diatomic gas at room temperature.
 - H₂ is sometimes referred to as *dihydrogen*, but is more commonly called either *molecular hydrogen* or simply hydrogen.
- Since H₂ is nonpolar and has only two electrons, its intermolecular forces are weak (boiling point −253 °C, melting point −250 °C).
- The H–H bond enthalpy is high (436 kJ/mol).
 - Therefore, reactions with hydrogen are slow at room temperature.
 - Often the molecules must be activated with heat, irradiation, or a catalyst.
- Hydrogen forms strong covalent bonds with many elements.
- When hydrogen is ignited in air, an explosion results:



Production of Hydrogen⁴

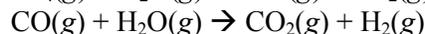
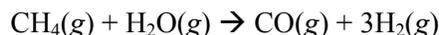
- In the laboratory, hydrogen is usually prepared by the reduction of an acid.

⁴ “Making Hydrogen Gas from an Acid and a Base” from Live Demonstrations

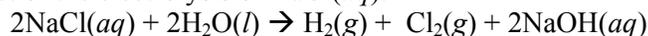
- For example, Zn is added to an acidic solution and hydrogen bubbles form.
- The hydrogen bubbles out of solution and is collected in a flask.
- The collection flask is usually filled with water, so the volume of hydrogen collected is the volume of water displaced.



- Hydrogen can be prepared in larger quantities by the reduction of methane in the presence of steam at 1100 °C:

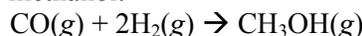


- Alternatively,
 - hydrogen gas can be prepared by reacting carbon with steam at high temperatures to make *water gas* (a mixture of H₂ and CO).
 - H₂ is a by-product of the electrolysis of NaCl(aq):



Uses of Hydrogen

- About two-thirds of the 2×10^8 kg of hydrogen produced in the United States is used for ammonia production via the Haber process.
- Hydrogen is used to manufacture methanol:



Binary Hydrogen Compounds^{5,6}

- Three types of binary hydrogen compounds are formed:
 - **ionic hydrides** (e.g., LiH)
 - contain H and alkali metals or heavier alkaline earth metals.
 - H⁻ is very reactive and basic.
 - Example: $\text{H}^-(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{H}_2(g) + \text{OH}^-(aq)$
 - They are generally stored in an environment free from water and air.
 - **metallic hydrides** (e.g., TiH₂)
 - contain transition metals and H.
 - *Interstitial* hydrides can be made with less than stoichiometric amounts of H.
 - An example is TiH_{1.8}.
 - **molecular hydrides** (e.g., CH₄)
 - Contain nonmetals or semimetals and H.
 - The thermal stability of molecular hydrides (measured by ΔG°_f) decreases as we go down a group and increases from left to right across a period.

22.3 Group 8A: The Noble Gases^{7,8}

- The noble gases are all gases at room temperature.
 - He is the most important noble gas.
 - Liquid helium is used as a coolant.
 - It has the lowest boiling point of any substance.
 - Ar is the most abundant noble gas.

Noble-Gas Compounds

- The noble gases are very unreactive.

⁵ “What’s the Use? Hydrogen” from Further Readings

⁶ “Formation of Water” Movie from Instructor’s Resource CD/DVD

⁷ “Electronegativities of the Noble Gases” from Further Readings

⁸ Table 22.1 from Transparency Pack

- All noble gases have high ionization energies.
- The heavier noble gases react more readily than the lighter ones.
- The first compounds of noble gases were prepared by Neil Bartlett in 1962.
 - He prepared xenon fluorides.
- Oxygen-containing compounds are formed when the fluorides react with water.

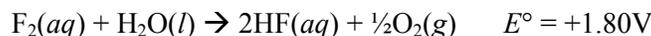
$$\text{XeF}_6(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{XeO}_3(aq) + 6\text{HF}(aq)$$
- Another known noble gas compound is KrF₂.
 - It decomposes to its elements at -10 °C.

22.4 Group 7A: The Halogens

- The outer electron configurations are ns^2np^5 .
- All halogens have large electron affinities.
 - They achieve a noble-gas configuration by gaining one electron.
 - Their most common oxidation state is -1, but oxidation states of +1, +3, +5, and +7 are possible.
- In the positive oxidation states, halogens are good oxidizing agents.
- Chlorine, bromine, and iodine are found as halides in seawater and salt deposits.
- Fluorine occurs in several minerals (e.g., fluor spar, CaF₂).
- All isotopes of At are radioactive.

Properties and Preparation of the Halogens^{9,10,11,12}

- The properties of the halogens vary regularly with their atomic number.
- Each halogen is the most electronegative element in its row.
- Halogens exist as diatomic molecules.
 - In solids and liquids, the molecules are held together by weak London-dispersion forces.
 - Iodine has the highest melting point and the strongest intermolecular forces.
 - At room temperature, I₂ is a solid, Br₂ is a liquid, and Cl₂ and F₂ are gases.
- The bond enthalpy of F₂ is low.
 - Hence, fluorine is very reactive.
 - The reduction potential of fluorine is very high.
 - Water is oxidized more readily than fluorine, so F₂ cannot be prepared by electrolysis of a salt solution.



