Notes: Chapter 14

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Chapter 14: Periodic Patterns in the Main-Group Elements

Homework:**2,3,11,15,16,22,27,28,42,47,52,53,57,61,68,69,80,83,87,92,105,109,111,112,127,132,138,154,172**

General Trends for Metals and Nonmetals

Metals form positive ions while nonmetals form negative ions.

Oxides of metals tend to be basic while nonmetals form acidic oxides.

Exceptions: The basic character of metallic oxides decreases as the charge of the positive ion increases. (Electronegativity increases causing the oxide to be less ionic. Aluminum oxide is amphoteric and has both acidic and basic properties.

Metallic character increases to the left and down.

Nonmetallic character increases up and to the right.

Oxidation States

The maximum positive oxidation state for any main group element is equal to the group number. The maximum negative oxidation state for the more electronegative elements (group 4A to group 7A) is the group number - 8.

Problem 1: $PbCl_2$ and $PbCl_4$ are the two chlorides of lead. One of these compounds is a liquid at room temperature and explodes near its boiling point of 105°C, the other is a stable crystalline substance having a melting point of 501°C. Which is which.

Compounds containing elements having higher oxidation states low on the periodic table are less stable. Bonds have more covalent character causing $PbCl_4$ to behave as a molecular solid and not as an ionic crystal lattice. i.e. $PbCl_4$ explodes near its B.P. of 100°C

Differences in behavior of the Second-Row Elements

Second row group IA to IIIA elements are small and tend to polarize the bonds in their compounds giving polar covalent bonds. The second row nonmetals have high electronegativities and generally form ionic compounds with metals and covalent (molecular) compounds with nonmetals.

Since the second row nonmetallic elements are small, many tend to form double and triple bonds because of effective p-orbital overlap. The halogens do not tend to form double and triple bonds. As you move down the periodic table the size of the atoms increases and double and triple bonding becomes less likely since the p-orbitals have a less effective orbital overlap.

Problem 2: Describe the bonding in CO_2 , SiO_2 and PbO_2.

Diagonal Relationship: Chemical properties of third-row elements to the right and below the second-row elements tend to have similar properties to those second row elements. The primary reason is that the size and ionization energies are very close for these diagonal elements.

Group IA: The Alkali Metals

Alkali metals are extremely reactive since they have very low ionization energies and can readily loose their ns^1 electrons. Hydrogen is placed in this family mainly because it has the same electron configuration; however, it could just as easily be placed in the halogen family since it can form the negative hydride ion, H^-.

In nature, alkali metals are always found as ions or ionic compounds, never as the free elements. They are all soft, silver colored metals with low densities and low melting points. They all react with water to form hydroxides and hydrogen gas. They all burn in air to form oxygen compounds: Lithium oxide (O^{-2}), sodium peroxide (O_2^{-2}), and potassium superoxide (O_2^{-1}). The general trend in reactivity for the alkali metals increases as you move down the periodic table. All alkali metals react with halogens and hydrogen forming ionic salts (i.e. NaH, KCl, LiBr). The alkali metals must be stored under kerosene to prevent oxidation by air.

Nearly all group IA salts are soluble in water. Lithium's small size and high charge density imparts considerable covalent character to the bonds it forms with nonmetals making it more difficult for it to form ions in water, and hence reducing the solubility.

Preparation of the Elements.

Sodium and lithium are prepared by electrolysis from molten salts. Potassium and the other alkali metals are prepared by a single replacement reaction process using sodium.

$Na_{(l)} + KCl \rightarrow NaCl + K_{(g)}$

Uses of the Alkali Metals

Na Production of Tetra Ethyl Lead (TEL), $NaNH_2$, Na_2O_2, reduction of other metals.

Li Aluminum alloys, lithium batteries, $LiAlH_4$.

K KO_2, KOH

Group IIA: The Alkaline Earth Metals

Alkaline earth metals are fairly reactive since they have very low ionization energies and can readily loose their ns^2 electrons.

In nature, alkaline earth metals are always found in compounds, never as the free elements. Be is gray and the others are silver colored metals. Their densities range from 2.5 to 3.5 g/ml. Magnesium and below all react with water to form hydroxides and hydrogen gas. Magnesium and below all burn in air to form oxides. The general trend in reactivity for the alkaline earth metals increases as you move down the periodic table. All alkaline earth metals react with halogens and hydrogen forming ionic salts (i.e. MgH_2, $CaCl_2$, $SrBr_2$).

Preparation of the Elements.

All alkaline earth metals can be prepared by electrolysis from molten chloride salts; however, they can also be prepared by a single replacement process using a more active metal.

