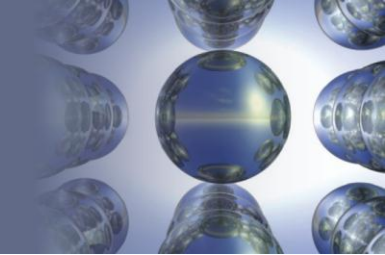


Chapter 20

The Representative Elements

Chapter 19

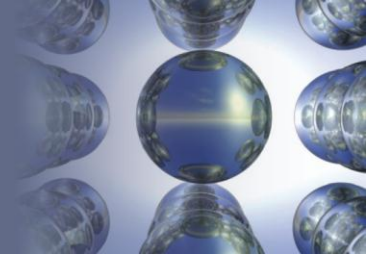
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- (20.1) A survey of the representative elements
- (20.2) The group 1A elements
- (20.3) The chemistry of hydrogen
- (20.4) The group 2A elements
- (20.5) The group 3A elements
- (20.6) The group 4A elements
- (20.7) The group 5A elements
- (20.8) The chemistry of nitrogen

Chapter 19

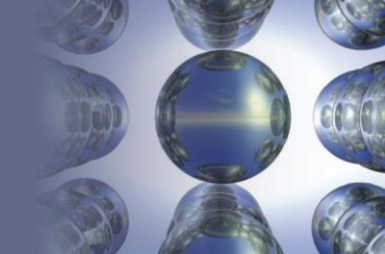
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- (20.9) The chemistry of phosphorus
- (20.10) The group 6A elements
- (20.11) The chemistry of oxygen
- (20.12) The chemistry of sulfur
- (20.13) The group 7A elements
- (20.14) The group 8A elements

Section 20.1

A Survey of the Representative Elements

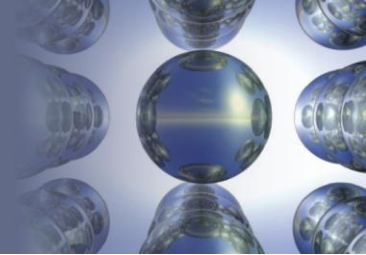


Reviewing the Periodic Table

- **Representative elements:** Chemical properties are determined by the valence-level s and p electrons
 - Designated Groups 1A–8A
- **Transition metals:** Result from the filling of d orbitals
 - Present at the center of the periodic table

Section 20.1

A Survey of the Representative Elements

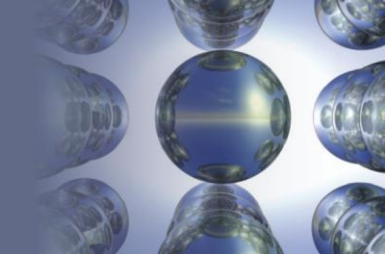


Reviewing the Periodic Table (Continued)

- **Lanthanides**: Correspond to the filling of the $4f$ orbitals
- **Actinides**: Correspond to the filling of the $5f$ orbitals
- **Metalloids (semimetals)**: Elements along the division line between metals and nonmetals in the periodic table
 - Exhibit both metallic and nonmetallic characteristics

Section 20.1

A Survey of the Representative Elements



Differentiating Metals from Nonmetals

Metals

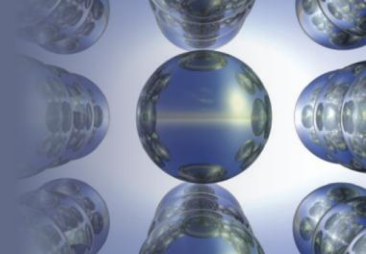
- Form cations by losing valence electrons
- Exhibit electron configuration of the noble gas from the preceding period

Nonmetals

- Form anions by gaining electrons
- Exhibit electron configuration of the noble gas in the same period

Section 20.1

A Survey of the Representative Elements

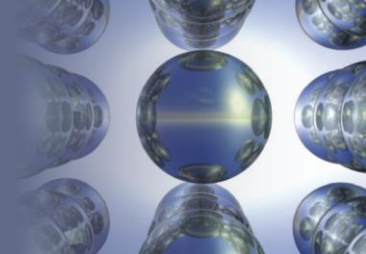


Atomic Size and Group Anomalies

- Difference in atomic radii between the first and the second member of a group causes the first element to exhibit different properties
 - Group 1A - Hydrogen is a nonmetal and lithium is an active metal
 - Hydrogen can form covalent bonds with nonmetals
 - Other members of Group 1A lose their valence electrons to nonmetals to form 1+ cations in ionic compounds

Section 20.1

A Survey of the Representative Elements

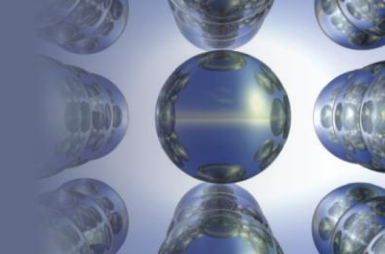


Atomic Size and Group Anomalies (Continued 1)

- Group 2A - Oxides of metals are basic except for beryllium oxide, which is amphoteric
 - All the oxides of the Group 2A metals are highly ionic except for beryllium oxide, which has considerable covalent character
- Group 3A - Boron acts as a nonmetal, or sometimes as a semimetal
 - All the other members are active metals

Section 20.1

A Survey of the Representative Elements

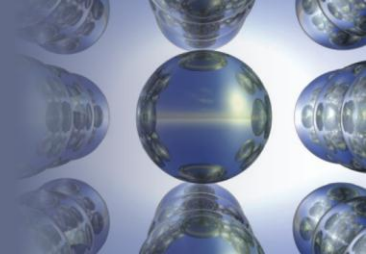


Atomic Size and Group Anomalies (Continued 2)

- Group 4A - Carbon and silicon have different chemical properties
 - Carbon compounds contain chains of C—C bonds, but silicon compounds mainly contain Si—O bonds
 - Differ in their ability to form π bonds
- Group 5A - Elemental nitrogen exists as a diatomic molecule, but elemental phosphorus forms larger aggregates of atoms
 - Elemental nitrogen can form strong π bonds, but phosphorus atoms cannot

Section 20.1

A Survey of the Representative Elements



Atomic Size and Group Anomalies (Continued 3)

- Group 6A
 - Elemental oxygen exists in its most stable form as O_2 molecule with a double bond
 - Sulfur atom forms bigger aggregates that contain only single bonds
- Group 7A - Fluorine has a smaller electron affinity than chlorine
 - The small size of the fluorine $2p$ orbitals causes large electron–electron repulsions

Section 20.1

A Survey of the Representative Elements

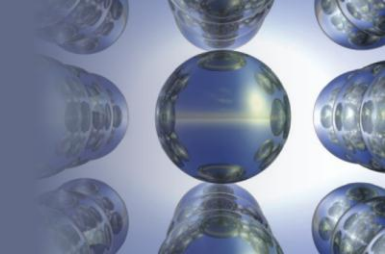


Table 20.1 - Distribution of the 18 Most Abundant Elements in the Earth's Crust

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

Section 20.1

A Survey of the Representative Elements

Table 20.2 - Abundance of Elements in the Human Body

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

Section 20.1

A Survey of the Representative Elements

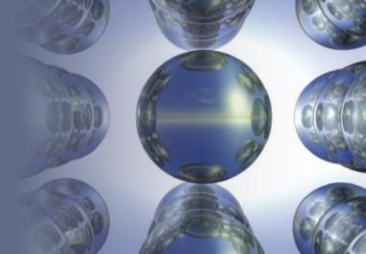


Abundance and Preparation

- One-fourth of all elements exist naturally in their free state
 - Most elements are found in a combined state
- **Metallurgy**: Process of obtaining a metal from its ore
 - Involves reducing ions to their elemental metal
 - Carbon is the most common reducing agent used

Section 20.1

A Survey of the Representative Elements

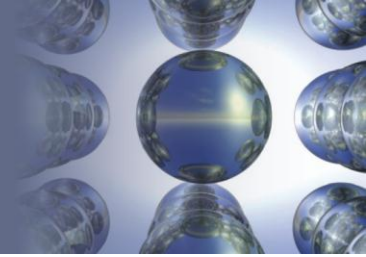


Preparation

- Most active metals are reduced using electrolysis
- Oxygen and nitrogen
 - Converted to liquid through **liquefaction**
 - Based on the principle that gas cools as it expands
 - Separated by distilling liquid air
- Hydrogen can be obtained from:
 - Electrolysis of water
 - Decomposition of methane in natural gas

Section 20.1

A Survey of the Representative Elements

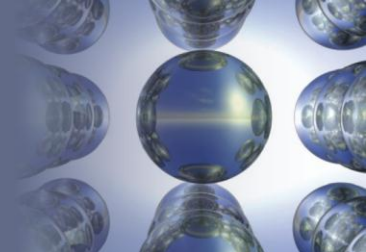


Preparation (Continued)

- Sulfur
 - Elemental form is found underground
 - Recovered by the Frasch process
- Halogens
 - Obtained via oxidation of anions from halide salts

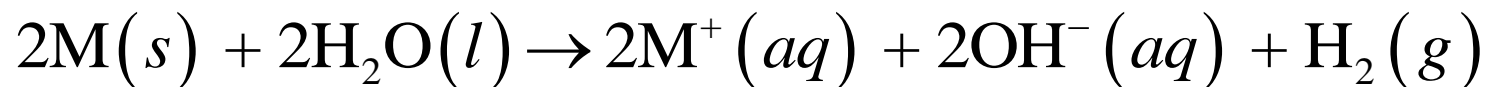
Section 20.2

The Group 1A Elements



Alkali Metals

- Elements with ns^1 valence electron configuration
 - Exception - Hydrogen
- React vigorously with H_2O to release hydrogen gas



- Essential for the proper functioning of nerves and muscles

1A

H

Li

Na

K

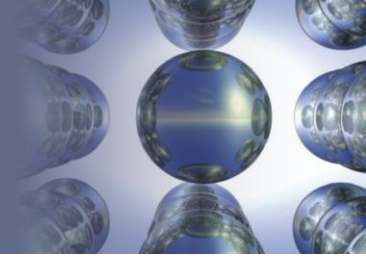
Rb

Cs

Fr

Section 20.2

The Group 1A Elements



Concentration of Na⁺ and K⁺ Ions in the Human Body

- Concentrations in human blood plasma
 - [Na⁺] ≈ 0.15 M
 - [K⁺] ≈ 0.005 M
- Concentrations in fluids inside cells
 - [Na⁺] ≈ 0.005 M
 - [K⁺] ≈ 0.16 M
- To transport Na⁺ and K⁺ ions through the cell membranes, an elaborate mechanism involving selective ligands is required

Section 20.2

The Group 1A Elements

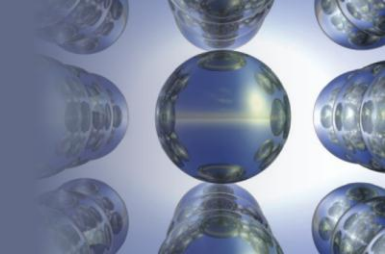


Table 20.3 - Sources and Methods of Preparation of the Pure Alkali Metals

Element	Source	Method of Preparation
Lithium	Silicate minerals such as spodumene, $\text{LiAl}(\text{Si}_2\text{O}_6)$	Electrolysis of molten LiCl
Sodium	NaCl	Electrolysis of molten NaCl
Potassium	KCl	Electrolysis of molten KCl
Rubidium	Impurity in lepidolite, $\text{Li}_2(\text{F},\text{OH})_2\text{Al}_2(\text{SiO}_3)_3$	Reduction of RbOH with Mg and H_2
Cesium	Pollucite ($\text{Cs}_4\text{Al}_4\text{Si}_9\text{O}_{26} \cdot \text{H}_2\text{O}$) and an impurity in lepidolite (Fig. 20.4)	Reduction of CsOH with Mg and H_2

Section 20.2

The Group 1A Elements

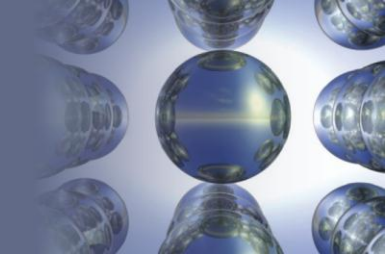


Table 20.4 - Selected Physical Properties of the Alkali Metals

Element	Ionization Energy (kJ/mol)	Standard Reduction Potential (V) for $M^+ + e^- \rightarrow M$	Radius of M^+ (pm)	Melting Point ($^{\circ}\text{C}$)
Lithium	520	-3.05	60	180
Sodium	495	-2.71	95	98
Potassium	419	-2.92	133	64
Rubidium	409	-2.99	148	39
Cesium	382	-3.02	169	29

Section 20.2

The Group 1A Elements

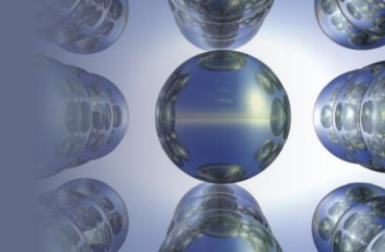
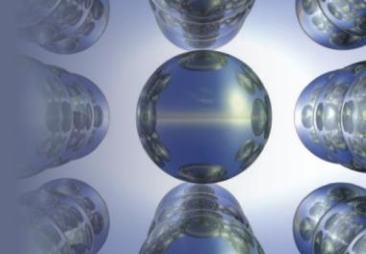


Table 20.5 - Selected Reactions of the Alkali Metals

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

Section 20.2

The Group 1A Elements

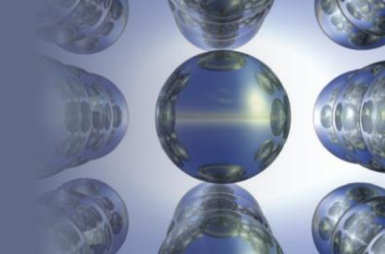


Exercise

- Refer to Table 20.5 and give examples of the three types of alkali metal oxides that form
 - How do they differ?

Section 20.2

The Group 1A Elements

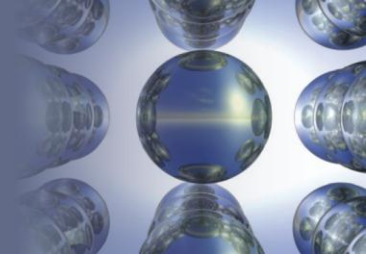


Exercise - Solution

- When lithium reacts with excess oxygen, Li_2O forms
 - Li_2O is composed of Li^+ and O_2^- ions
 - This is called an oxide salt
- When sodium reacts with oxygen, Na_2O_2 forms
 - Na_2O_2 is composed of Na^+ and O_2^{2-} ions
 - This is called a peroxide salt

Section 20.2

The Group 1A Elements



Exercise - Solution (Continued)

- When potassium (or rubidium or cesium) reacts with oxygen, KO_2 forms
 - KO_2 is composed of K^+ and O_2^- ions
 - This is called a superoxide salt
- The alkali metal oxides differ in the oxygen anion part of the formula (O^{2-} vs. O_2^{2-} vs. O_2^-)
 - Each of these anions have unique bonding arrangements and oxidation states

Section 20.3

The Chemistry of Hydrogen

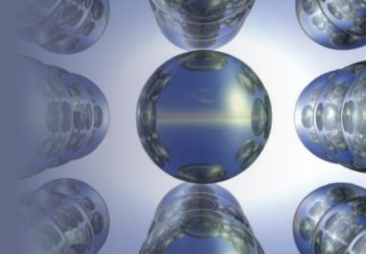


Hydrogen - Physical Properties

- Colorless, odorless gas composed of H₂ molecules
- Low molar mass and nonpolarity
 - Low boiling point (-235° C)
 - Low melting point (-260° C)
- Highly flammable
 - Air that contains 18% to 60% hydrogen by volume is considered to be explosive

Section 20.3

The Chemistry of Hydrogen



Hydrogen - Sources

- Industrial source

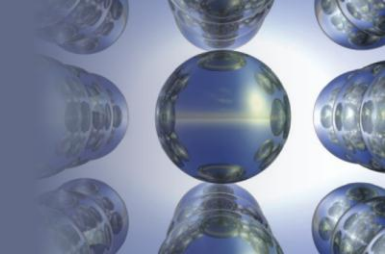
- Reaction of methane with water at high temperatures (800–1000° C) and pressures (10–50 atm) in the presence of a metallic catalyst (nickel)



- Electrolysis of water produces pure hydrogen

Section 20.3

The Chemistry of Hydrogen

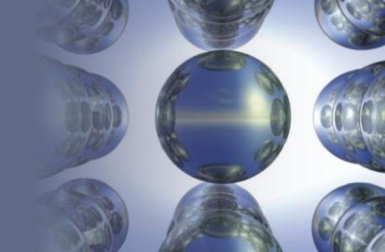


Hydrogen - Sources (Continued)

- **By-product of gasoline production**
 - Hydrocarbons with high molecular masses are cracked to produce smaller molecules that can be used as motor fuel