- Cl₂ is produced by electrolysis of NaCl(l) or NaCl(aq).

Uses of the Halogens^{13,14,15,16}

- Fluorine is an important industrial chemical.
 - It is used to make fluorocarbons [used as lubricants and plastics (Teflon)].
- Chlorine is used in plastics (PVC), dichloroethane, and other organic chemicals; it is also used as a bleaching agent in the paper and textile industries.
 - NaClO is the active ingredient in bleach.
- NaBr is used in photography.

⁹ Table 22.2 from Transparency Pack

¹⁰ “An Overhead Demonstration of Some Descriptive Chemistry of the Halogens and Le Châtelier’s Principle” from Live Demonstrations

¹¹ “Discovery and Early Uses of Iodine” from Further Readings

¹² “Physical Properties of the Halogens” Movie from Instructor’s Resource CD/DVD

¹³ “Demonstrating a Lack of Reactivity Using a Teflon-Coated Pan” from Live Demonstrations

¹⁴ “Preparation of Chlorine Gas from Laundry Bleach” from Live Demonstrations

¹⁵ “Dentifrice Fluoride” from Further Readings

¹⁶ “Teflon” 3-D Model from Instructor’s Resource CD/DVD

- Iodine is a necessary nutrient.
 - It is used by the body in the synthesis of thyroid hormone.
 - Lack of iodine in the diet results in a thyroid condition called *goiter*.

The Hydrogen Halides

- All halogens form diatomic molecules with hydrogen.
- Most hydrogen halides are prepared by treating a salt with a strong nonvolatile acid.
 - For example, we can utilize sulfuric acid in such a reaction to form HF or HCl:

$$\text{CaF}_2(s) + \text{H}_2\text{SO}_4(l) \rightarrow 2\text{HF}(g) + \text{CaSO}_4(s)$$

$$\text{NaCl}(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{HCl}(g) + \text{NaHSO}_4(s)$$
 - These reactions cannot be used to prepare HBr or HI.
- Hydrogen halides form hydrohalic acid solutions when dissolved in water.
- HF(aq) also reacts with **silica** (SiO₂) to form hexafluorosilicic acid:

$$\text{SiO}_2(s) + 6\text{HF}(aq) \rightarrow \text{H}_2\text{SiF}_6(aq) + 2\text{H}_2\text{O}(l)$$
- HF must be stored in wax or plastic containers because it will react with the silicates in glass.

Interhalogen Compounds

- Diatomic molecules containing two different halogens are called **interhalogen compounds**.
- Most higher interhalogen compounds have Cl, Br, or I as the central atom surrounded by 3, 5, or 7 F atoms.
 - The larger the halogen, the more interhalogen compounds it can form.
 - The compound ICl₃ is unique.
 - The large size of the I atom allows it to accommodate the three Cl atoms.
 - No other halogen is large enough to accommodate three Cl atoms.
- Interhalogen compounds are very reactive; they are powerful oxidizing agents.

Oxyacids and Oxyanions

- Acid strength increases as the oxidation state of the halogen increases.
- All are strong oxidizing agents.
- They are generally unstable and decompose readily.
 - The oxyanions are more stable than oxyacids.
- Oxyacids and oxyanions of chlorine include:
 - hypochlorite salts (used in bleaches and disinfectants)
 - perchlorates (particularly unstable when heated in the presence of organic material)
 - Ammonium perchlorate is a potent oxidizer.
 - In the presence of powdered aluminum, NH₄ClO₄ is used to launch the space shuttle.
 - Each launch uses 700 tons of ammonium perchlorate.

FORWARD REFERENCES

- The role of chlorides in the coordination chemistry of transition metals will be tabulated in Chapter 23 (section 23.1).

22.5 Oxygen

Properties of Oxygen^{17,18}

- Oxygen has two allotropes: O₂ (*dioxygen*) and O₃ (*ozone*).
- O₂ is a colorless, odorless gas at room temperature.
 - The electron configuration is [He]2s²2p⁴, which means the dominant oxidation state is -2.
 - It can complete an octet by gaining two e⁻ to form an oxide anion (O²⁻) or by sharing 2e⁻.

¹⁷ “Joseph Priestley, Preeminent Amateur Chemist” from Further Readings

¹⁸ “The Discovery of Oxygen and Other Priestley Matters” from Further Readings

- In covalent compounds, it forms either two single bonds or a double bond.
- The O=O bond is strong (bond enthalpy 495 kJ/mol).

Production of Oxygen

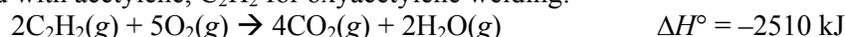
- Laboratory preparation of oxygen often involves the catalytic decomposition of KClO_3 in the presence of MnO_2 :



- Atmospheric oxygen is replenished by photosynthesis.