$Mg_{(l)} + BeF_{2(l)} \rightarrow MgF_{2(l)} + Be_{(s)}$ or

$3CaO_{(s)} + 2\ Al_{(l)} \rightarrow Al2O_{3(s)} + 3Ca_{(g)}$

Uses of the Alkaline Earth Metals

Mg	Strong aluminum alloys, aircraft parts, reducing agent for other metals
Be	Hard copper alloys, electric contacts, x-ray windows, n moderator in nuclear power plants.
Ca	Purifying agent for producing certain metals, lead alloy agent for lead-acid batteries
Ba	T.V. picture tubes, x-ray absorber as $BaSO_4$

Group IIIA: The Boron and the Aluminum Family Metals

Boron, the first element of this group is a metalloid. As such, it is a semiconductor. All group three elements have a +3 charge state; however, some +1 compounds exist for gallium, indium and thallium. Group III metals are not nearly as reactive as groups I and II since they have higher ionization energies, but they can readily loose their ns^2, np^1 electrons.

In nature, group III metals are always found in compounds, never as the free elements. Be is gray and the others are silver colored metals. Their densities range from 2.3 to 11.8 g/ml. Group III elements do not with water. All the metals form oxides spontaneously forming an oxide coating, which prevents further oxidation. The general trend in reactivity for the group III metals increases as you move down the periodic table. All group III metals react with halogens and hydrogen forming ionic salts (i.e. AlH_3, $GaCl_3$, $ThBr_3$).

Preparation of the Elements.

Aluminum is prepared by an electrolytic process called the Hall process. Aluminum oxide (bauxite ore) is dissolved in molten cryolite and an electric current is passed through it. The molten aluminum sinks to the bottom where it is drained from the bottom as nearly pure metal.

Boron is prepared by a single replacement reaction involving magnesium as a reducing agent.

$Be_2O_{3(l)} + 3\ Mg_{(l)} \rightarrow 2B_{(s)} + 3MgO_{(s)}$

Uses of the group III Metals

Al	Aircraft parts, cans, building materials, explosives and incendiaries
B	Special filaments, plastics, semiconductor doping agent
Ga	Semiconductors
In	Semiconductors
Tl	Not many uses.

Group IV: The Carbon Family

All group IV elements have compounds where the group IV element has a +4 oxidation state; however only carbon and silicon have compounds where they are in the -4 charge state. Many charge states between these extremes exist for the group IV elements. All the group IV elements can have sp^3 (tetrahedral) hybridization, and all but carbon can have sp^3d^2 (octahedral) hybridized.

Physical Properties of the Elements

Carbon exists in three allotropes (look up the word) graphite, diamond and amorphous. In graphite, the atoms are sp^2 hybridized where the remaining p-orbital forms _-bonds with adjacent carbon atoms. The hexagonal sheets of atoms are much like a honeycomb. This structure accounts for the slippery nature of graphite. Diamond forms a continuous sp^3 (tetrahedral) lattice structure where each carbon is bonded to 4 adjacent carbons. All bonds are strong s-bonds leading the hard but brittle diamond structure. Conductivity: graphite is a semiconductor and diamond is an insulator. A new set of cage forms of carbon has recently been discovered. C_{60} is a spherical shaped molecule with the appearance of a soccer ball. It is called Buckminster Fullerine after the architect who discovered the geodesic dome. Chemical slang for these compounds is Buckey balls. Several other C_x molecules have been characterized.

Silicon, germanium and one allotrope of tin, gray tin, are found in the diamond-type lattice. These elements are semiconductors. Silicon and germanium are silvery-gray and brittle.

White tin in and lead are metals and as such are lustrous, good conductors of heat and electricity, malleable, and ductile.

Chemical Properties of the Elements

Reactivity toward oxygen at normal temperatures is low; however, at elevated temperatures all group IV elements will burn forming oxides. None of these elements are reactive toward water; however, carbon and silicon will react with steam. The reaction of carbon with steam results in a mixture, which is used as a fuel.

$C + H_2O_{(g)} \rightarrow CO + H_2$

$CO + H_2 + O_2 \rightarrow CO_2 + H_2O$

The group IV nonmetals are unreactive toward strong acids. The group IV metals are both above hydrogen on the electrochemical series and therefore react with acids, albeit slowly, forming hydrogen.

Preparation and Uses of the Elements

Amorphous carbon can be prepared by heating hydrocarbons in the absence of oxygen.

$C_6H_{14} \xrightarrow{\Delta} 6C + 7H_2$

Graphite is prepared by heating amorphous carbon at 3500°C using SiO_2 and Fe as catalysts.