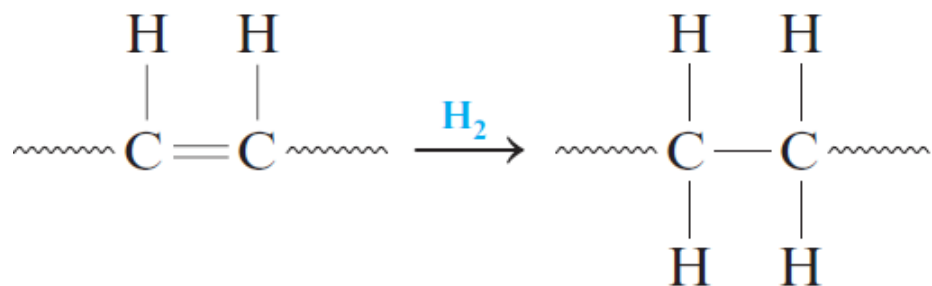
Section 20.3

The Chemistry of Hydrogen



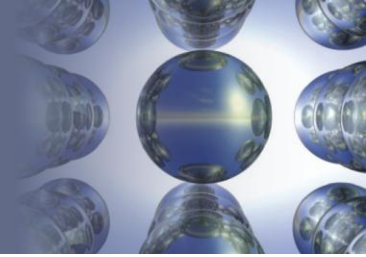
Hydrogen - Uses

- Industrial use
 - Production of ammonia by the Haber process
- Hydrogenation of unsaturated vegetable oils
 - Hydrogen is used in large quantities to produce carbon–carbon single bonds



Section 20.3

The Chemistry of Hydrogen

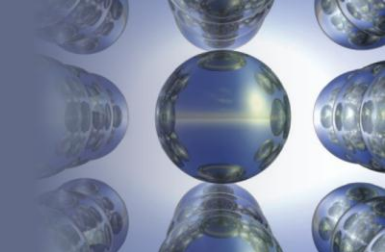


Hydrogen and Hydrides

- Hydrogen forms:
 - Covalent compounds with other nonmetals
 - Salts with active metals
- **Hydrides:** Binary compounds containing hydrogen
 - Classified into ionic hydrides, covalent hydrides, and metallic (interstitial) hydrides

Section 20.3

The Chemistry of Hydrogen

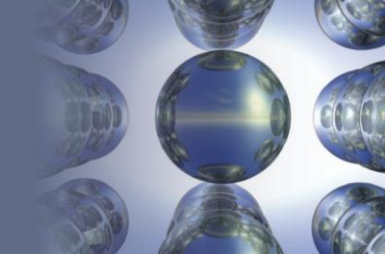


Ionic (Saltlike) Hydrides

- Formed when hydrogen combines with the most active metals (Groups 1A and 2A)
- Examples
 - LiH and CaH₂
- Hydride ion acts as a strong reducing agent
 - Presence of 2 electrons in the 1s orbital produces large electron–electron repulsions
 - Nucleus will have a +1 charge

Section 20.3

The Chemistry of Hydrogen



Covalent Hydrides

- Formed when hydrogen combines with other nonmetals
- Examples - HCl, CH₄, and NH₃
- Most important covalent hydride - Water (H₂O)
 - Polarity of molecules attribute to water's unusual properties

Section 20.3

The Chemistry of Hydrogen



Unusual Properties of Water

- High boiling point in comparison to what is expected from its molar mass
- Large heat of vaporization and heat capacity
- Higher density in liquid form than in solid form
 - Caused by the open structure of ice
 - Results from maximizing hydrogen bonding
- Excellent solvent for ionic and polar substances
 - Effective medium for life processes

Section 20.3

The Chemistry of Hydrogen

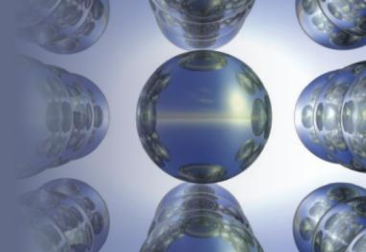
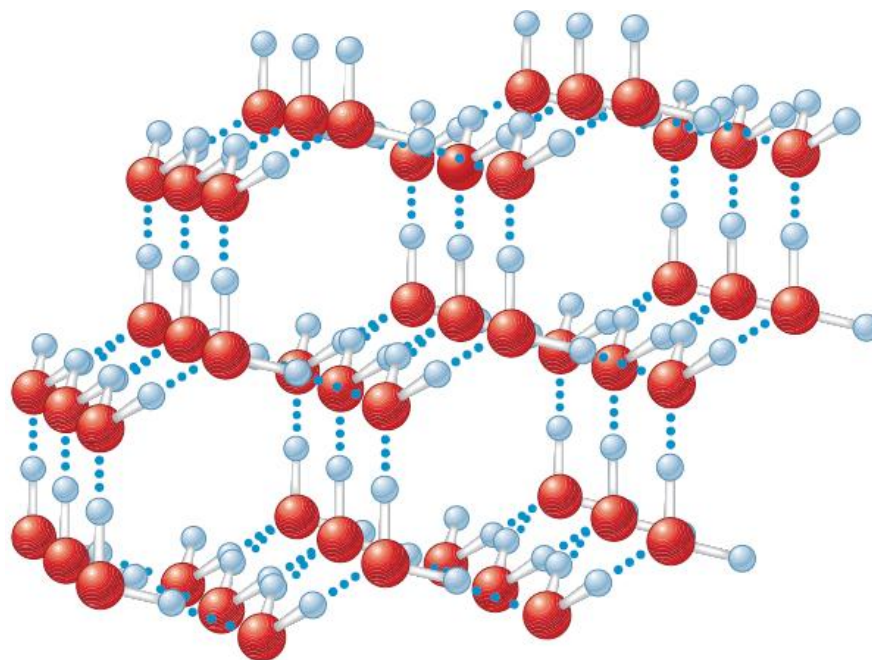


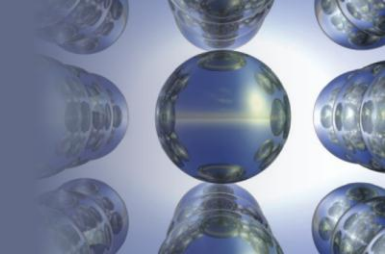
Figure 20.5 - The Structure of Ice



Ice

Section 20.3

The Chemistry of Hydrogen



Metallic (Interstitial) Hydrides

- Formed when transition metal crystals are treated with hydrogen gas
 - Hydrogen molecules dissociate at the metal's surface
 - Small hydrogen atoms migrate into the crystal structure and occupy interstices (holes)
- Appear to be solid solutions

Section 20.3

The Chemistry of Hydrogen

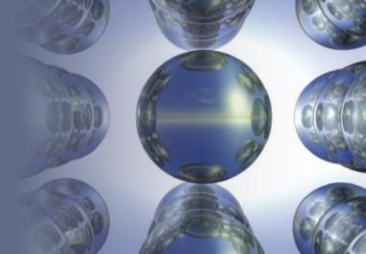


Metallic (Interstitial) Hydrides (Continued)

- Compositions of nonstoichiometric hydrides vary with the length of exposure of the metal to hydrogen gas
- Lose much of the absorbed hydrogen as gas when heated
 - Offer possibilities for storing hydrogen for use as a portable fuel

Section 20.4

The Group 2A Elements



Alkaline Earth Metals

- Valence electron configuration - ns^2
- Very reactive
 - Lose two valence electrons to form ionic compounds containing M^{2+} cations
- Group 2A elements are called alkaline earth metals due to the basicity of their oxides
 - Exception - Beryllium oxide (BeO)

2A

Be

Mg

Ca

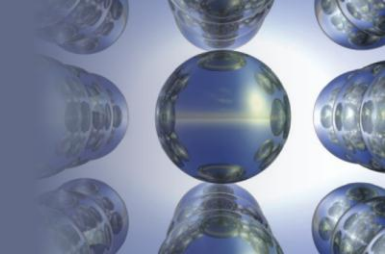
Sr

Ba

Ra

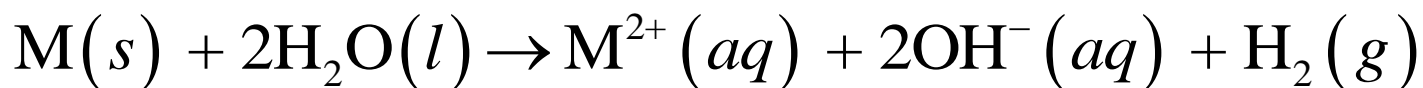
Section 20.4

The Group 2A Elements



Alkaline Earth Metals' Reaction with Water

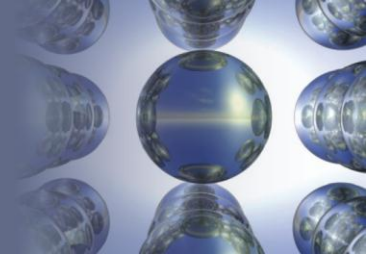
- More active alkali metals react with water
 - Results in the production of H₂ gas



- At 25° C
 - Ca, Sr, and Ba react vigorously
 - Be and Mg show no reaction
 - Mg reacts with boiling water

Section 20.4

The Group 2A Elements



Alkaline Earth Metals - Importance

- Calcium (Ca)
 - Found in the structural minerals that compose bones and teeth
- Magnesium (Mg^{2+} ion)
 - Essential in metabolism and muscle function
 - Useful structural material due to its low density and moderate strength

Section 20.4

The Group 2A Elements

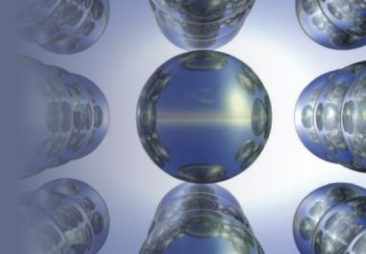


Table 20.6 - Selected Physical Properties, Sources, and Methods of Preparation of the Group 2A Elements

Element	Radius of M^{2+} (pm)	Ionization Energy (kJ/mol)		\mathcal{E}° (V) for $M^{2+} + 2e^- \longrightarrow M$	Source	Method of Preparation
		First	Second			
Beryllium	≈ 30	900	1760	-1.70	Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$)	Electrolysis of molten BeCl_2
Magnesium	65	735	1445	-2.37	Magnesite (MgCO_3), dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$), carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$)	Electrolysis of molten MgCl_2
Calcium	99	590	1146	-2.76	Various minerals containing CaCO_3	Electrolysis of molten CaCl_2
Strontium	113	549	1064	-2.89	Celestite (SrSO_4), strontianite (SrCO_3)	Electrolysis of molten SrCl_2
Barium	135	503	965	-2.90	Baryte (BaSO_4), witherite (BaCO_3)	Electrolysis of molten BaCl_2
Radium	140	509	979	-2.92	Pitchblende (1 g of Ra/7 tons of ore)	Electrolysis of molten RaCl_2

Section 20.4

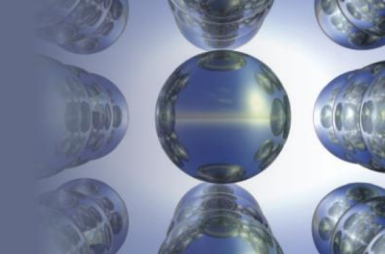
The Group 2A Elements

Table 20.7 - Selected Reactions of the Group 2A Elements

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

Section 20.4

The Group 2A Elements



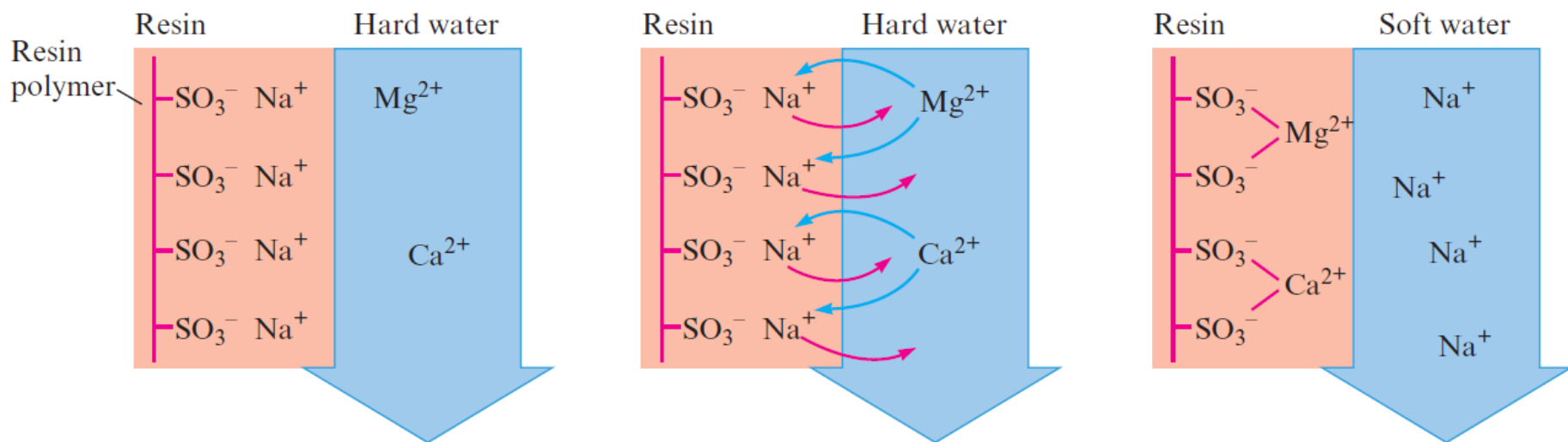
Alkaline Earth Metals and Ion Exchange

- **Hard water:** Natural water that contains Ca^{2+} and Mg^{2+}
 - **Ion exchange:** Process that removes Ca^{2+} and Mg^{2+}
 - Na^+ is released into the solution
 - **Ion-exchange resin:** Large molecules that have many ionic sites

Section 20.4

The Group 2A Elements

Figure 20.6 - Converting Hard Water to Soft Water



a

Typical cation-exchange resin

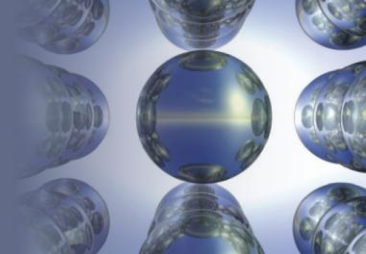
b

When hard water is passed over the cation-exchange resin, the Ca^{2+} and Mg^{2+} bind to the resin

c

Section 20.5

The Group 3A Elements



Group 3A Elements

- Valence electron configuration
 - ns^2np^1
- Exhibit increase in metallic character in going down the group that is characteristic of the representative elements

3A

B

Al

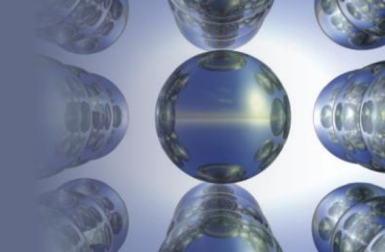
Ga

In

Tl

Section 20.5

The Group 3A Elements



Boron

- Typical nonmetal
- Forms covalent compounds
- **Boranes:** Covalent hydride compounds of boron
 - Extremely electron-deficient
 - Highly reactive
 - React exothermically with oxygen
 - Once considered to be potential fuels for rockets in the U.S. space program

Section 20.5

The Group 3A Elements

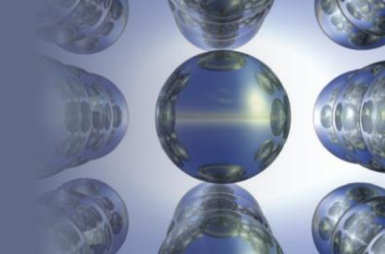
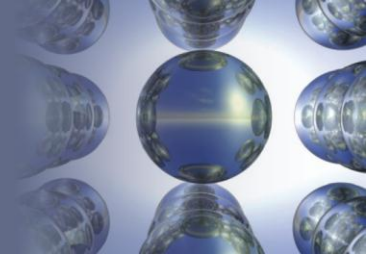


Table 20.8 - Selected Physical Properties, Sources, and Methods of Preparation of the Group 3A Elements

Element	Radius of M^{3+} (pm)	Ionization Energy (kJ/mol)	\mathcal{E}° (V) for $M^{3+} + 3e^- \longrightarrow M$	Source	Method of Preparation
Boron	20	798	—	Kernite, a form of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$)	Reduction by Mg or H_2
Aluminum	50	581	-1.66	Bauxite (Al_2O_3)	Electrolysis of Al_2O_3 in molten Na_3AlF_6
Gallium	62	577	-0.53	Traces in various minerals	Reduction with H_2 or electrolysis
Indium	81	556	-0.34	Traces in various minerals	Reduction with H_2 or electrolysis
Thallium	95	589	0.72	Traces in various minerals	Electrolysis

Section 20.5

The Group 3A Elements

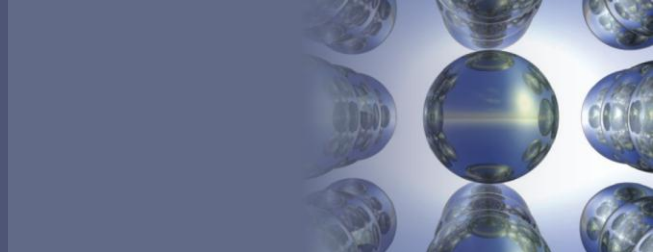


Aluminum

- Most abundant metal on earth
- Contains metallic properties
 - Conducts heat and electricity
 - Lustrous appearance
- Forms covalent bonds with nonmetals
 - Responsible for the amphoteric nature of Al_2O_3 and the acidic nature of $\text{Al}(\text{H}_2\text{O})_6^{3+}$