Uses of Oxygen

- Oxygen is one of the most widely used oxidizing agents.
 - More than half of the oxygen produced is used in the steel industry to remove impurities.
- Oxygen is also used in medicine.
 - It is used with acetylene, C_2H_2 for oxyacetylene welding:



Ozone¹⁹

- Ozone is a pale blue poisonous gas.
- Ozone dissociates to form oxygen:

$$\text{O}_3(g) \rightarrow \text{O}_2(g) + \text{O}(g) \quad \Delta H^\circ = 105 \text{ kJ.}$$
- Ozone is a stronger oxidizing agent than oxygen:

$$\begin{array}{l} \text{O}_3(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{O}_2(g) + \text{H}_2\text{O}(l) \quad E^\circ = 2.07 \text{ V} \\ \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l) \quad E^\circ = 1.23 \text{ V} \end{array}$$
- Ozone can be made by passing an electric current through dry O_2 :

$$3\text{O}_2(g) \rightarrow 2\text{O}_3(g) \quad \Delta H^\circ = 285 \text{ kJ}$$
- Ozone is used to kill bacteria and to prepare pharmaceuticals and lubricants.
- Ozone is an important component of the atmosphere.
 - In the upper atmosphere, ozone forms a shield to screen out harmful radiation.
 - In the lower atmosphere, ozone is considered an air pollutant.

Oxides^{20,21,22,23,24}

- Oxygen is the second most electronegative element.
- *Oxides* are compounds with oxygen in the -2 oxidation state.
- Nonmetal oxides are covalent.
 - Most metal oxides combine with water to give oxyacids.
 - Oxides that react with water to form acids are called **acidic anhydrides**, or **acidic oxides**.
 - Anhydride means without water.
 - Example:

$$\text{SO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_3(aq)$$
- Metal oxides are ionic.
 - Oxides that react with water to form hydroxides are called **basic anhydrides**, or **basic oxides**.
 - Example: BaO in water produces $\text{Ba}(\text{OH})_2$.

$$\text{BaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ba}(\text{OH})_2(aq)$$
- Oxides that exhibit both acidic and basic properties are said to be *amphoteric* (e.g., Cr_2O_3).

¹⁹ “Ozone” 3-D Model from Instructor’s Resource CD/DVD

²⁰ “Combining Volume of Oxygen with Sulfur” from Live Demonstrations

²¹ “Periodic Trends: Acid-Base Behavior of Oxides” Animation from Instructor’s Resource CD/DVD

²² “Three Forms of Molecular Oxygen” from Further Readings

²³ “An Acidity Scale for Binary Oxides” from Further Readings

²⁴ “Water” 3-D Model from Instructor’s Resource CD/DVD

Peroxides and Superoxides²⁵

- *Peroxides* have an O–O bond and O in the –1 oxidation state.
 - An example is hydrogen peroxide (H₂O₂).
- *Superoxides* have an O–O bond and O in an oxidation state of –½.
 - The superoxide ion is O₂[–].
 - Superoxides usually form with very active metals (KO₂, RbO₂ and CsO₂).
- Uses of superoxides:
 - Superoxides generate oxygen gas when dissolved in water.
 - This process is used in oxygen masks used in rescue work.
- Properties and uses of peroxides
 - Hydrogen peroxide is unstable and decomposes into water and oxygen:

$$2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \quad \Delta H^\circ = -196.1 \text{ kJ.}$$
 - This is an example of a **disproportionation reaction** in which an element is simultaneously oxidized and reduced.
 - In dilute aqueous solution it is used as a mild antiseptic.
 - Peroxide is a by-product of some cellular metabolic processes.
 - These peroxides are reactive and potentially damaging to tissues.
 - Cells contain enzymes (peroxidases, catalase) that convert peroxides into less harmful species.
 - Peroxides are formed when active metals such as Na or Ca react with O₂ (i.e., to form metallic peroxides such as Na₂O₂, CaO₂).

FORWARD REFERENCES

- Several oxide minerals of transition metals will be tabulated in Chapter 23 (section 23.1).

22.6 The Other Group 6A Elements: S, Se, Te, and Po

General Characteristics of Group 6A Elements

- The outermost electron configuration is ns^2np^4 .
- The dominant oxidation state is –2 (ns^2np^6).
- Other observed oxidation states are up to +6 (e.g., SF₆, SeF₆, TeF₆).
- There is a regular change in properties with increasing atomic number.

Occurrences and Production of S, Se, and Te^{26,27}

- Sulfur, selenium, and tellurium can all be mined from the earth.
- S occurs widely as sulfates and in sulfide minerals.
 - Its presence in coal and petroleum poses an environmental problem when these fuels are burned.
- Se and Te occur in rare minerals (Cu₂Se, PbSe, Ag₂Se, Cu₂Te, PbTe, Ag₂Te, and Au₂Te) and are minor constituents in sulfide ores (usually of Cu, Fe, Ni, and Pb).

Properties and Uses of Sulfur, Selenium, and Tellurium

- Sulfur is yellow, tasteless, and almost odorless.
 - Sulfur is insoluble in water.
 - Sulfur exists in allotropes (rhombic S₈ rings, plastic sulfur).
 - Sulfur is used in the manufacture of sulfuric acid and in vulcanizing rubber.
- Se and Te both form helical chains of atoms in crystals.
 - There is some sharing of electron pairs between chains.
 - Se is used in photoelectric cells, photocopiers, and light meters.