Diamond can be prepared by heating graphite at high temperature, 3000°C, and pressure, 100,000 atm. Diamond films have recently been developed for coating metals. These films make metal surfaces as hard as diamond and might someday be used to eliminate engine wear.

Silicon and germanium are metalloids and are produced by reduction of the oxides with carbon. I.e.

$SiO_2 + 2C \rightarrow Si + CO_2$

The impure silicon is refined by passing a cylinder of silicon slowly through a heating element where a small zone of the element is melted. As the molten zone cools, it forms pure crystals while the impurities remain in the molten zone. This method of refining is called zone refining. Silicon prepared in this manner is used for manufacturing electronic devices called silicon chips used in computers.

Important Compounds

Carbon forms an infinite number of compounds and is unique in that it can form multiple bonds to itself. Other elements in this group cannot readily form π-bonds since their large atomic radius prevents effective p-orbital overlap. The chemistry of carbon is called organic chemistry.

CO is important as a fuel and reducing agent.

$2CO + O_2 \rightarrow 2CO_2$

$3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$

CO_2 is the main product of the combustion of hydrocarbons such as methane, gasoline, and oil. CO_2 is relatively soluble in water and forms the basis of all carbonated drinks.

Methane is a major source of energy in the world.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Silicon Dioxide and Silicates

Un like CO_2, SiO_2 is a covalent network without double bonds. SiO_2 is a main constituent of the earth's crust. An abundant source is SiO_2 is sand. Silicates have a common constituent SiO_4^{4-}, or polymers of this basic unit. $ZrSiO_4$ is the formula of zircon, a hard crystalline substance used to make fake jewelry. Polymeric strings of silicates form stringy or sheet-like minerals.

Aluminosilicates are silicates in which a portion of the silicon atoms has been replaced by aluminum. Consider replacing 50% of the silicon atoms in typical silicate:

SiO_4 x 4 = Si_4O_8; 25% Si replace with Al = $AlSi_3O_8^-$; $NaAlSi_3O_8$

Problem 3: Give the formula for a magnesium silicate in which 25% of the silicon is replaced by aluminum.

Problem: Make a calcium aluminum silicate in which 2/3 of the Si has been replaced with Al

$SiO_2 \times 3 = Si_3O_6 \Rightarrow Al_2SiO_6^{-2} \Rightarrow \underline{CaAl_2SiO_6}$

Group IV A Tin and Lead

Tin is prepared by reduction of the oxide with carbon.

$SnO_2 + C \rightarrow Sn + CO_2$ <— SnO_2 & C are solid so alt. use CO(g) instead of C

Tin is extensively used as a protective coating on steel and as an alloying agent for bronze and lead solder. An alloy of lead and tin forms a solder, which is stronger and has a lower melting point than either lead or tin separately.

Lead is prepared by roasting galena, PbS, in oxygen.

$PbS + O_2 \rightarrow Pb + SO_2$

The symbol for lead, Pb, is derived from plumbum, the Latin word for waterworks, because of lead's extensive use in ancient water pipes. Lead is a cumulative poison causing dain bramage and is only slowly excreted. The fall of the Roman Empire may have been due in part to lead poisoning and the resulting stupidification of the population. Lead is an excellent absorber of radiation and is used as a protective shielding against gamma and x-rays. The largest use of lead today is in the plates of lead-acid storage batteries for automobiles.

Hydroxides of Sn and lead are amphoteric; that is the both dissolve in acids and bases.

Group VA: Nitrogen and the Phosphorous Family

The oxidation state for the group VA elements range from -3 to +5 except for Bi, which only has the +3 charge. Nitrogen is a gas at room temperature and is extremely inert due to its triple bond. Phosphorous forms two common allotropes, red and white phosphorous. Red phosphorous consists of long polymer chains of P_4 units and is relatively stable. White phosphorous consists of P_4 molecules and has a yellowish cast with a waxy consistency. White phosphorous spontaneously burns in air giving P_2O_5 , the acid anhydride of phosphoric acid.

Preparation and Uses of the Elements

Nitrogen is prepared by fractional distillation of air. It is used primarily as a blanketing gas for welding to reduce or eliminate oxidation of the metal surface. One of the most important compounds of nitrogen is sodium nitrate used in the manufacture of explosives such as gunpowder. It is also used extensively in the Haber process to produce ammonia and fertilizers.

Phosphorous is prepared by heating phosphate ores (known as apatite minerals) with coke (C) and sand. Gaseous phosphorous is condensed and stored under water. Phosphorous is mainly used to produce phosphoric acid.