Section 20.5

The Group 3A Elements



Gallium

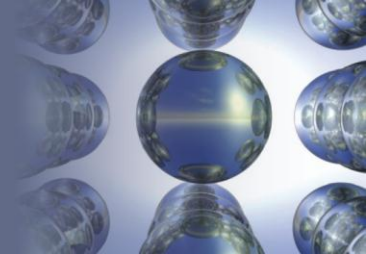
- **Properties**
 - Unusually low melting point (29.8° C)
 - Boiling point - About 2400° C
 - Used in thermometers
 - Expands when it freezes
- **Chemistry is similar to that of aluminum**
 - Ga_2O_3 is amphoteric



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Section 20.5

The Group 3A Elements



Indium and Thallium

- Indium
 - Has a chemistry similar to that of aluminum and gallium
 - Compounds containing 1+ and 3+ ions are known
- Thallium
 - Chemistry is completely metallic

Section 20.5

The Group 3A Elements

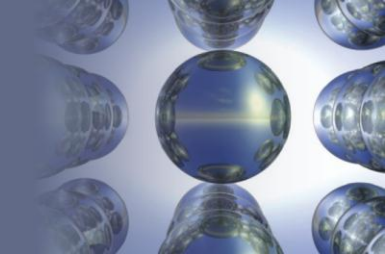
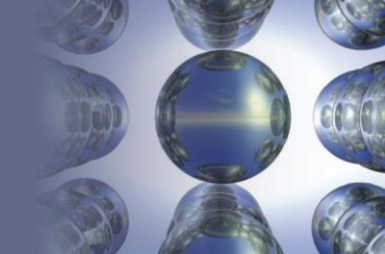


Table 20.9 - Selected Reactions of the Group 3A Elements

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

Section 20.5

The Group 3A Elements



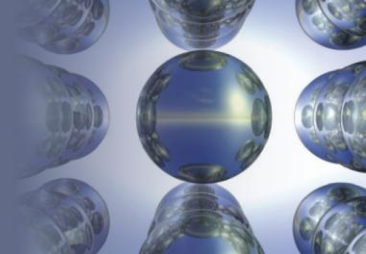
Exercise

- Write equations describing the reactions of Ga with each of the following: F₂, O₂, S, and HCl



Section 20.6

The Group 4A Elements



Group 4A Elements - An Introduction

- Valence electron configuration - ns^2np^2
- Include
 - Carbon - Fundamental constituent of molecules that are necessary for life
 - Silicon - Forms the basis for the geological world

4A

C

Si

Ge

Sn

Pb

Section 20.6

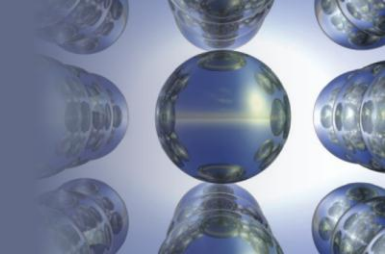
The Group 4A Elements

Table 20.10 - Some Physical Properties, Sources, and Methods of Preparation of the Group 4A Elements

Element	Electronegativity	Melting Point (°C)	Boiling Point (°C)	Source	Method of Preparation
Carbon	2.6	3727 (sublimes)	—	Graphite, diamond, petroleum, coal	—
Silicon	1.9	1410	2355	Silicate minerals, silica	Reduction of K_2SiF_6 with Al, or reduction of SiO_2 with Mg
Germanium	2.0	937	2830	Germanate (mixture of copper, iron, and germanium sulfides)	Reduction of GeO_2 with H_2 or C
Tin	2.0	232	2270	Cassiterite (SnO_2)	Reduction of SnO_2 with C
Lead	2.3	327	1740	Galena (PbS)	Roasting of PbS with O_2 to form PbO_2 and then reduction with C

Section 20.6

The Group 4A Elements

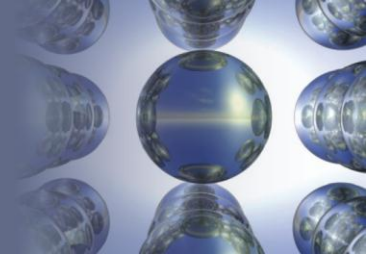


Group 4A Elements - Properties

- Form four covalent bonds to nonmetals
 - Examples - CH_4 , SiF_4 , GeBr_4 , SnCl_4 , and PbCl_4
 - In each tetrahedral molecule, the central atom is described as sp^3 hybridized
- Carbon forms π bonds
 - Accounts for different structures and properties of CO_2 and SiO_2
 - Chemistry of carbon is dominated by carbon–carbon bonds
 - Chemistry of silicon is dominated by silicon–oxygen bonds

Section 20.6

The Group 4A Elements

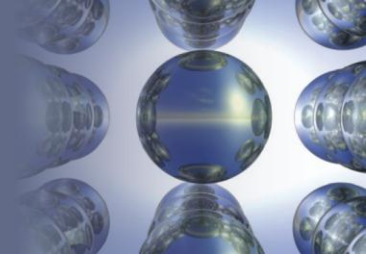


Group 4A Elements

- Carbon
 - Occurs in the allotropic forms of graphite, diamond, and fullerenes
- Silicon - Semimetal that is found widely distributed in silica and silicates
- Germanium - Rare element and a semimetal
 - Used in the manufacturing of semiconductors for transistors and similar electronic devices

Section 20.6

The Group 4A Elements

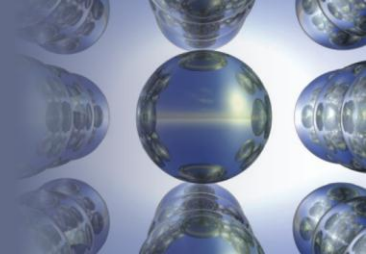


Group 4A Elements (Continued 1)

- Tin - Soft, silvery metal that can be rolled into thin sheets
 - Used in alloys and as protective coating for steel
 - Tin disease - Tin turns powdery gray and crumbles when exposed to low temperatures
 - Allotropes of tin
 - White tin - Stable at normal temperatures
 - Gray tin - Stable at temperatures below 13.2°C
 - Brittle tin - Found in temperatures above 161°C

Section 20.6

The Group 4A Elements



Group 4A Elements (Continued 2)

- Lead
 - Ore - Galena (PbS)
 - Melts at low temperatures
 - Has been in use since 3000 B.C.
 - Toxic in nature

Section 20.6

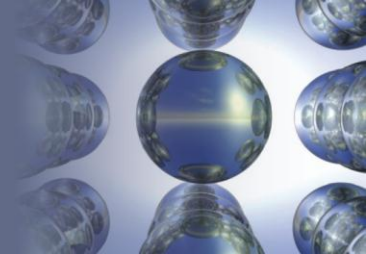
The Group 4A Elements

Table 20.12 - Selected Reactions of the Group 4A Elements

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

Section 20.7

The Group 5A Elements



Group 5A Elements - An Introduction

- Valence electron configuration - ns^2np^3
- Exhibit varied chemical properties
 - Nitrogen and phosphorus gain three electrons to form 3⁻ anions in salts with active metals
 - Bismuth and antimony exhibit metallic properties
 - Readily lose electrons to form cations

5A

N

P

As

Sb

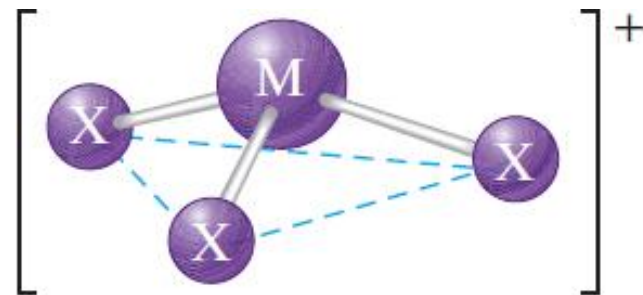
Bi

Section 20.7

The Group 5A Elements

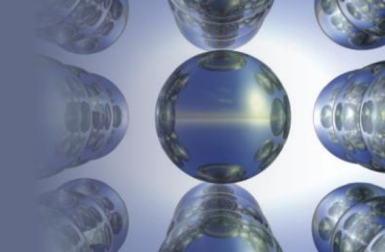
Group 5A Elements and Covalent Bonds

- Capable of forming molecules or ions that involve 3, 5, or 6 covalent bonds
 - Examples - NH_3 , PH_3 , NF_3 , AsCl_3
 - Have a lone pair of electrons
 - VSEPR model structure - Pyramidal



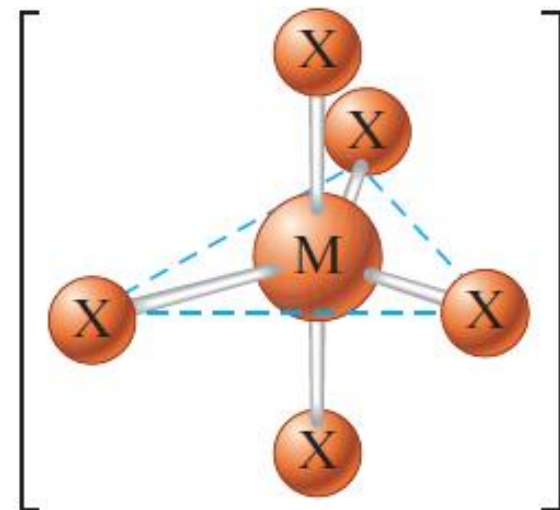
Section 20.7

The Group 5A Elements



Group 5A Elements and Covalent Bonds (Continued)

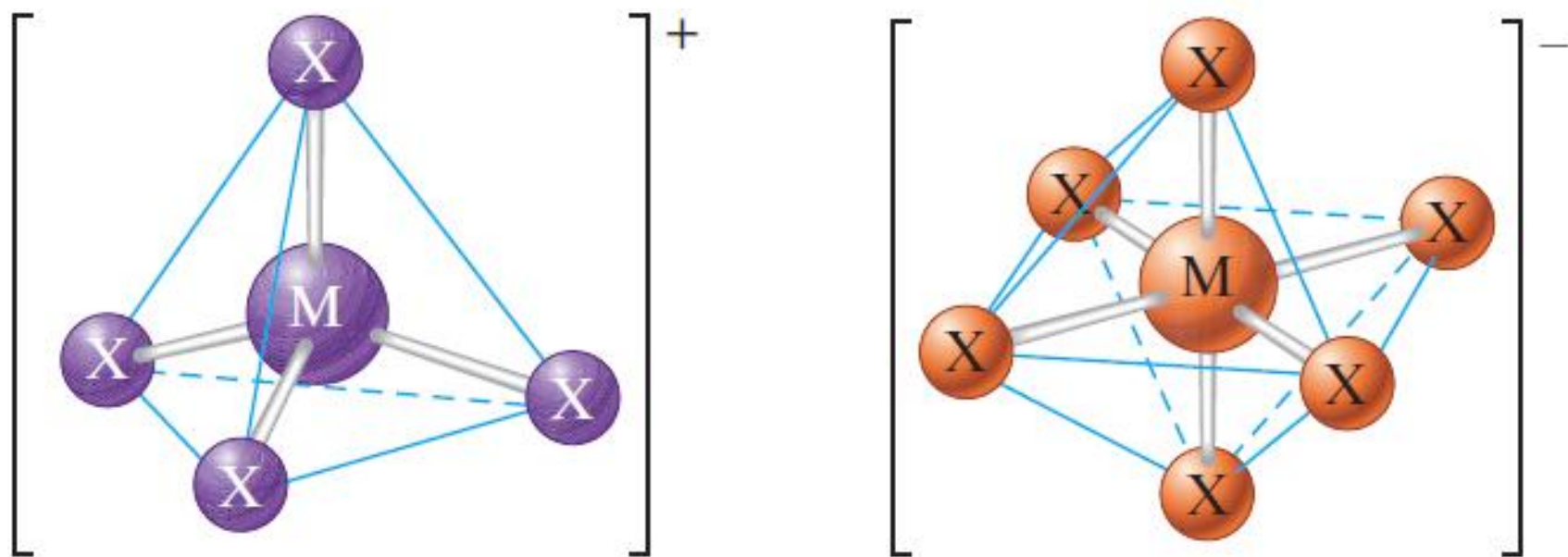
- Capable of forming molecules with five covalent bonds
 - Exception - Nitrogen
 - VSEPR model - Trigonal bipyramidal
 - Central atom is dsp^3 hybridized



Section 20.7

The Group 5A Elements

Figure 20.10 - The Structures of the Tetrahedral MX_4^+ and the Octahedral MX_6^- Ions



Section 20.7

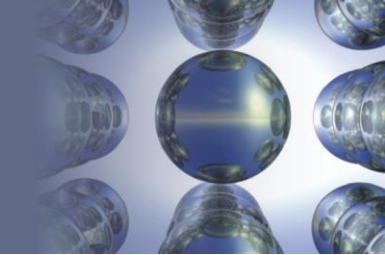
The Group 5A Elements

Table 20.13 - Selected Physical Properties, Sources, and Methods of Preparation of the Group 5A Elements

Element	Electronegativity	Source	Method of Preparation
Nitrogen	3.0	Air	Liquefaction of air
Phosphorus	2.2	Phosphate rock [Ca ₃ (PO ₄) ₂], fluorapatite [Ca ₅ (PO ₄) ₃ F]	$2\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 \longrightarrow 6\text{CaSiO}_3 + \text{P}_4\text{O}_{10}$ $\text{P}_4\text{O}_{10} + 10\text{C} \longrightarrow 4\text{P} + 10\text{CO}$
Arsenic	2.2	Arsenopyrite (Fe ₃ As ₂ , FeS)	Heating arsenopyrite in the absence of air
Antimony	2.1	Stibnite (Sb ₂ S ₃)	Roasting Sb ₂ S ₃ in air to form Sb ₂ O ₃ and then reduction with carbon
Bismuth	2.0	Bismite (Bi ₂ O ₃), bismuth glance (Bi ₂ S ₃)	Roasting Bi ₂ S ₃ in air to form Bi ₂ O ₃ and then reduction with carbon

Section 20.8

The Chemistry of Nitrogen

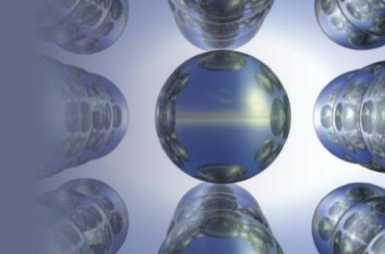


Nitrogen

- All elemental nitrogen exists as N_2 molecules with strong triple bonds (941 kJ/mol)
 - N_2 molecule is unreactive
 - N_2 can coexist with almost all other elements without undergoing reaction under normal conditions
 - Useful medium for experiments conducted using an inert atmosphere box

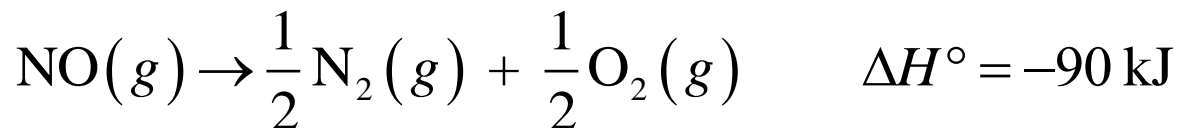
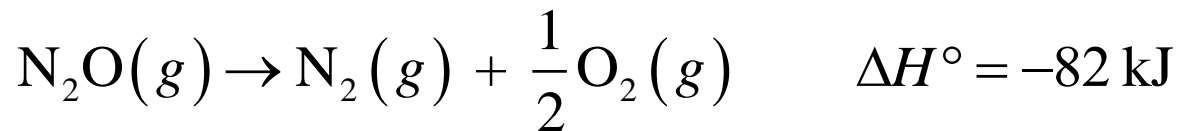
Section 20.8

The Chemistry of Nitrogen



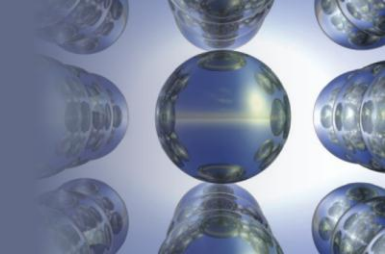
Nitrogen - A Thermodynamic Perspective

- Stability of the $\text{N}\equiv\text{N}$ implies that most binary compounds containing nitrogen decompose exothermically to the elements

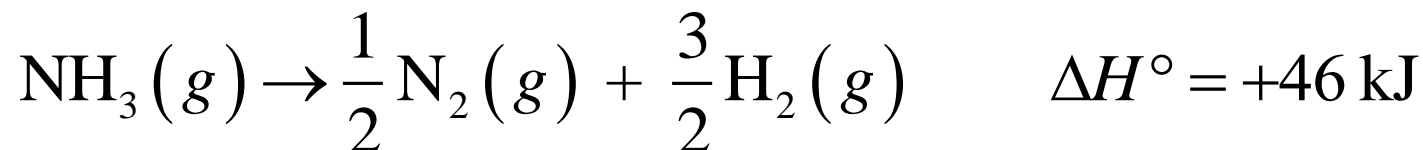


Section 20.8

The Chemistry of Nitrogen



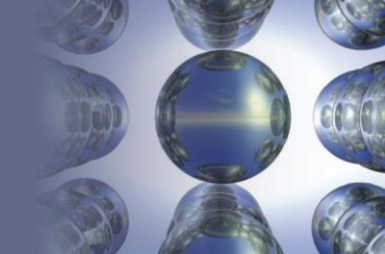
Nitrogen - A Thermodynamic Perspective (Continued)