²⁵ “Hydrogen Peroxide” 3-D Model from Instructor’s Resource CD/DVD

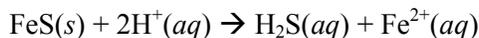
²⁶ “Plastic Sulfur” from Live Demonstrations

²⁷ Table 22.5 from Transparency Pack

- Its electrical conductivity is poor in the dark and increases greatly when exposed to light.

Sulfides²⁸

- S is in the -2 oxidation state in *sulfides*.
- Many metals are found in the form of sulfides in ores.
 - Examples are PbS (galena) and HgS (cinnabar).
- S in *pyrites* is in the -1 oxidation state, S_2^{2-} .
 - FeS₂ is iron pyrite, often called “fool’s gold.”
- Hydrogen sulfide (used for qualitative analysis of certain metals) is prepared by treating iron(II) sulfide with dilute acid:



- Hydrogen sulfide is responsible for the odor of rotten eggs and is quite toxic.

Oxides, Oxyacids, and Oxyanions of Sulfur²⁹

- SO₂ is produced when sulfur is combusted in air.
- SO₂ in water produces sulfurous acid, H₂SO₃, a weak diprotic acid.
- SO₂ is toxic to fungi and is used to sterilize dried fruit and wine.
 - Na₂SO₃ and NaHSO₃ are used as preservatives.
 - Many people are allergic to these agents and must avoid foods treated with them.
- When sulfur burns in air, both SO₂ (major product) and SO₃ are formed.
- The oxidation of SO₂ to SO₃ requires a catalyst (usually V₂O₅ or Pt).
- SO₃ is used to produce H₂SO₄:

$$\text{SO}_3(g) + \text{H}_2\text{SO}_4(l) \rightarrow \text{H}_2\text{S}_2\text{O}_7(l) \text{ [pyrosulfuric acid]}$$

$$\text{H}_2\text{S}_2\text{O}_7(l) + \text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{SO}_4(l)$$
 - Commercially, sulfuric acid is 98% H₂SO₄.
 - Sulfuric acid is a powerful dehydrating agent, a strong acid, and a moderate oxidizing agent.
 - In aqueous solutions of H₂SO₄ only the first proton is completely ionized:

$$\text{H}_2\text{SO}_4(aq) \rightarrow \text{HSO}_4^-(aq) + \text{H}^+(aq)$$
- Bisulfate (HSO₄⁻) salts are important components of “dry acids” used in toilet bowl cleaners and in adjusting the pH of swimming pools and hot tubs.
- The sulfite ion, SO₃²⁻, and the *thiosulfate* ion, S₂O₃²⁻, are other important sulfur-containing ions:

$$8\text{SO}_3^{2-}(aq) + \text{S}_8(s) \rightarrow 8\text{S}_2\text{O}_3^{2-}(aq)$$

FORWARD REFERENCES

- Several sulfide minerals of transition metals will be tabulated in Chapter 23 (section 23.1).

22.7 Nitrogen

Properties of Nitrogen³⁰

- It is a colorless, odorless, tasteless gas composed of N₂ molecules.
- It is unreactive because of the strong triple bond.
- Exception: Burning Mg or Li in air (78% nitrogen) forms nitrides:

$$3\text{Mg}(s) + \text{N}_2(g) \rightarrow \text{Mg}_3\text{N}_2(s)$$

$$6\text{Li}(s) + \text{N}_2(g) \rightarrow 2\text{Li}_3\text{N}(s)$$
- N³⁻ is a strong Brønsted-Lowry base (forms NH₃ in water):

$$\text{Mg}_3\text{N}_2(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{NH}_3(aq) + 3\text{Mg}(\text{OH})_2(s)$$
- Nitrogen exhibits all formal oxidation states from -3 to $+5$.

²⁸ “Herman Frasch, Sulfur King” from Further Readings

²⁹ “Sulfate Ion” 3-D Model from Instructor’s Resource CD/DVD

³⁰ Table 22.6 from Transparency Pack

- The most common oxidation states are +5, 0, and -3 (nitrogen has an $[\text{He}]2s^22p^3$ electron configuration).

Production and Uses of Nitrogen

- N_2 is produced by fractional distillation of air.
- Nitrogen is used as an inert gas to exclude oxygen from packaged foods and in the manufacture of chemicals, fabrication of metals, and production of electronics.
- Liquid nitrogen is an important coolant.
- The largest use of N_2 is in the manufacture of nitrogen-containing fertilizers to provide a source of *fixed* nitrogen.
 - Nitrogen is fixed by forming NH_3 (Haber Process).
 - NH_3 is converted into other useful chemicals.

Hydrogen Compounds of Nitrogen³¹

- Ammonia* is one of the most important compounds of nitrogen.
 - Ammonia is a colorless toxic gas with an irritating aroma.
 - In the laboratory, ammonia is produced by the reaction between NaOH and an ammonium salt:

$$\text{NH}_4\text{Cl}(aq) + \text{NaOH}(aq) \rightarrow \text{NH}_3(g) + \text{H}_2\text{O}(l) + \text{NaCl}(aq)$$
 - Commercially, ammonia is prepared by the Haber process.

$$\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$$
- Hydrazine* contains an N-N single bond (N_2H_4).
 - Hydrazine (poisonous) is prepared by the reaction of ammonia and hypochlorite:

$$2\text{NH}_3(aq) + \text{OCl}^-(aq) \rightarrow \text{N}_2\text{H}_4(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l)$$
 - Poisonous chloramine, NH_2Cl , is an intermediate in the reaction.
 - It bubbles out of solution when household ammonia and bleach are mixed.
 - Pure hydrazine is an oily liquid that explodes on heating.
 - Hydrazine and related compounds are used as a component of rocket fuels.