- In ammonia, energy is required to decompose the molecule into its constituent elements
 - Makes ammonia more stable than its component elements

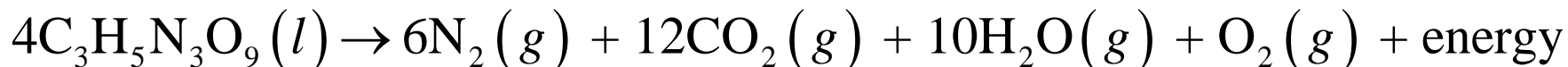
Section 20.8

The Chemistry of Nitrogen



Nitrogen-Based Explosives

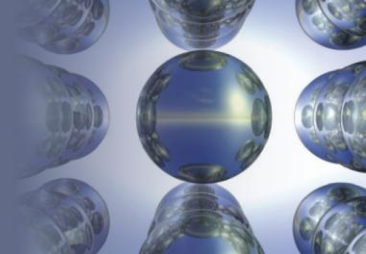
- Stability of N_2 contributes to the power of such explosives
- Example - Nitroglycerin ($\text{C}_3\text{H}_5\text{N}_3\text{O}_9$)
 - When subjected to sudden impact or when ignited, it decomposes rapidly and exothermically, causing an explosion



- 4 moles of liquid nitroglycerin produce 29 moles of gaseous products

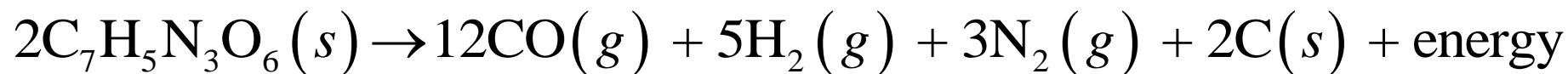
Section 20.8

The Chemistry of Nitrogen



Nitrogen-Based Explosives (Continued)

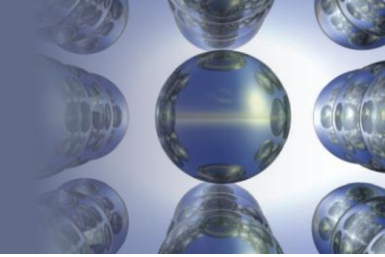
- Trinitrotoluene (TNT)
 - Solid at normal temperature
 - Decomposes as follows:



- 2 moles of solid TNT produce 20 moles of gaseous products and energy

Section 20.8

The Chemistry of Nitrogen



Nitrogen Fixation

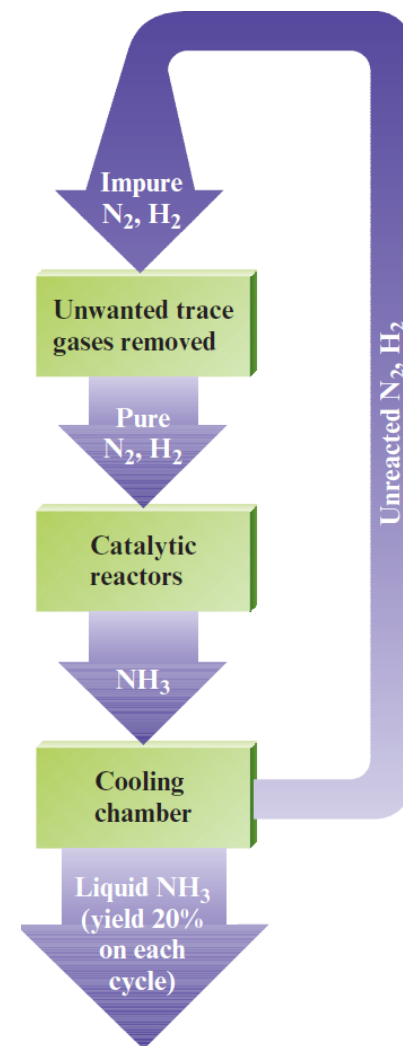
- Process of transforming N_2 to other nitrogen-containing compounds
- Example - The Haber process
 - **Haber process:** Used for manufacturing ammonia
 - High pressure forces the equilibrium to the right
 - High temperatures produce a reasonable rate of reaction

Section 20.8

The Chemistry of Nitrogen

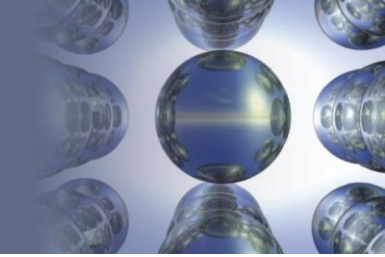
The Haber Process

- Carried out at a temperature of approximately 400°C and a pressure of about 250 atm
- Uses a catalyst
 - Solid iron oxide mixed with small quantities of aluminum oxide and potassium oxide



Section 20.8

The Chemistry of Nitrogen

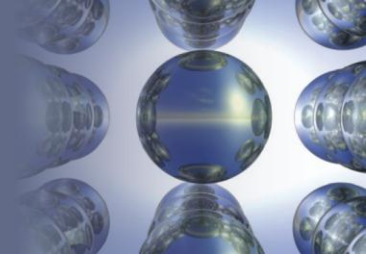


Nitrogen Fixation and Combustion

- Nitrogen fixation can result from high-temperature combustion that occurs in automobile engines
 - Nitrogen in the air is drawn into the engine
 - Reacts at a significant rate along with oxygen to form nitric oxide
 - Nitric oxide further reacts with oxygen to form nitrogen dioxide, which contributes to photochemical smog

Section 20.8

The Chemistry of Nitrogen



Nitrogen Fixation in Nature

- Lightning provides energy to disrupt N_2 and O_2 molecules in the air
 - Results in highly reactive nitrogen and oxygen atoms
 - Atoms further react with other N_2 and O_2 to form nitrogen oxides that eventually become nitrates

Section 20.8

The Chemistry of Nitrogen



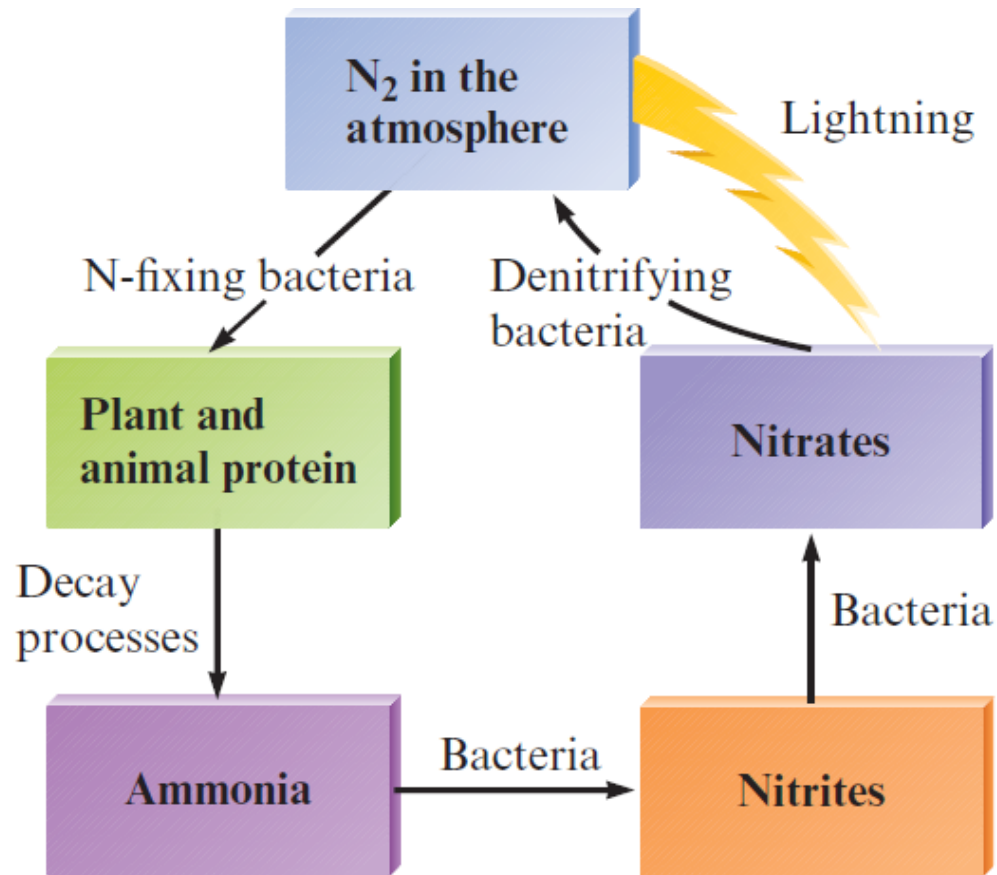
Nitrogen Fixation in Nature (Continued)

- **Nitrogen-fixing bacteria:** Readily convert nitrogen to ammonia and other nitrogen-containing compounds that are useful for plants
 - Reside in the root nodules of plants
 - Capable of producing NH_3 at soil temperatures and 1 atm pressure

Section 20.8

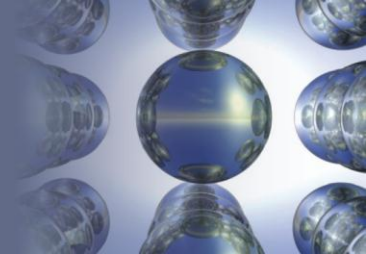
The Chemistry of Nitrogen

Figure 20.13 - The Nitrogen Cycle



Section 20.8

The Chemistry of Nitrogen

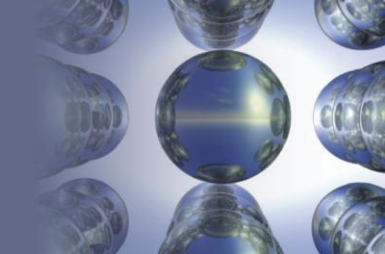


Nitrogen Hydrides - Ammonia (NH_3)

- Physical properties
 - Toxic and colorless gas
 - Pungent odor
- Used in fertilizers
- Pyramidal ammonia molecule has a lone pair of electrons on its nitrogen atom and polar N—H bonds

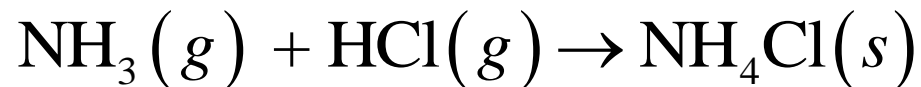
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The Chemistry of Nitrogen



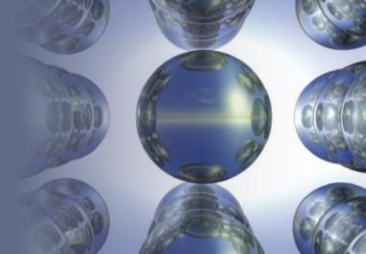
Nitrogen Hydrides - Ammonia (NH₃) (Continued)

- The structure leads to a high degree of intermolecular interaction by hydrogen bonding in its liquid state
 - Results in a high boiling point (−33.4° C)
- Behaves as a base
 - Reacts with acids to produce ammonium salts



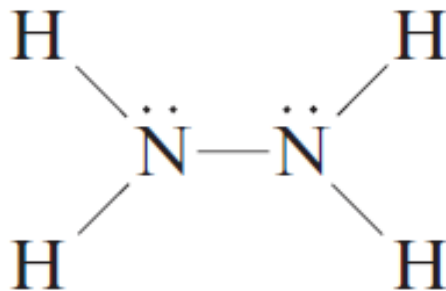
Section 20.8

The Chemistry of Nitrogen



Nitrogen Hydrides - Hydrazine (N_2H_4)

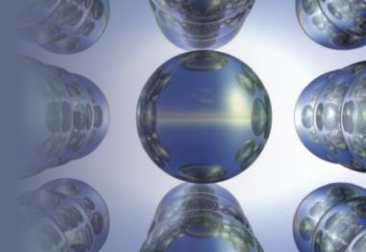
- Lewis structure



- Each nitrogen atom should be sp^3 hybridized with bond angles close to 109.5°
- Colorless liquid with ammoniacal odor

Section 20.8

The Chemistry of Nitrogen

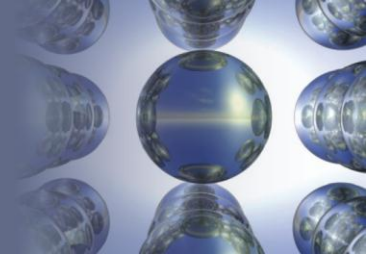


Nitrogen Hydrides - Hydrazine (N_2H_4) (Continued 1)

- Boiling point - 113.5°C
 - Suggests that considerable hydrogen bonding occurs among the polar hydrazine molecules
- Freezing point - 2°C
- Powerful reducing agent
- Uses
 - Rocket propellant
 - Blowing agent in the manufacture of plastics
 - Production of agricultural pesticides

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The Chemistry of Nitrogen

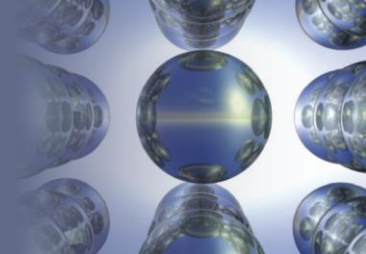


Nitrogen Hydrides - Hydrazine (N_2H_4) (Continued 2)

- Reacts vigorously with halogens
 - Used as the oxidizer in rocket engines
- Substituted hydrazines
 - When one or more hydrogen atoms in the compound are replaced by other groups
 - Used as rocket fuel
 - Example - Monomethylhydrazine

Section 20.8

The Chemistry of Nitrogen



Nitrogen Oxides

- Nitrogen forms a series of oxides
 - Oxidation states range from +1 to +5

Section 20.8

The Chemistry of Nitrogen

Table 20.14 - Some Common Nitrogen Compounds

Oxidation State of Nitrogen	Compound	Formula	Lewis Structure*
-3	Ammonia	NH ₃	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$
-2	Hydrazine	N ₂ H ₄	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\ddot{\text{N}}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$
-1	Hydroxylamine	NH ₂ OH	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\ddot{\text{O}}-\text{H} \\ \\ \text{H} \end{array}$
0	Nitrogen	N ₂	$:\text{N}\equiv\text{N}:$
+1	Dinitrogen monoxide (nitrous oxide)	N ₂ O	$:\ddot{\text{N}}=\text{N}=\ddot{\text{O}}:$

*In some cases additional resonance structures are needed to fully describe the electron distribution.

Section 20.8

The Chemistry of Nitrogen

Table 20.14 - Some Common Nitrogen Compounds

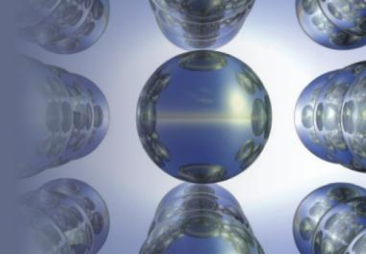
(Continued)

Oxidation State of Nitrogen	Compound	Formula	Lewis Structure*
+2	Nitrogen monoxide (nitric oxide)	NO	$:\ddot{\text{N}}=\ddot{\text{O}}:$
+3	Dinitrogen trioxide	N ₂ O ₃	$\begin{array}{c} :\ddot{\text{O}}: \\ \diagdown \\ \text{N} - \ddot{\text{N}} = \ddot{\text{O}}: \\ \diagup \\ :\ddot{\text{O}}: \end{array}$
+4	Nitrogen dioxide	NO ₂	$:\ddot{\text{O}} - \ddot{\text{N}} = \ddot{\text{O}}:$
+5	Nitric acid	HNO ₃	$\begin{array}{c} :\ddot{\text{O}} - \text{N} - \ddot{\text{O}} - \text{H} \\ \parallel \\ :\ddot{\text{O}}: \end{array}$

*In some cases additional resonance structures are needed to fully describe the electron distribution.