Oxides and Oxyacids of Nitrogen^{32,33,34,35,36,37,38,39}

- There are three common oxides of nitrogen:
 - N_2O (*nitrous oxide*).
 - This is also known as laughing gas and is used as an anesthetic.
 - NO (*nitric oxide*).
 - This is a toxic, colorless gas; it is an important neurotransmitter.
 - NO_2 (*nitrogen dioxide*).
 - This is a poisonous yellowish-brown gas, which is major constituent of smog.
- Some of the reactions used in their preparation include:

$$\text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(g)$$

$$3\text{Cu}(s) + 2\text{NO}_3^-(aq) + 8\text{H}^+(aq) \rightarrow 3\text{Cu}^{2+}(aq) + 2\text{NO}(g) + 4\text{H}_2\text{O}(l)$$
- The **Ostwald process** is the commercial route to HNO_3 .
 - It takes place in 3 steps:

³¹ “Hydrazine” 3-D Model from Instructor’s Resource CD/DVD

³² “Some History of Nitrates” from Further Readings

³³ “Nitrogen Dioxide and Dinitrogen Tetroxide” Movie from Instructor’s Resource CD/DVD

³⁴ “Dinitrogen Trioxide” 3-D Model from Instructor’s Resource CD/DVD

³⁵ “Dinitrogen Tetroxide” 3-D Model from Instructor’s Resource CD/DVD

³⁶ “Nitrogen Dioxide” 3-D Model from Instructor’s Resource CD/DVD

³⁷ “The Discovery of Nitroglycerine: Its Preparation and Therapeutic Utility” from Further Readings

³⁸ “Bad Rap of Nitrate” from Further Readings

³⁹ “Biological Roles of Nitric Acid” from Further Readings

- oxidation of NH_3 by oxygen to form NO (usually using a Pt catalyst).

$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$
- oxidation of NO by oxygen to form NO_2 (unreacted NO is recycled).
- NO_2 dissolution in water to form nitric acid.
- The common oxyacids of nitrogen are HNO_3 (*nitric*) and HNO_2 (*nitrous*).
 - Nitric acid is a strong acid and a powerful oxidizing agent.
 - Concentrated nitric acid will oxidize most metals (exceptions are Au, Pt, Rh and Ir):

$$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \quad E^\circ = 0.96\text{V}$$
 - Nitric acid is used to manufacture fertilizers (NH_4NO_3), drugs, plastics, and explosives [such as nitroglycerin and TNT (trinitrotoulene)].
 - Nitrous acid (weak, $K_a = 4.5 \times 10^{-4}$) is not stable and disproportionates into NO and HNO_3 .

FORWARD REFERENCES

- Ammonia complexes of cobalt will be discussed in Chapter 23 (section 23.2).

22.8 The Other Group 5A Elements: P, As, Sb, and Bi**General Characteristics of the Group 5A Elements^{40,41,42,43}**

- The outermost shell electron configuration is ns^2np^3 .
- The most common oxidation state is -3 . Other common oxidation states are -1 , $+1$, $+3$, and $+5$.
- The variation in atomic properties is very striking.
 - This group contains all three types of elements: metallic, nonmetallic, and semimetallic.
 - Size and metallic character increase with increasing atomic number within the group.
- The X–X bond enthalpies are difficult to measure.

Occurrence, Isolation, and Properties of Phosphorus⁴⁴

- Occurs mainly in phosphorus minerals [e.g., phosphate rock, $\text{Ca}_3(\text{PO}_4)_2$].
- Elemental P_4 is produced by reduction:

$$2\text{Ca}_3(\text{PO}_4)_2(\text{s}) + 6\text{SiO}_2(\text{s}) + 10\text{C}(\text{s}) \rightarrow \text{P}_4(\text{g}) + 6\text{CaSiO}_3(\text{l}) + 10\text{CO}(\text{g})$$
- There are two allotropes of phosphorus: red and white.
 - P_4 is white phosphorus.
 - All P–P–P bond angles are 60° (small), therefore, the molecule is strained and unstable.
 - White phosphorus is poisonous and highly reactive (spontaneously reacts with oxygen in air).
 - Therefore, white phosphorus is stored under water.
 - If white phosphorus is heated to 400°C in the absence of air, it converts into red phosphorus.
 - Red phosphorus is the more stable allotrope and is not usually stored under water.