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The Chemistry of Nitrogen

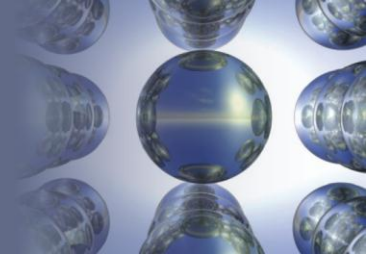


Dinitrogen Monoxide - N₂O

- Commonly known as laughing gas
- Used as a mild anesthetic by dentists
- Highly soluble in fats
 - Used as a propellant in aerosol cans
- Concentration is gradually increasing in the atmosphere
 - Produced by microorganisms in soil
 - Controls the earth's atmosphere by absorbing infrared radiation

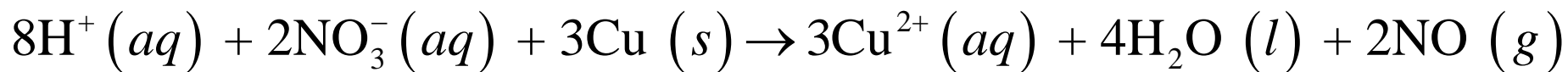
Section 20.8

The Chemistry of Nitrogen



Nitrogen Monoxide - NO

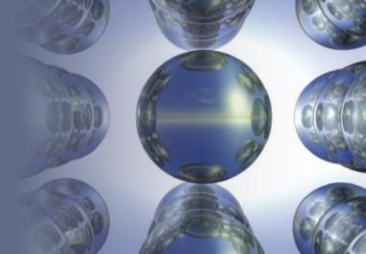
- Known as nitric oxide
- Regulator in biological systems
- Colorless gas under normal conditions
- Produced in a lab by reacting 6 *M* nitric acid with copper



- Nitric oxide is immediately oxidized by O_2 in the air to a reddish brown NO_2

Section 20.8

The Chemistry of Nitrogen



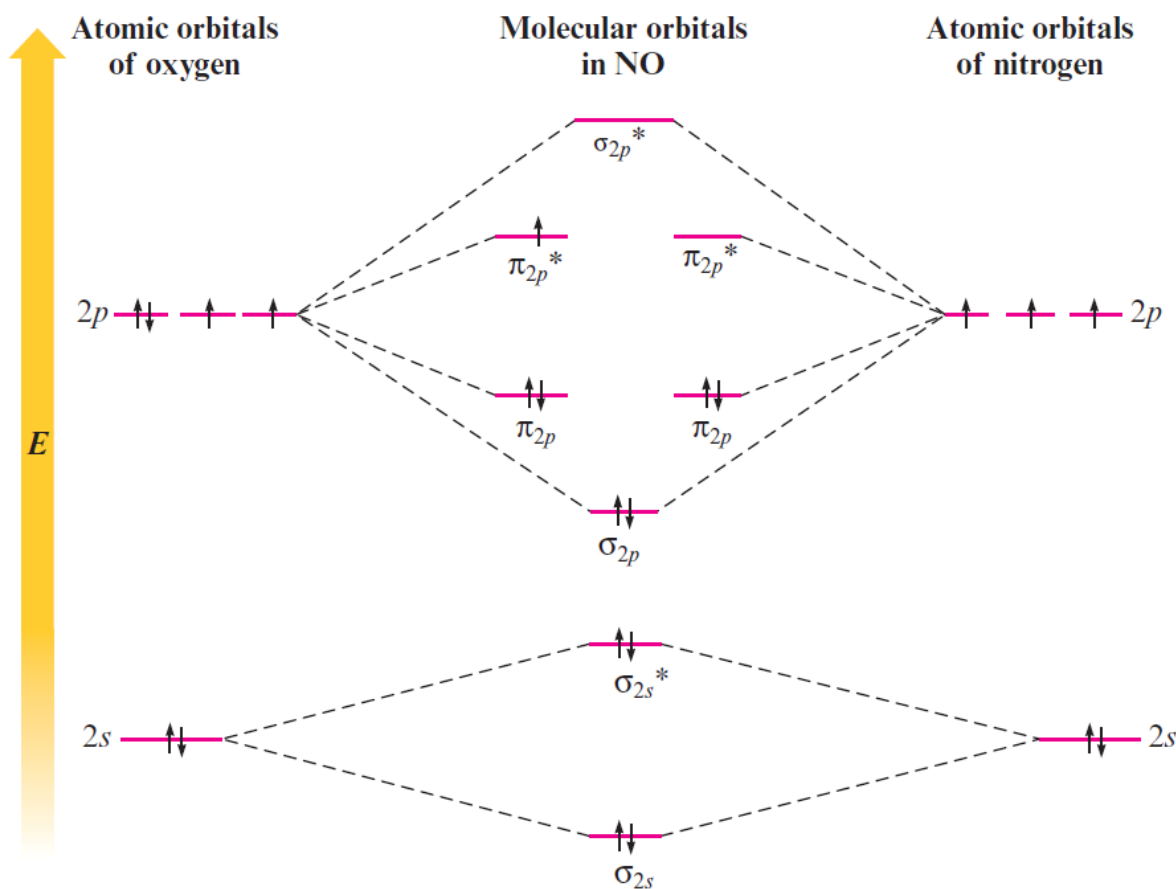
Structure of NO - Molecular Orbital Model

- NO contains an odd number of electrons
 - Has a bond order of 2.5
 - Since NO has one high-energy electron, it can be easily oxidized to form the nitrosyl ion (NO^+)
 - An antibonding electron is removed when NO is converted to NO^+
 - Resulting ion should have a stronger bond than NO

Section 20.8

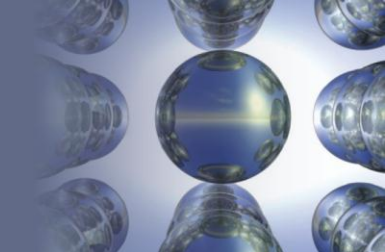
The Chemistry of Nitrogen

Figure 20.15 - Molecular Orbital Energy-Level Diagram for Nitric Oxide (NO)



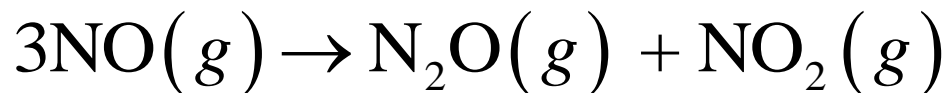
Section 20.8

The Chemistry of Nitrogen



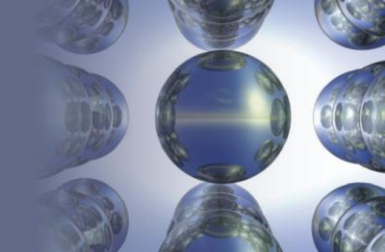
Nitric Oxide - Thermodynamic Perspective

- Considered to be thermodynamically unstable
 - Decomposes to form nitrous oxide and nitrogen dioxide



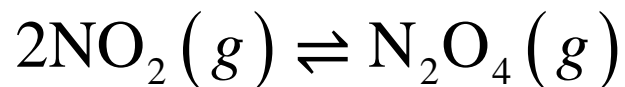
Section 20.8

The Chemistry of Nitrogen



Nitrogen Dioxide (NO₂)

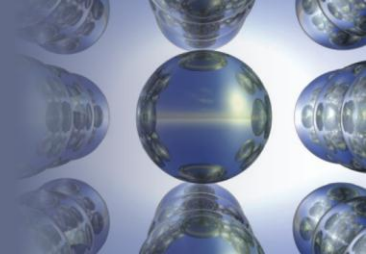
- Paramagnetic, odd-electron molecule with a V-shaped structure
 - Appearance - Reddish brown
- Readily dimerizes to form dinitrogen tetroxide



- Resulting product is diamagnetic and colorless
- K is approximately 1 for this process at 55° C
 - K decreases as the temperature increases

Section 20.8

The Chemistry of Nitrogen



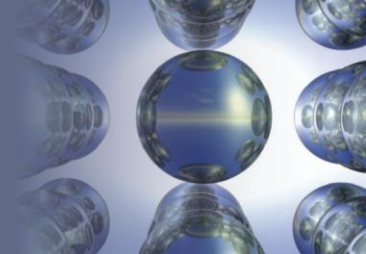
Least Common Nitrogen Oxides

- Dinitrogen trioxide (N_2O_3)
 - Blue liquid that readily dissociates to gaseous nitric oxide and nitrogen dioxide
- Dinitrogen pentoxide (N_2O_5)
 - Solid mixture of NO_2^+ and NO_3^- ions in normal conditions
 - Dissociates to nitrogen dioxide and oxygen via a reaction that follows first-order kinetics



Section 20.8

The Chemistry of Nitrogen



Oxyacids of Nitrogen - Nitric Acid (HNO_3)

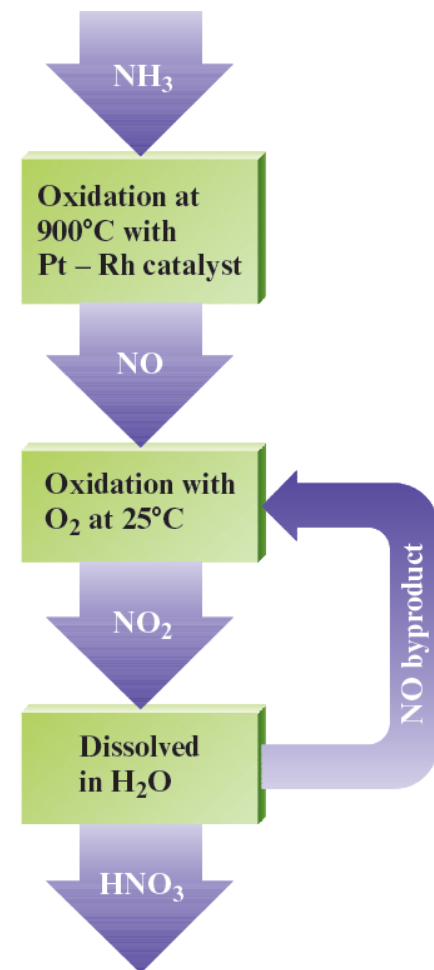
- Used to manufacture nitrogen-based explosives and ammonium nitrate
- Commercially produced by the **Ostwald process**
- Colorless, fuming liquid with a pungent odor
 - Boiling point = 83°C

Section 20.8

The Chemistry of Nitrogen

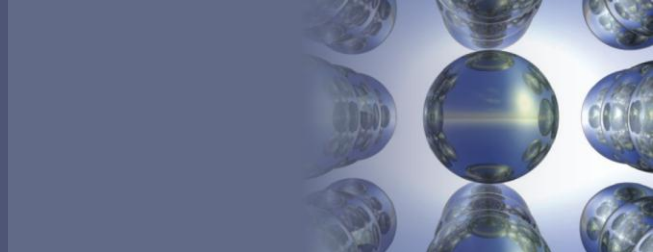
Oxyacids of Nitrogen - Nitric Acid (HNO_3) (Continued 1)

- The Ostwald process
 - Step 1 - Ammonia is oxidized to nitric oxide
 - Step 2 - Nitric oxide reacts with oxygen to produce nitrogen dioxide
 - Step 3 - Nitrogen dioxide is absorbed by water
 - Gaseous nitric oxide is recycled so that it can be oxidized to nitrogen dioxide



Section 20.8

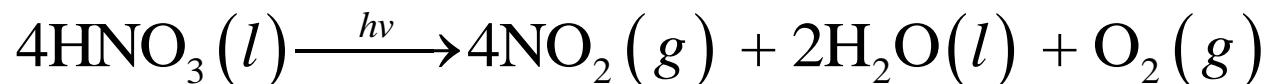
The Chemistry of Nitrogen



Oxyacids of Nitrogen - Nitric Acid (HNO₃) (Continued 2)

- Aqueous nitric acid from Ostwald process is about 50% HNO₃ by mass
 - Can be increased to 68% by distillation and to 95% by treatment with concentrated sulfuric acid

- Decomposes in sunlight

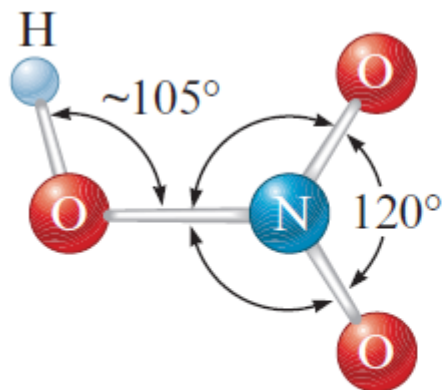


- Concentrated nitric acid (15.9 M HNO₃)
 - Common laboratory reagent and a strong oxidizing agent

Section 20.8

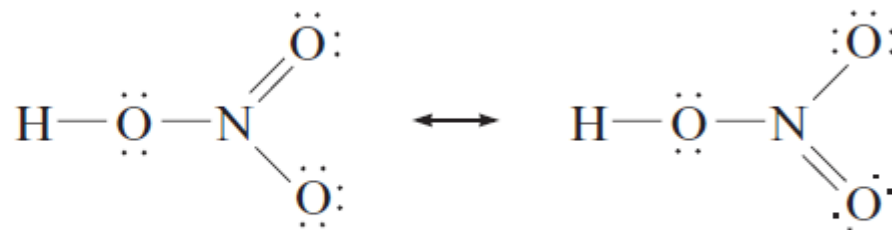
The Chemistry of Nitrogen

Figure 20.17 - Structures of Nitric Acid



a

The molecular structure of HNO_3

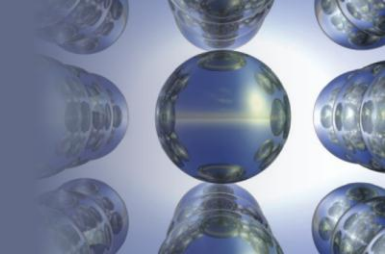


b

The resonance structures of HNO_3

Section 20.9

The Chemistry of Phosphorus

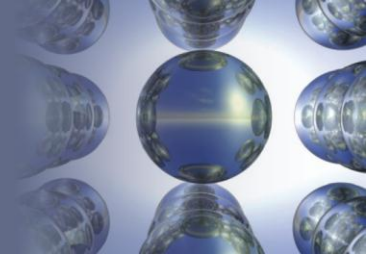


Phosphorus and Nitrogen

- Differ significantly in chemical properties due to:
 - Ability of nitrogen to form stronger π bonds
 - Greater electronegativity of nitrogen
 - Larger size of phosphorus atoms
 - Possible availability of empty valence d orbitals on phosphorus

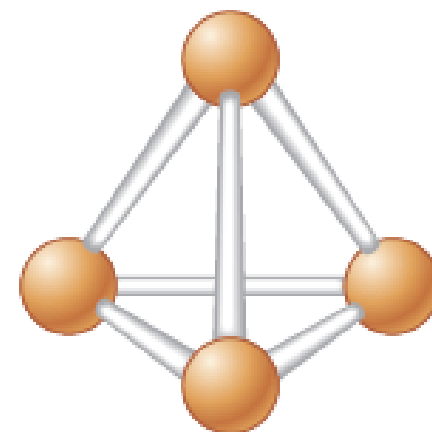
Section 20.9

The Chemistry of Phosphorus



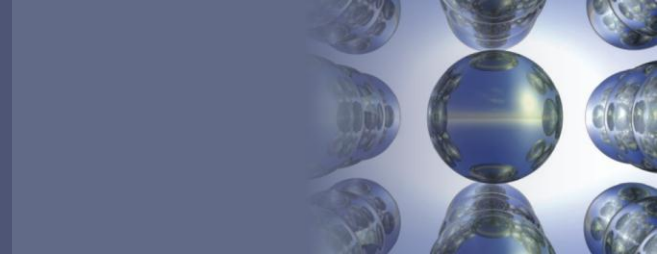
Allotropes of Phosphorus

- **White phosphorus**
 - Contains tetrahedral P_4 molecules
 - Highly reactive and toxic
 - Pyrophoric - Bursts into flames on contact with air
 - Commonly stored under water



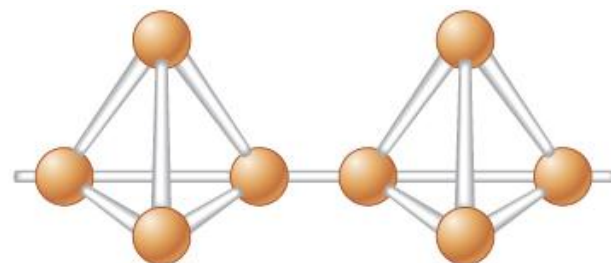
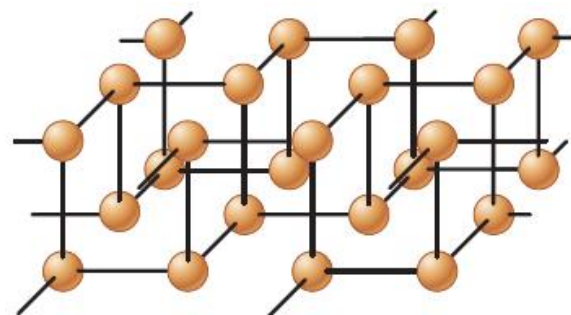
Section 20.9

The Chemistry of Phosphorus



Allotropes of Phosphorus (Continued)

- **Black phosphorus - Has a crystalline structure**
 - Less reactive
 - Obtained by heating white or red phosphorus at high pressures
- **Red phosphorus - Amorphous**
 - Contains chains of P_4 units
 - Obtained by heating white phosphorus at 1 atm in the absence of air



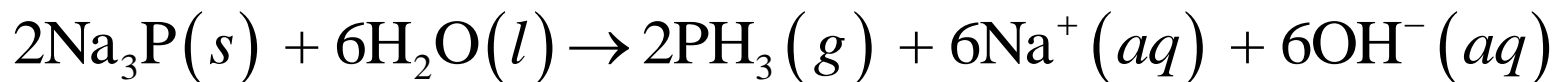
Section 20.9

The Chemistry of Phosphorus



Phosphides

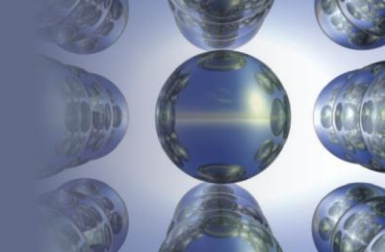
- Ionic substances that contain P^{3-} anions
- Examples - Na_3P and Ca_3P
- Phosphide salts react vigorously with water to produce phosphine (PH_3)



- Colorless, toxic gas that is analogous to ammonia
- Contains a pyramidal structure and has bond angles of 94°

Section 20.9

The Chemistry of Phosphorus



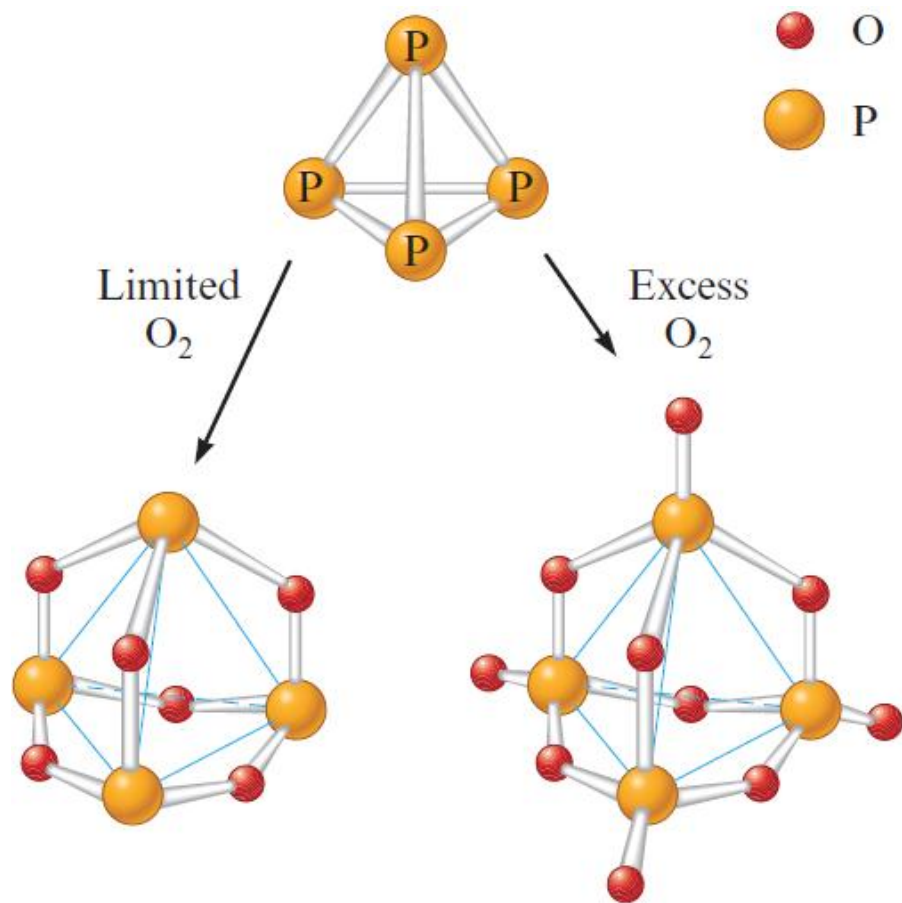
Phosphorus Oxides

- Phosphorus reacts with O_2 to form oxides in which its oxidation states are +5 and +3
- P_4O_6 - Formed by burning elemental phosphorus in a limited supply of O_2
- P_4O_{10} - Formed when O_2 is in excess

Section 20.9

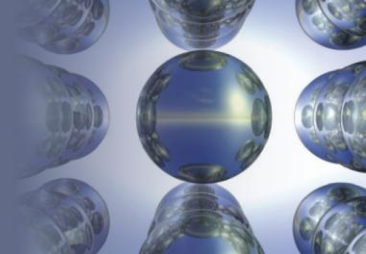
The Chemistry of Phosphorus

Figure 20.19 - The Structures of P_4O_6 and P_4O_{10}



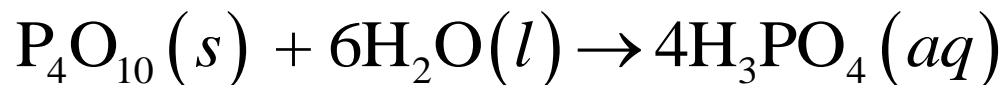
Section 20.9

The Chemistry of Phosphorus



Phosphorus Oxyacids - Phosphoric Acid

- Known as **orthophosphoric acid**
 - Product of the reaction between tetraphosphorus decoxide (P_4O_{10}) and water



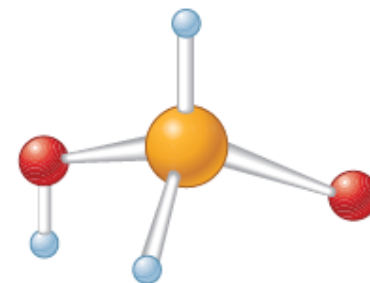
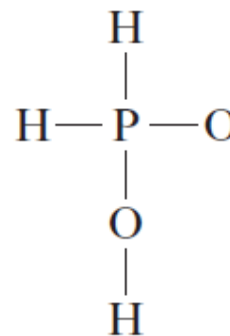
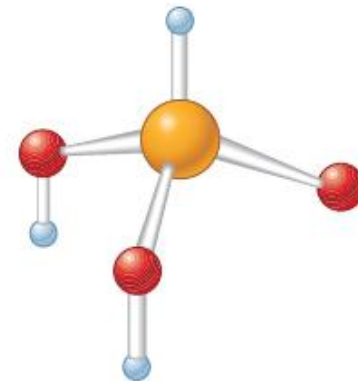
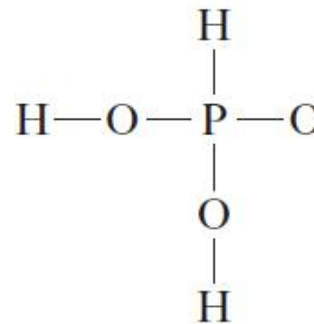
- Pure H_3PO_4 is a white solid
 - Melting point = $42^\circ C$
- Aqueous H_3PO_4 is a weak acid ($K_{a_1} \approx 10^{-2}$)
 - Poor oxidizing agent

Section 20.9

The Chemistry of Phosphorus

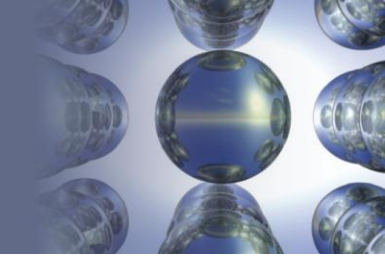
Phosphorus Oxyacids - Phosphorus Acid and Hypophosphorus Acid

- **Phosphorus acid** (H_3PO_3)
 - Resulting product of a reaction involving P_4O_6 and water
 - Diprotic acid
- Hypophosphorus acid (H_3PO_2)
 - Monoprotic acid



Section 20.9

The Chemistry of Phosphorus

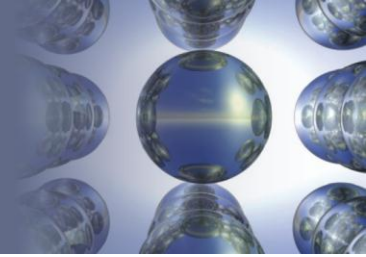


Phosphorus in Fertilizers

- Phosphorus is essential for the growth of plants
 - Soil contains large amounts of phosphorus in the form of insoluble minerals
 - Makes it inaccessible to plants
- **Superphosphate of lime:** Product manufactured by treating phosphate rock with sulfuric acid
 - Contains a mixture of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

Section 20.9

The Chemistry of Phosphorus

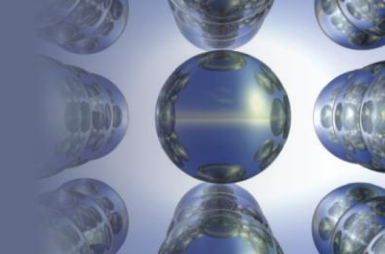


Phosphorus in Fertilizers (Continued)

- Triple phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$
 - Formed when phosphate rock is treated with phosphoric acid
- Ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$)
 - Formed when ammonia reacts with phosphoric acid

Section 20.10

The Group 6A Elements



Group 6A - Trends

- None of the Group 6A elements behave as typical metals
- Common chemical behavior
 - React with a metal to attain noble gas configuration by adding 2 electrons to become a 2- anion in ionic compounds

6A

O

S

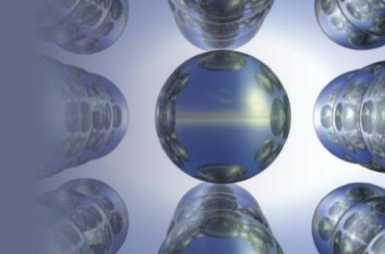
Se

Te

Po

Section 20.10

The Group 6A Elements

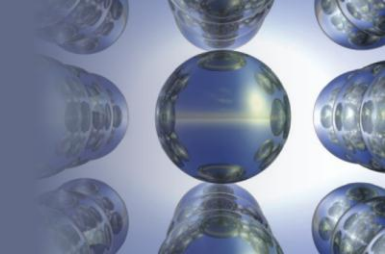


Group 6A - Trends (Continued)

- Elements form covalent bonds with other nonmetals
 - Combine with hydrogen to form a series of covalent hydrides with the general formula H_2X
- Elements with available valence d orbitals form molecules in which they are surrounded by more than 8 electrons
 - Examples - SF_4 , $SeBr_4$, and TeI_4

Section 20.10

The Group 6A Elements



Selenium and Polonium

- Selenium

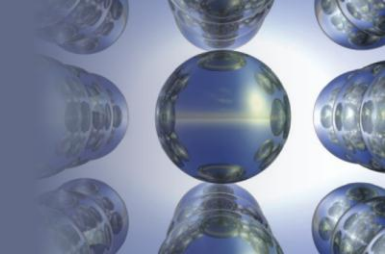
- Medical studies show an inverse relationship between the incidence of cancer and the selenium levels in soil
- Used in the electronic industry

- Polonium

- Highly toxic and radioactive
- Polonium-210 - A natural contaminant of tobacco and an α -particle producer

Section 20.11

The Chemistry of Oxygen

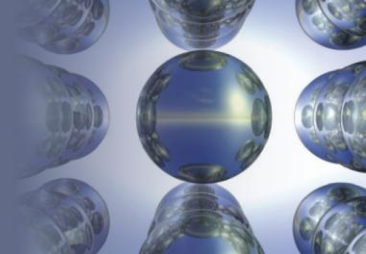


Oxygen

- Present in:
 - The atmosphere as oxygen gas and ozone
 - Soil and rocks in oxide, silicate, and carbonate minerals
 - Water bodies
 - The human body
- Reacts with carbon-containing molecules to provide energy required for survival

Section 20.11

The Chemistry of Oxygen



Common Elemental Form of Oxygen - O₂

- Comprises 21% of the volume of the earth's atmosphere
- Pale blue liquid
 - Freezing point = -219° C
 - Boiling point = -183° C
- Paramagnetic in nature

Section 20.11

The Chemistry of Oxygen

Ozone (O_3)

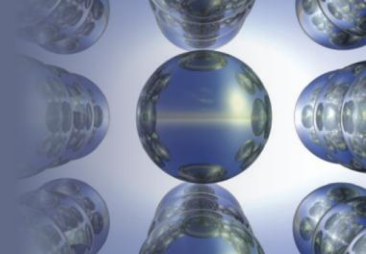
- Represented by the following resonance structures:



- Bond angle - 117°
 - More space is required for the lone pair than for the bonding pairs

Section 20.11

The Chemistry of Oxygen

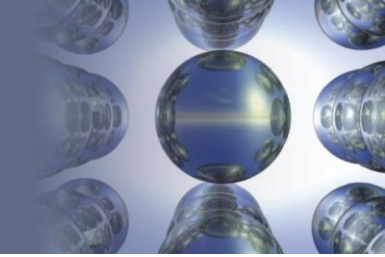


Ozone (O_3) (Continued 1)

- Prepared by passing an electrical discharge through pure oxygen gas
 - Electric energy will disrupt the bonds in some O_2 molecules
 - Produce oxygen atoms that react with other O_2 molecules to form O_3
- Less stable than oxygen at 25°C and 1 atm
- Pale blue, highly toxic gas

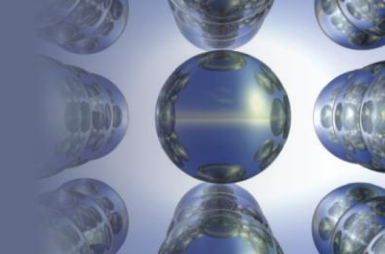
Section 20.11

The Chemistry of Oxygen



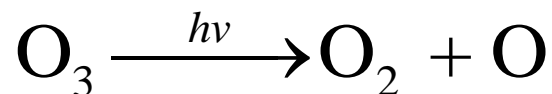
Ozone (O_3) (Continued 2)

- Powerful oxidizing agent
 - Used to killing bacteria in pools and aquariums
 - Used in municipal water treatment and for washing produce after it comes out of the fields
 - Advantage - Does not leave toxic residues
 - Disadvantage - Possibility of recontamination
- Exists naturally in the upper atmosphere
 - Absorbs ultraviolet light and acts prevents radiation from reaching the earth's surface



Ozone Layer

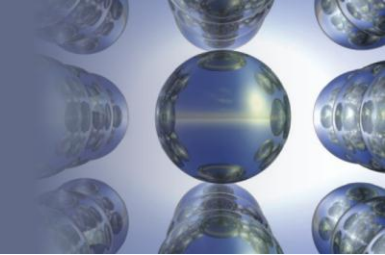
- When an O_3 molecule absorbs energy, it splits into O_2 and O



- If O_2 and O collide, they will not remain as O_3 unless there is a third body
 - The third body will absorb the energy as kinetic energy
 - Ultraviolet radiation is converted to thermal energy

Section 20.11

The Chemistry of Oxygen

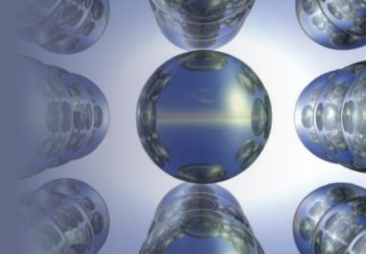


Exercise

- How can the paramagnetism of O_2 be explained using the molecular orbital model?
 - The molecular orbital electron configuration of O_2 has two unpaired electrons in the degenerate pi antibonding (π^*_{2p}) orbitals
 - A substance with unpaired electrons is paramagnetic

Section 20.12

The Chemistry of Sulfur



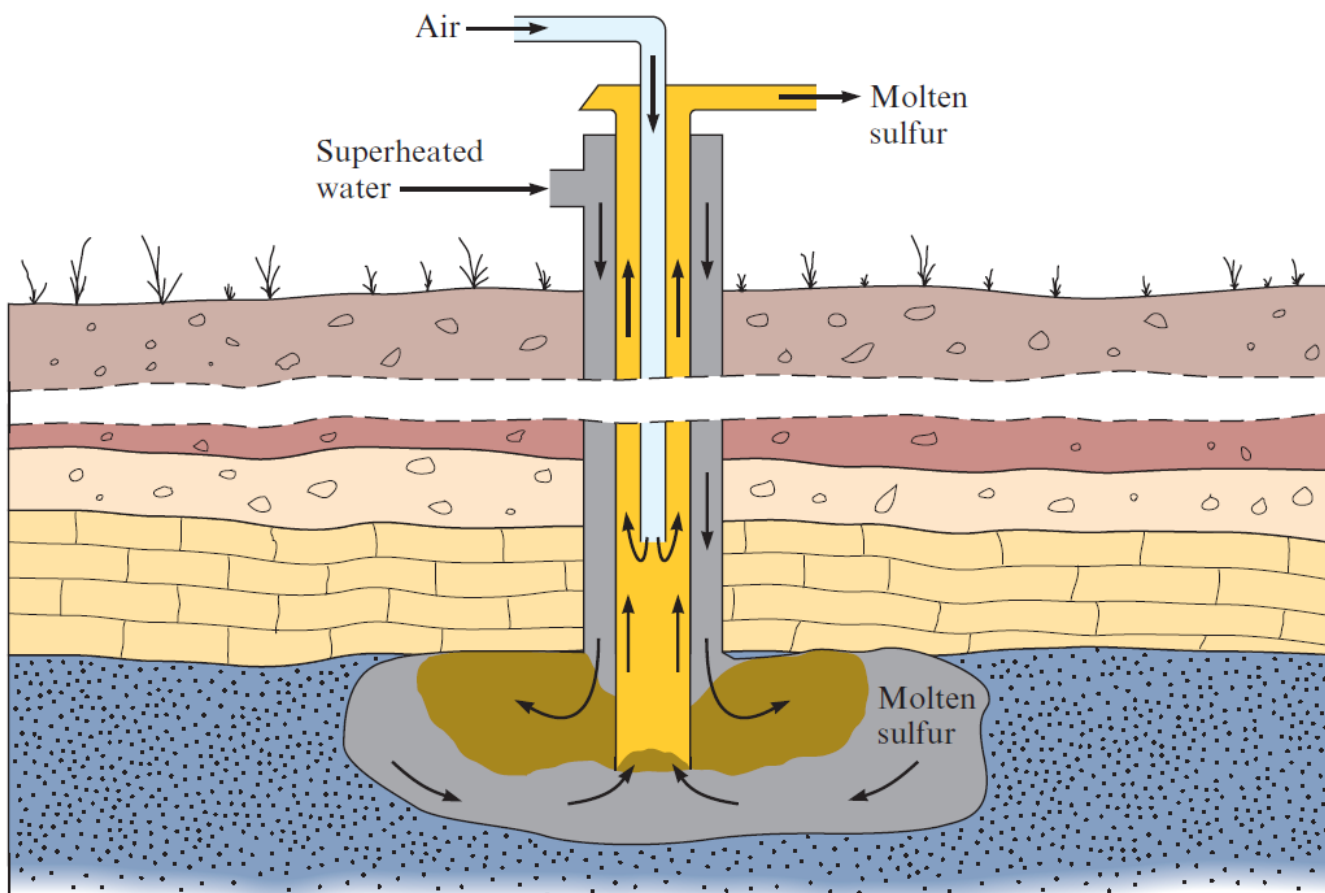
Sulfur

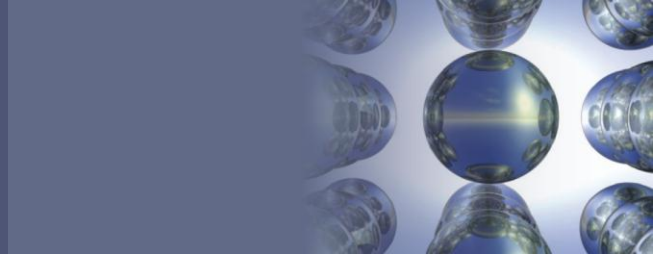
- Found in nature in:
 - Large deposits of the free element
 - Ores such as galena, cinnabar, pyrite, gypsum, epsomite, and glauberite
- Recovered using the **Frasch process**
 - Superheated water is pumped into a deposit to melt sulfur
 - Sulfur is forced to the surface by air pressure