Phosphorus Halides

- Phosphorus forms a variety of compounds with halogens with the tri- and pentahalides being the most important.
- The most important is PCl_3 which is used in soap, detergent, plastic, and insecticide production.
- Preparation of phosphorus halides involves direct oxidation of elemental phosphorous with elemental halogen.
 - For example:

$$2\text{P}(\text{s}) + 3\text{Cl}_2(\text{g}) \rightarrow 2\text{PCl}_3(\text{l})$$
 - In the presence of excess chlorine:

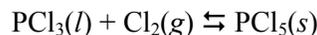
⁴⁰ “Arsenic: Not So Evil After All?” from Further Readings

⁴¹ Table 22.7 from Transparency Pack

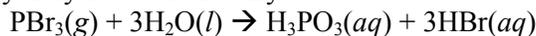
⁴² “Arsenic in Drinking Water—A Global Environmental Problem” from Further Readings

⁴³ “Phosphorus” 3-D Model from Instructor’s Resource CD/DVD

⁴⁴ “Keeping the Fire Cold” from Further Readings



- In the presence of water hydrolysis occurs readily:



Oxy Compounds of Phosphorus^{45,46,47,48}

- Oxygen-containing phosphorus compounds are extremely important.
 - Phosphorus(III) oxide, P_4O_6 is made by reacting white phosphorus with a limited supply of oxygen.
 - Phosphorus(V) oxide, P_4O_{10} is made by reacting phosphorus with excess oxygen.
 - Phosphorus(III) oxide, P_4O_6 produces phosphorous acid, H_3PO_3 in water.
- The oxides of phosphorus are acidic.
 - H_3PO_3 is a weak *diprotic* acid (the H attached to P is not acidic).
 - Phosphorus(V) oxide, P_4O_{10} produces phosphoric acid, H_3PO_4 .
 - H_3PO_4 is a weak *triprotic* acid.
 - P_4O_{10} is used as a drying agent because of its affinity for water.
- Phosphoric and phosphorous acids undergo condensation reactions.
 - A condensation reaction is one in which two or more molecules combine to form a larger molecule with the elimination of a smaller molecule.
 - For example:



- Phosphoric acid and its salts are used in detergents (as $\text{Na}_5\text{P}_3\text{O}_{10}$) and fertilizers (from mined phosphate rock).
- Phosphorus compounds are important in biological systems [e.g., RNA, DNA, and adenosine triphosphate (ATP)].

FORWARD REFERENCES

- Phosphate groups in RNA and DNA will be discussed in Chapter 24 (section 24.10).

22.9 Carbon

Elemental Forms of Carbon

- Carbon constitutes about 0.027% of the Earth's crust.
- Carbon is the main constituent of living matter.
- The study of carbon compounds (*organic compounds*) is called *organic chemistry*.
- There are five allotropic forms of carbon: two of these are graphite and diamond:
 - *graphite* (soft, slippery, and black),
 - *diamond* (clear, hard, and forms a covalent network),
- Microcrystalline and amorphous forms of C include:
 - **carbon black**, formed when hydrocarbons are heated in a very limited supply of oxygen:

$$\text{CH}_4(g) + \text{O}_2(g) \rightarrow \text{C}(s) + 2\text{H}_2\text{O}(g)$$
 - Carbon black is used as a pigment in black inks and automobile tires.
 - **charcoal**, formed by heating wood in the absence of air.
 - Activated charcoal is used to remove odors and impurities from air and water.

Oxides of Carbon

- Carbon forms two principal oxides: CO and CO_2 .

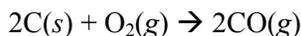
⁴⁵ "Tetraphosphorus Hexoxide" 3-D Model from Instructor's Resource CD/DVD

⁴⁶ "Tetraphosphorus Decoxide" 3-D Model from Instructor's Resource CD/DVD

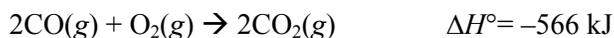
⁴⁷ "Phosphoric Acid" 3-D Model from Instructor's Resource CD/DVD

⁴⁸ "Phosphorous Acid" 3-D Model from Instructor's Resource CD/DVD

- CO (*carbon monoxide*) is formed when carbon or hydrocarbons are burned in a limited supply of oxygen.



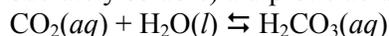
- CO is very toxic (binds irreversibly to hemoglobin, interfering with oxygen transport).
 - It is odorless, colorless, and tasteless.
- CO also has a lone pair of electrons on C, which is unusual.
- CO is a good Lewis base and forms metal carbonyls with transition metals.
 - For example, Ni(CO)₄ forms readily when Ni is warmed in CO.
- CO can be used as a fuel:



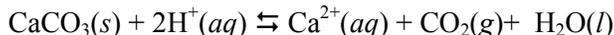
- CO is a good reducing agent
 - $\text{Fe}_3\text{O}_4(s) + 4\text{CO}(g) \rightarrow 3\text{Fe}(s) + 4\text{CO}_2(g)$
- CO₂ (*carbon dioxide*) is produced when organic compounds are burned in excess oxygen:
 - $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(g)$
- CO₂ is produced by either heating carbonates or treating them with acids:
 - $\text{CaCO}_3(s) \rightarrow \text{CO}_2(g) + \text{CaO}(s)$
 - $\text{CO}_3^{2-}(aq) + 2\text{H}^+(aq) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$
- Fermentation of sugar to produce alcohol also produces CO₂:
 - $\text{C}_6\text{H}_{12}\text{O}_6(aq) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(aq) + 2\text{CO}_2(g)$
- Some of the major uses of CO₂ are in refrigeration (using Dry Ice™), in the carbonation of beverages, and in the production of both *washing soda* (Na₂CO₃·10H₂O) and *baking soda* (NaHCO₃).