Section 20.12

The Chemistry of Sulfur

Figure 20.21 - The Frasch Process





Aggregates of Sulfur and Their Stability

- Elemental sulfur exists as S_2 molecules in gas phase at high temperatures
- Sulfur atoms form stronger σ bonds than π bonds
 - S_2 is less stable at 25°C than its larger aggregates such as S_6 and S_8 rings
 - Most stable form of sulfur at 25°C and 1 atm is the rhombic sulfur with stacked S_8 rings
 - If rhombic sulfur is melted and heated to 120°C , it forms monoclinic sulfur as it slowly cools

Section 20.12

The Chemistry of Sulfur

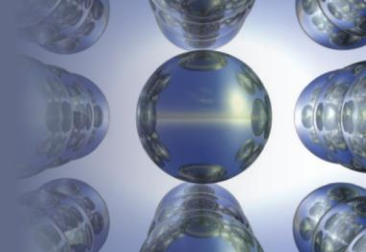
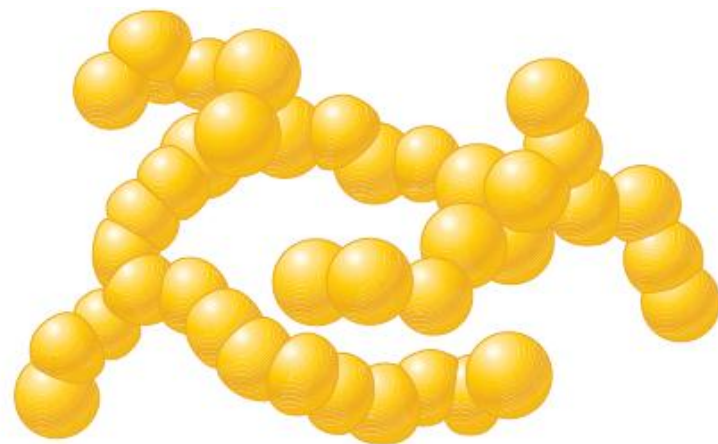
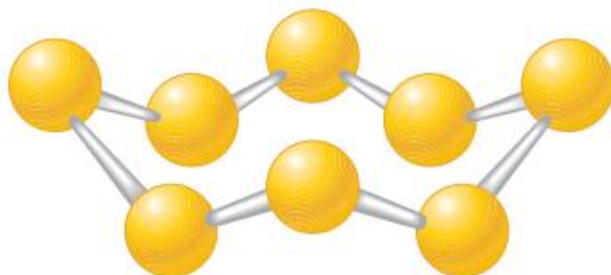


Figure 20.22 - Aggregates of Sulfur



a

The S_8 molecule

b

Chains of sulfur atoms in viscous liquid sulfur

Section 20.12

The Chemistry of Sulfur

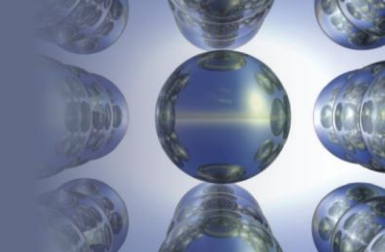
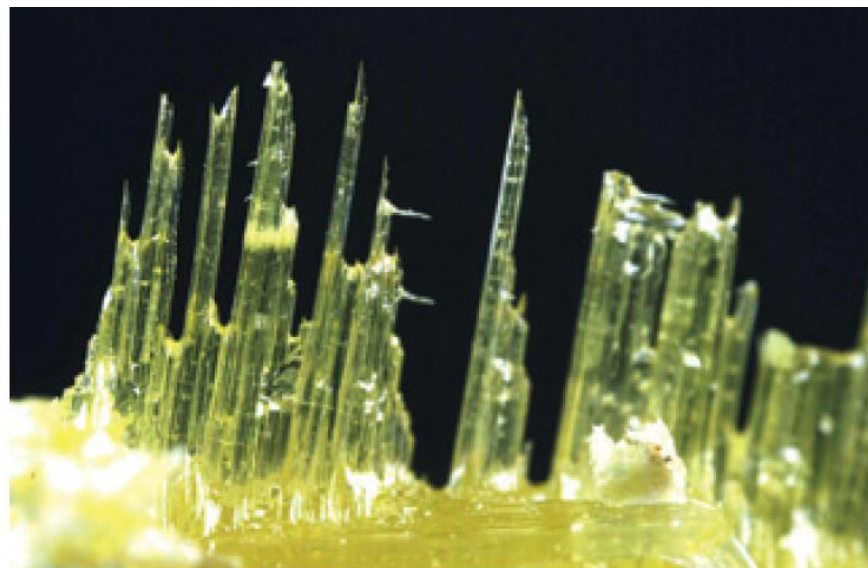


Figure 20.23 - Crystals of Rhombic and Monoclinic Sulfur



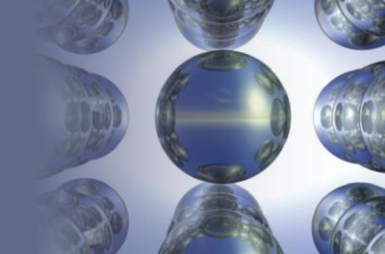
Ken O'Donoghue

a



Dr. Ryoji Tanaka/Sagami Chemical Research Center

b

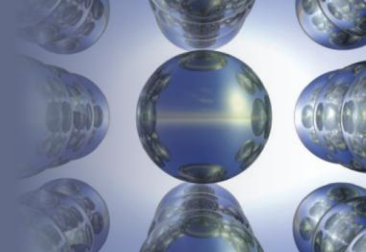


Sulfur Oxides

- Sulfur monoxide (SO)
 - Highly unstable
 - Weak π bonding between S and O atoms in SO than between O atoms in O₂
- Sulfur dioxide (SO₂)
 - Produced when sulfur is burned in air
 - Colorless gas with pungent odor
 - Condenses to liquid state at -10° C and 1 atm

Section 20.12

The Chemistry of Sulfur

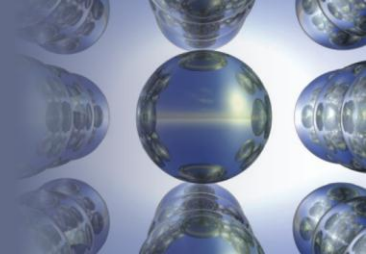


Sulfur Oxides (Continued)

- Efficient antibacterial agent
 - Used for preserving stored fruit
- Sulfur trioxide (SO_3)
 - Product of the reaction between SO_2 and O_2
 - Reaction is slow in the absence of a catalyst

Section 20.12

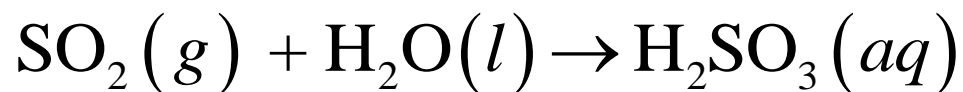
The Chemistry of Sulfur



Oxyacids of Sulfur

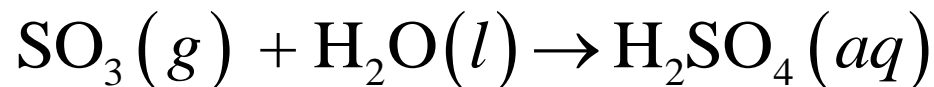
- Sulfurous acid

- Product of the reaction in which SO_2 dissolves in H_2O



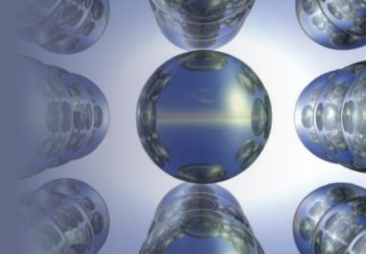
- **Sulfuric acid**: Product of the violent reaction between SO_3 and H_2O

- Diprotic in nature



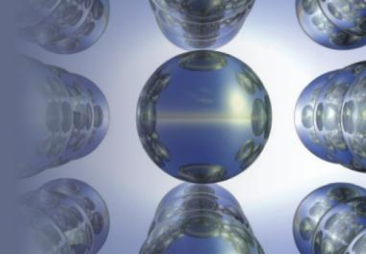
Section 20.12

The Chemistry of Sulfur



Sulfuric Acid

- Usually produced by the contact process
- Uses
 - To produce fertilizers from phosphate rock
 - Lead storage batteries
 - Petroleum refining
 - Steel manufacturing

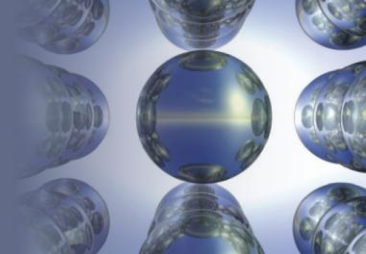


Sulfuric Acid as a Dehydrating Agent

- Caused due to high affinity for water
 - Used for separating gases that do not react with it
 - Gases include oxygen, nitrogen, and carbon
 - Separation process involves bubbling the gases through concentrated solutions of the acid
- Removes H and O from a substance that does not contain molecular H₂O
 - Removal is done at a ratio of 2:1

Section 20.13

The Group 7A Elements



Halogens

- Valence electron configuration - ns^2np^5
- Nonmetals whose properties vary smoothly while going down the group
 - Exceptions
 - Low electron affinity of fluorine
 - Small bond energy of F_2 molecules

7A

F

Cl

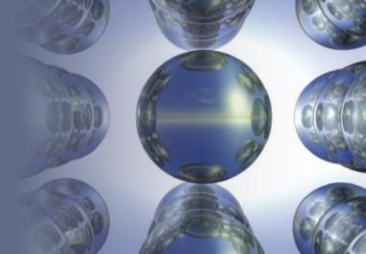
Br

I

At

Section 20.13

The Group 7A Elements



Halogens (Continued)

- Have high reactivities
 - Cannot be found as free elements in nature
 - Found as halide ions (X^-) in various minerals and in seawater
- Have high electronegativity values
 - Form polar covalent bonds with nonmetals
 - Form ionic bonds with metals in their low oxidation states

Section 20.13

The Group 7A Elements

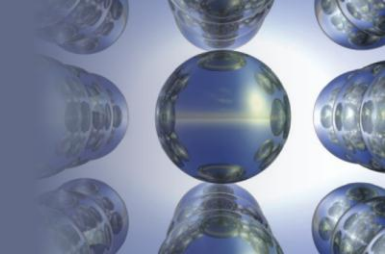


Table 20.17 - Trends in Selected Physical Properties of the Group 7A Elements

Element	Electronegativity	Radius of X^- (pm)	\mathcal{E}° (V) for $X_2 + 2e \rightarrow 2X^-$	Bond Energy of X_2 (kJ/mol)
Fluorine	4.0	136	2.87	154
Chlorine	3.2	181	1.36	239
Bromine	3.0	195	1.09	193
Iodine	2.7	216	0.54	149
Astatine	2.2	—	—	—

Section 20.13

The Group 7A Elements

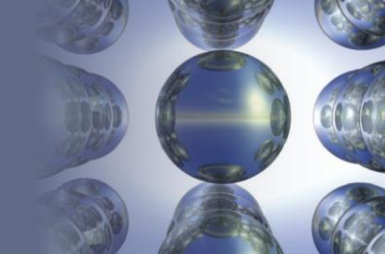
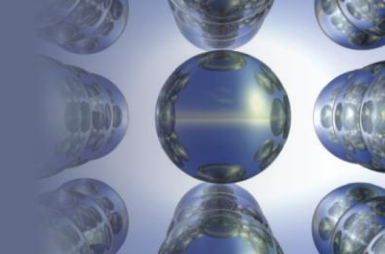


Table 20.18 - Some Physical Properties, Sources, and Methods of Preparation of the Group 7A Elements

Element	Color and State	Percentage of Earth's Crust	Melting Point (°C)	Boiling Point (°C)	Source	Method of Preparation
Fluorine	Pale yellow gas	0.07	-220	-188	Fluorospar (CaF_2), cryolite (Na_3AlF_6), fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$]	Electrolysis of molten KHF_2
Chlorine	Yellow-green gas	0.14	-101	-34	Rock salt (NaCl), halite (NaCl), sylvite (KCl)	Electrolysis of aqueous NaCl
Bromine	Red-brown liquid	2.5×10^{-4}	-7.3	59	Seawater, brine wells	Oxidation of Br^- by Cl_2
Iodine	Violet-black solid	3×10^{-5}	113	184	Seaweed, brine wells	Oxidation of I^- by electrolysis or MnO_2

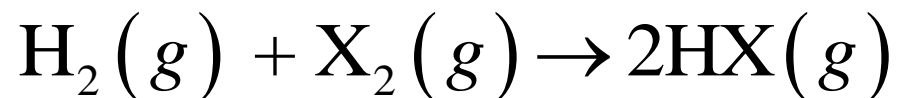
Section 20.13

The Group 7A Elements



Hydrogen Halides

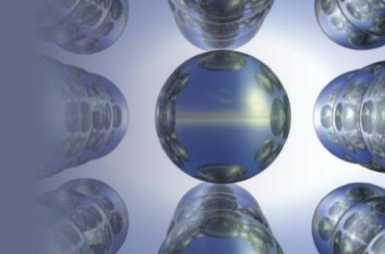
- Preparation can be represented as follows:



- Reaction occurs with explosive vigor when fluorine and hydrogen are mixed
- Hydrogen and chlorine coexist in the dark with little reaction
 - React rapidly in the presence of ultraviolet light
- Bromine and iodine react with hydrogen at a slow rate

Section 20.13

The Group 7A Elements



Hydrogen Halides (Continued)

- Behave as acids and completely dissociate when dissolved in water
 - Exception - Hydrogen fluoride
 - Strength of acids can be presented as follows:



Strongest
acid

Weakest
acid

Section 20.13

The Group 7A Elements

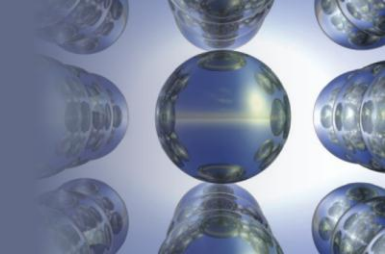
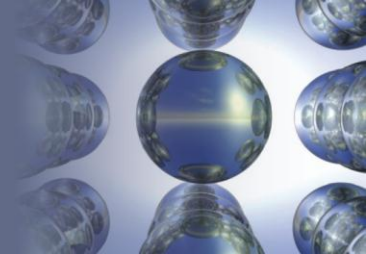


Table 20.19 - Some Physical Properties of the Hydrogen Halides

HX	Melting Point (°C)	Boiling Point (°C)	H—X Bond Energy (kJ/mol)
HF	-83	20	565
HCl	-114	-85	427
HBr	-87	-67	363
HI	-51	-35	295

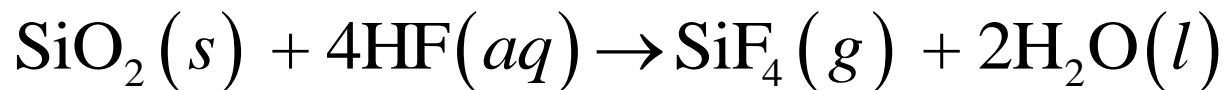
Section 20.13

The Group 7A Elements



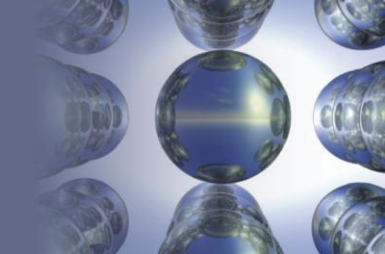
Hydrohalic Acids

- Aqueous solutions of hydrogen halides
- **Hydrochloric acid**
 - Used for cleaning steel prior to galvanization
- Hydrofluoric acid is used to etch glass
 - Reacts with silica in glass to form SiF_4



Section 20.13

The Group 7A Elements



Halogen Oxyacids and Oxyanions

- All halogens except F combine with O atoms to form a series of oxyacids
 - Strengths of the acids vary in direct proportion to the number of oxygen atoms attached to the halogen
 - Acid strength increases as more oxygen atoms are added

Section 20.13

The Group 7A Elements

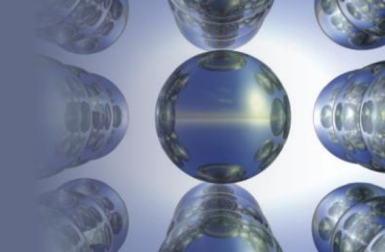


Table 20.21 - The Known Oxyacids of the Halogens

Oxidation State of Halogen	Fluorine	Chlorine	Bromine	Iodine*	General Name of Acids	General Name of Salts
+1	HOF [†]	HOCl	HOBr	HOI	Hypohalous acid	Hypohalites, MOX
+3	‡	HOClO	‡	‡	Halous acid	Halites, MXO ₂
+5	‡	HOClO ₂	HOBrO ₂	HOIO ₂	Halic acid	Halates, MXO ₃
+7	‡	HOClO ₃	HOBrO ₃	HOIO ₃	Perhalic acid	Perhalates, MXO ₄

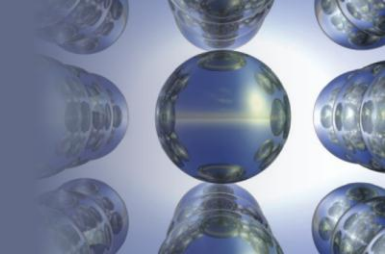
*Iodine also forms H₄I₂O₉ (mesodiperiodic acid) and H₅IO₆ (paraperiodic acid).

[†]HOF oxidation state is best represented as -1.

[‡]Compound is unknown.

Section 20.13

The Group 7A Elements



Chlorine Series - Oxyacids and Oxyanions

- Perchloric acid (HOClO_3)
 - Strong acid and a powerful oxidizing agent
 - Only member of the chlorine series that can be obtained in its pure state
- Other oxyacids are known only in solution
 - Salts containing their anions are widely known

Section 20.13

The Group 7A Elements

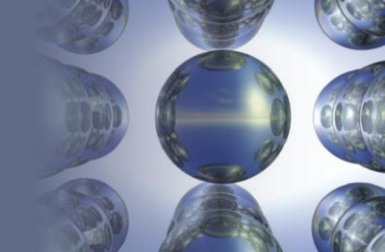
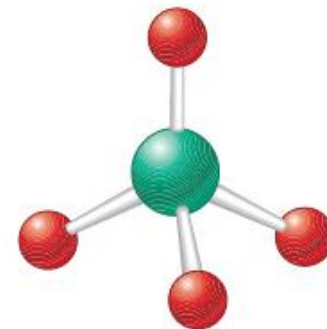
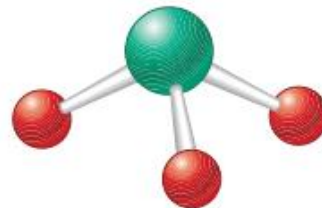
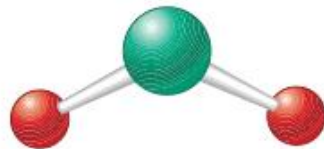
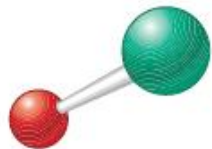
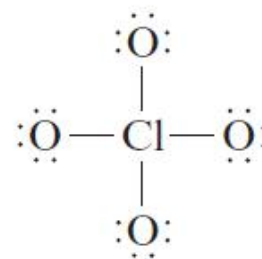
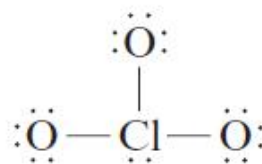
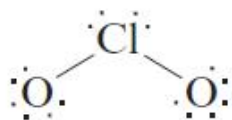
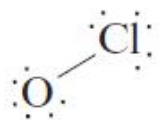


Figure 20.6 - The Structures of the Oxychloro Anions



Hypochlorite ion,
 OCl^-

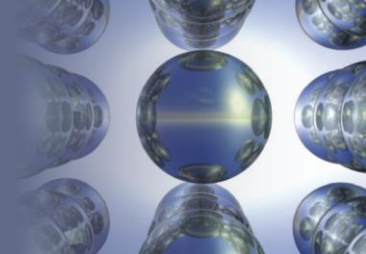
Chlorite ion,
 ClO_2^-

Chlorate ion,
 ClO_3^-

Perchlorate ion,
 ClO_4^-

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The Group 7A Elements

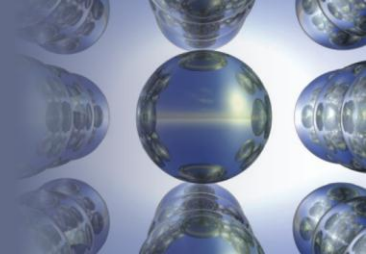


Chlorine Series - Oxyacids and Oxyanions (Continued)

- Hypochlorous acid (HOCl)
 - Formed when chlorine gas is dissolved in cold water
$$\text{Cl}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOCl}(aq) + \text{H}^+(aq) + \text{Cl}^-(aq)$$
 - **Disproportionation reaction:** A given element is both oxidized and reduced in the reaction
 - HOCl acid and its salts are strong oxidizing agents
 - Solutions are used as disinfectants and household bleaches

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The Group 7A Elements

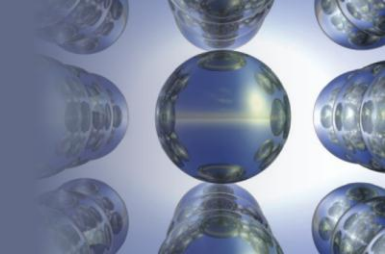


Chlorine Series - Chlorate Salts

- Strong oxidizing agents
- Used as:
 - Weed killers
 - Oxidizers in fireworks and explosives

Section 20.13

The Group 7A Elements

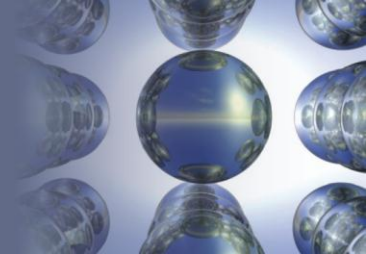


Fluorine Series - Oxyacids and Oxides

- Forms one oxyacid, hypofluorous acid (HOF)
- Forms two oxides
 - Oxygen difluoride (OF₂)
 - Formed when fluorine gas is bubbled into a dilute solution of sodium hydroxide
$$4\text{F}_2(g) + 3\text{H}_2\text{O}(l) \rightarrow 6\text{HF}(aq) + \text{OF}_2(g) + \text{O}_2(g)$$
 - Pale yellow gas
 - Boiling point = -145°C
 - Strong oxidizing agent

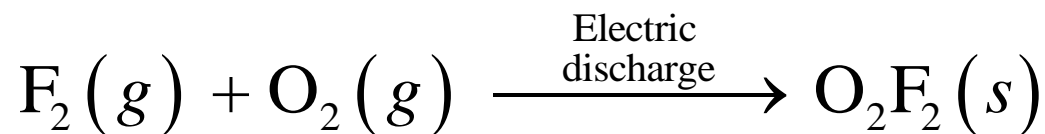
Section 20.13

The Group 7A Elements



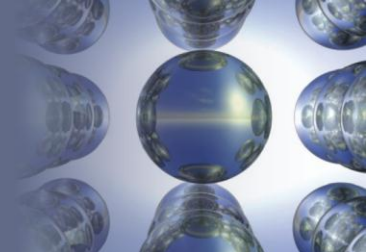
Fluorine Series - Oxyacids and Oxides (Continued)

- Dioxygen difluoride (O_2F_2)
 - An orange solid
 - Prepared by an electric discharge in an equimolar mixture of fluorine and oxygen gases



Section 20.14

The Group 8A Elements



Noble Gases

- Characterized by filled s and p valence orbitals
 - Highly unreactive
- Electron configuration
 - $2s^2$ for He
 - ns^2np^6 for other elements

8A

He

Ne

Ar

Kr

Xe

Rn

Section 20.14

The Group 8A Elements

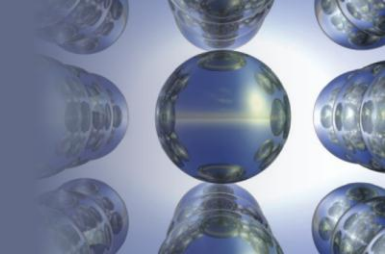
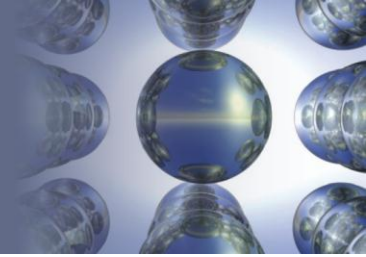


Table 20.22 - Selected Properties of Group 8A Elements

Element	Melting Point (°C)	Boiling Point (°C)	Atmospheric Abundance (% by volume)	Examples of Compounds
Helium	-270	-269	5×10^{-4}	None
Neon	-249	-246	1×10^{-3}	None
Argon	-189	-186	9×10^{-1}	HArF
Krypton	-157	-153	1×10^{-4}	KrF ₂
Xenon	-112	-107	9×10^{-6}	XeF ₄ , XeO ₃ , XeF ₆

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The Group 8A Elements

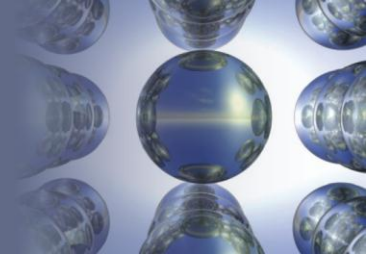


Noble Gas Element - Helium (He)

- Source - Natural gas deposits
 - Helium is formed by the α -particle decay of radioactive elements
- Does not form compounds
- Uses
 - Coolant
 - Pressurizing gas for rocket fuels
 - Diluent in gases used for deep-sea diving and spaceship atmospheres

Section 20.14

The Group 8A Elements

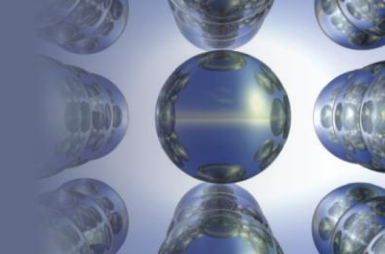


Noble Gas Elements - Neon and Argon

- Neon (Ne)
 - Does not form compounds
 - Used in neon signs
- Argon (Ar)
 - Forms chemical bonds under certain circumstances
 - Provides a noncorrosive atmosphere in incandescent light bulbs
 - Prolongs the life of the tungsten filament in bulbs

Section 20.14

The Group 8A Elements



Noble Gas Elements - Krypton and Xenon

- Form many stable chemical compounds
 - Example - Xenon tetrafluoride
 - Stable, colorless crystal that is formed by the reaction of xenon and fluorine gases in a nickel reaction vessel at 400° C and 6 atm
 - Xenon fluorides react with water to form hydrogen fluoride and oxycompounds
 - Other xenon fluorides - XeF_2 and XeF_6

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The Group 8A Elements

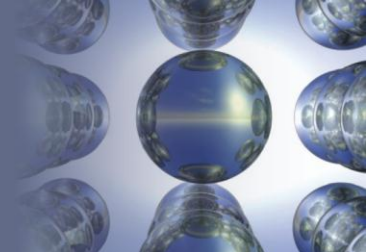
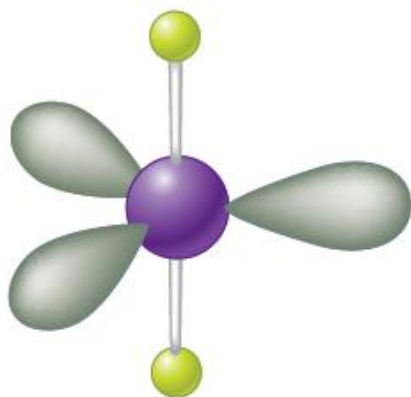
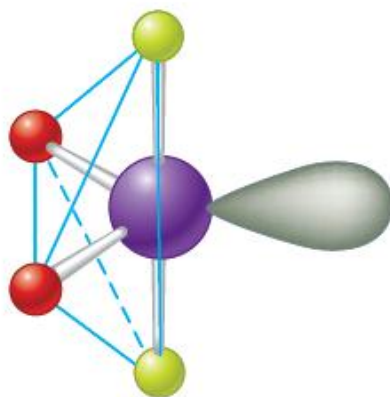


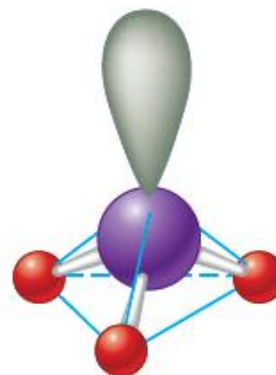
Figure 20.27 - The Structures of Known Xenon Compounds



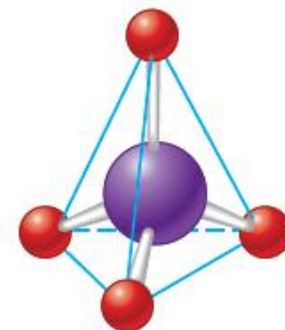
XeF₂
Linear



XeO₂F₂
See-saw



XeO₃
Pyramidal

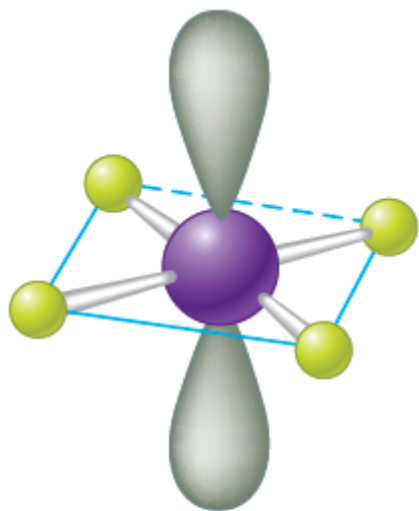


XeO₄
Tetrahedral

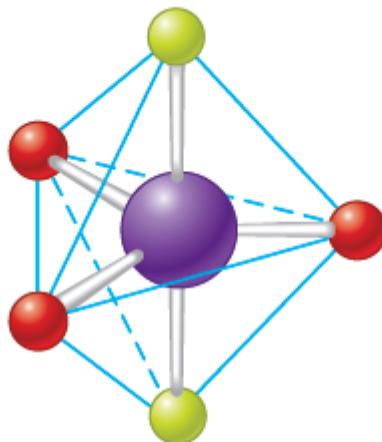
Section 20.14

The Group 8A Elements

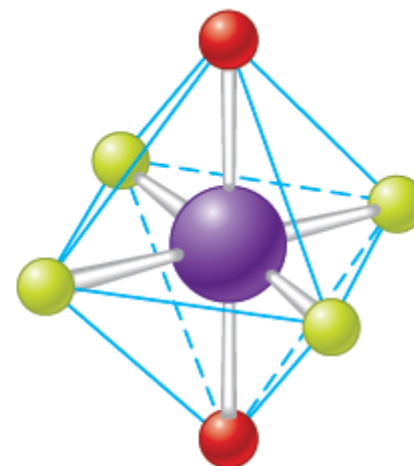
Figure 20.27 - The Structures of Known Xenon Compounds (Continued)



XeF₄
Square planar



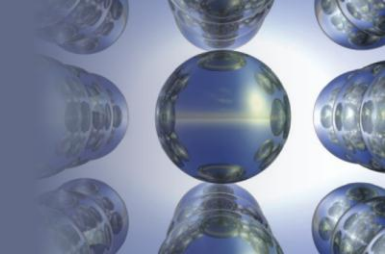
XeO₃F₂
Trigonal bipyramid



XeO₂F₄
Octahedral

Section 20.14

The Group 8A Elements



Exercise

- The xenon halides and oxides are isoelectronic with many other compounds and ions containing halogens
 - Give a molecule or ion in which iodine is the central atom that is isoelectronic with each of the following:
 - Xenon tetroxide IO_4^-
 - Xenon difluoride IF_2^-
 - Xenon hexafluoride IF_6^-