Carbonic Acid and Carbonates⁴⁹

- When CO₂ dissolves in water (moderately soluble) a diprotic acid, carbonic acid, forms:



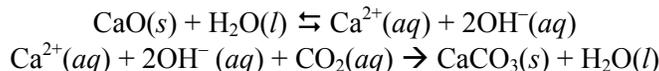
- Carbonic acid is responsible for giving carbonated beverages a sharp acidic taste.
- Two salts of carbonic acid may be obtained by neutralization.
 - Partial neutralization of H₂CO₃ gives hydrogen carbonates (bicarbonates): HCO₃⁻.
 - Aqueous solutions of bicarbonates are weakly basic.
 - Full neutralization gives carbonates: CO₃²⁻.
 - Aqueous solutions of carbonates are more strongly basic.
- Many minerals contain CO₃²⁻.
- Example: Calcite (CaCO₃) is the principal mineral in limestone, marble, etc..
- CaCO₃ reacts readily with acid:



- At elevated temperatures, CaCO₃ decomposes:



- This reaction is the commercial source of *lime*, CaO.
- CaO reacts with water and CO₂ to form CaCO₃, which binds the sand in mortar:



Carbides

- **Carbides** are binary compounds of C and metals, metalloids, and certain nonmetals.
- There are three types of carbides:
 - *Ionic carbides* (formed by active metals)
 - Most contain the *acetylide* ion, C₂²⁻.
 - An example is CaC₂.

⁴⁹ “Carbon Dioxide Behaves as an Acid in Water” Movie from Instructor’s Resource CD/DVD

- CaC_2 is used in the formation of acetylene:

$$\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(aq) + \text{C}_2\text{H}_2(g)$$
- *Interstitial carbides* are formed by many transition metals.
 - An example is tungsten carbide.
 - The carbon atoms occupy the spaces or interstices between metal atoms.
- *Covalent carbides* are formed by B and Si.
 - SiC is also called Carborundum. It is nearly as hard as diamond.

Other Inorganic Compounds of Carbon

- Two interesting inorganic compounds of carbon are HCN and CS_2 .
 - HCN (hydrogen cyanide) is an extremely toxic gas.
 - HCN is produced by reacting a salt, (e.g., NaCN) with acid.
 - Cyanides are used in the manufacture of plastics like nylon and Orlon.
 - CN^- forms very stable complexes with transition metals.
 - One cause of its toxicity is its ability to combine with the iron(III) of a key enzyme in respiration (cytochrome oxidase).
 - CS_2 is an important solvent for waxes and greases.
 - CS_2 vapor is very toxic, colorless, and highly flammable.

FORWARD REFERENCES

- Chemistry of carbon will be discussed in detail throughout Chapter 24.

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

General Characteristics of Group 4A Elements⁵⁰

- The outermost electron configuration is ns^2np^2 .
- The electronegativities are low.
- Carbon has a coordination number of 4, the other members have higher coordination numbers.
 - Carbides (C^{4-}) are rare.
 - C–C bonds are very strong, so C shows the unusual ability to bond to itself to form long chains.
- The dominant oxidation state for Ge, Sn, and Pb is +2.
- Because the Si–O bond is stronger than the Si–Si bond, Si tends to form oxides (silicates).

Occurrence and Preparation of Silicon

- Si is the second most abundant element in the Earth's crust.
- Elemental Si is prepared by reducing SiO_2 :

$$\text{SiO}_2(l) + 2\text{C}(s) \rightarrow \text{Si}(l) + 2\text{CO}(g)$$
- Silicon has many important uses in the electronics industry.
 - Wafers of Si are cut from cylindrical Si crystals.
 - Si must be extremely pure when used as a semiconductor.
 - Impure Si is converted to SiCl_4 (with Cl_2), distilled, and then reduced to pure Si:

$$\text{SiCl}_4(g) + 2\text{H}_2(g) \rightarrow \text{Si}(s) + 4\text{HCl}(g)$$
 - The Si is then further purified by zone refining.
 - *Zone refining* is used to produce ultrapure Si.
 - The silicon crystal is placed inside a tube with an inert atmosphere.
 - A heating coil is slowly moved down the Si.
 - As the coil melts the Si, any impurities dissolve and move down with the heating coil.
 - At the bottom of the crystal, the portion of Si containing all the impurities is cut off and discarded.
 - The remaining crystal is ultrapure.

⁵⁰ Table 22.8 from Transparency Pack

Silicates^{51,52,53,54}

- More than 90% of the Earth's crust is composed of compounds of Si and O.
- The most common oxidation state of Si is +4.
- **Silicates** are compounds in which Si has four O atoms surrounding it in a tetrahedral arrangement.
 - Other minerals like zircon, ZrSiO_4 have a similar structure.
 - The silicate tetrahedra are building blocks for more complicated structures.
 - If two SiO_4^{4-} (*orthosilicate* ions) link together, one O atom is shared.
 - This structure is the *disilicate* ion, $\text{Si}_2\text{O}_7^{6-}$.
 - The mineral *thortveitite* ($\text{Sc}_2\text{Si}_2\text{O}_7$) contains disilicate ions.
- Many silicate tetrahedra can link together to form sheets, chains, or three-dimensional structures.
 - Consider a structure with two vertices linked to two other tetrahedra.
 - A single-strand silicate chain can form with a $\text{Si}_2\text{O}_6^{4-}$ repeating unit.
 - An example is *enstatite* (MgSiO_3).
 - Consider a structure with two vertices linked to three other tetrahedra.
 - A two-dimensional sheet results.
 - The mineral *talc* [talcum powder, $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$] results.
- Many minerals are based on silicates.
 - Some are useful as clays, ceramics, and other materials.
 - Others have harmful effects on human health:
 - *Asbestos* is a general term applied to a group of fibrous silicate minerals.
 - They form chains or sheets of silicates.
 - The sheets in asbestos are formed into rolls.
 - The rolls make the asbestos fibrous.
 - The fibers can be woven into cloth (fireproof clothing).
 - Asbestos represents a significant health risk and has been linked to diseases such as lung cancer.
 - Three-dimensional silicate forms quartz.

Glass^{55,56,57}

- Glasses result when silicates are heated (Si–O bonds are broken) and then rapidly cooled.
 - The Si–O bonds are re-formed before the atoms are able to organize into an ordered arrangement.
 - The amorphous solid is called quartz glass or silica glass.
- Additives are used to lower the melting point of the SiO_2 .
 - **Glass** in windows and bottles is called *soda-lime glass* (CaO and Na_2O are used as additives).
 - The CaO and Na_2O are formed from limestone (CaCO_3) and soda ash (Na_2CO_3) when these inexpensive materials are heated.
- Other properties of glass may be altered by additives.
 - CoO produces blue cobalt glass.
 - K_2O produces a harder glass than glass made with Na_2O .
 - PbO produces lead crystal glass (high refractive index).
 - B_2O_3 is used to make Pyrex® and Kimax®.
 - Pyrex® and Kimax® glassware has a very high melting point and resists thermal shock.

⁵¹ Figure 22.34 from Transparency Pack

⁵² “Silicate Tetrahedron” 3-D Model from Instructor’s Resource CD/DVD

⁵³ “Disilicate Anion ($\text{Si}_2\text{O}_7^{6-}$)” 3-D Model from Instructor’s Resource CD/DVD

⁵⁴ “Single-Chain Silicate” 3-D Model from Instructor’s Resource CD/DVD

⁵⁵ “Glass-Sand + Imagination” from Further Readings

⁵⁶ “Glass Doesn’t Flow and Doesn’t Crystallize and It Isn’t a Liquid” from Further Readings

⁵⁷ “The Origin of Pyrex” from Further Readings

Silicones

- Silicones consist of O–Si–O chains with Si–R (R is an organic group such as CH₃) bonds filling the Si valency.
- Silicones can be oils or rubber-like materials depending on chain length and degree of cross-linking.
- Silicones are used in lubricants, car polishes, sealants, gaskets, and for waterproofing fabrics.

22.11 Boron^{58,59}

- **Boranes** are compounds of boron and hydrogen.
- BH₃ is the simplest borane.
 - It reacts with itself to form *diborane*, B₂H₆.
 - Hydrogen appears to form two bonds.
 - These are called *bridging hydrogens*.
 - Diborane is very reactive:

$$\text{B}_2\text{H}_6(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{g}) \quad \Delta H^\circ = -2030 \text{ kJ.}$$
 - Some boranes such as pentaborane (B₅H₉), are reactive while some are stable in air at room temperature (e.g., decaborane: B₁₀H₁₄).
- Boron and hydrogen form a series of anions called *borane anions* such as BH₄[−].
 - They are used as reducing agents.
 - Sodium borohydride, NaBH₄, is used very commonly in organic chemistry.
- Boric oxide, B₂O₃, is the only important boron oxide.
 - It is the anhydride form of boric acid, H₃BO₃, a weak acid ($K_a = 5.8 \times 10^{-10}$).
 - Boric acid is used as an eyewash.
 - Heating causes a dehydration of boric acid, yielding a diprotic acid called tetraboric acid:

$$4\text{H}_3\text{BO}_3(\text{s}) \rightarrow \text{H}_2\text{B}_4\text{O}_7(\text{s}) + 5\text{H}_2\text{O}(\text{g})$$
 - The hydrated sodium salt is called borax.
 - Solutions of borax are alkaline.
 - It is widely used as a cleaning agent.

⁵⁸ “Boron Clusters Come of Age” from Further Readings

⁵⁹ “Diborane” 3-D Model from Instructor’s Resource CD/DVD

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20. Russell N. Grimes, "Boron Clusters Come of Age," *J. Chem. Educ.*, Vol. 81, **2004**, 658–672.

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2. Robert C. Hansen, "An Overhead Demonstration of Some Descriptive Chemistry of the Halogens and Le Châtelier's Principle," *J. Chem. Educ.*, Vol. 65, **1988**, 264–265.
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