How do we obtain phosphorus?

$XPO_4 + SiO_2 + C \xrightarrow{\Delta} P_4(g)$ etc

Arsenic, Antimony, and Bismuth

Arsenic and antimony is prepared by roasting As_4S_6 in air and reducing the resulting As_4O_6 with coke. Arsenic exists in three allotropic forms, yellow (a), black (b) and metallic (g), which is the most stable. Arsenic is extremely toxic; however, 4-hydroxybenzene arsenic and 4-aminobenzene arsenic have been used as antisyphilis drugs. Arsenic is used to harden lead and copper.

How to we obtain arsenic?

$As_4S_6 + 9O_2 \rightarrow \underbrace{2As_2O_3}_{\text{dimer} = As_4O_6} + 6SO_2$

$As_4O_6 + 6CO \rightarrow 4As^\circ + 6CO_2$

Antimony exists in the same three allotropes as arsenic having essentially the same colors. The main use for antimony is as an alloying agent for the plates of lead-acid batteries, and in the manufacture of semiconductors. Antimony forms toxic compounds; however, some such as antimony potassium tartrate (tartar efetic) have been used medicinally for centuries.

Bismuth is a soft, brittle, highly lustrous metal with a melting point of 271°C. +3 and +5 compounds are known; however, +3 is the most stable of the two oxidation states. The relatively low toxicity of bismuth salts permits their use in the cosmetic and pharmaceutical industries. Peptobismol is one preparation containing bismuth and is used as an antidiareal.

Important Compounds

Ammonia is the most important nitrogen compound. Nitrogen is an extremely stable molecule due to its strong triple bond, and is difficult to "fix" into useful compounds. The Haber process fixes elemental nitrogen as ammonia where it can be reacted to form other compounds. A useful product comes from the reaction of ammonia with carbon dioxide: $2NH_3 + CO_2 \rightarrow NH_2CONH_2 + H_2O$. Urea is used as a fertilizer. Ammonia is oxidized to form nitric acid.

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ Platinum catalyst req.

$2NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Nitric acid is important in the production of explosives.

Phosphorous Oxides and Oxyacids

There are two common oxides of phosphorous. P_4O_6 and P_4O_{10}. P_4O_6 is the acid anhydride of phosphorous acid H_3PO_3, which is a diprotic acid since one of the hydrogens is attached to the phosphorous. P_4O_{10} is the acid anhydride of phosphoric acid, H_3PO_4. H_3PO_4 undergoes a condensation reaction to form poly phosphoric acids.

$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$ (diphosphoric acid, triphosphoric acid etc.)

Metaphosphoric acids are also polymers of phosphoric acid having the general formula $(HPO_3)_n$.

Group VIA: Oxygen and the Sulfur Family

The oxidation states of group VI range from -2 to +6.

Oxygen forms ions primarily in the -2 charge state (oxide O^{2-}), but also forms -1 (peroxide O_2^{2-}) and -.5 (superoxides O_2^{1-}). Oxygen only forms positive oxidation states with fluorine. Oxygen has two common allotropes O_3 ozone, and O_2. Oxygen radical (O) forms but is so reactive that it soon forms other compounds.

Sulfur

Sulfur forms all oxidation states of the group; S^{-2}, S°, SF_2, SO2, SO_3, and has four allotropes; S_8, S_6, S_4, and S_2. Melting sulfur results in a polymer S_n.

Selenium and tellurium are metalloids. Selenium, like sulfur, also exists in several allotropes Se_8 being the most common. Selenium is used in the manufacture of semiconductors, particularly rectifiers, and as a photo conductor in copy machines. Tellurium has few commercial applications. Polonium has the dubious distinction of being the only metal to have a simple cubic lattice.

Chemical Properties of the Elements.

Oxygen is very reactive and reacts with most elements directly to form oxides (O^{-2}), however peroxides (O_2^{2-}) and super oxides (O_2^{1-}) are also common.

Problem 4: Name the following compounds.

K_2O	Na_2O_2	LiO_2
CaO_2	CaO_4	MgO

Sulfur, Selenium and Tellurium

All three elements react with oxygen to form dioxides, and halogens to form halides, however only sulfur reacts easily with metals to form sulfides. Selenides and telurides are known, but not common.

Preparation and Uses of the Elements

Oxygen is commercially prepared by fractional distillation and in the lab by decomposition of $KClO_3$.
$KClO_3 \rightarrow KCl + O_2$
Oxygen's primary use is as an oxidizing agent.
Sulfur is mined by the Frasch process. The primary use of sulfur is the production of sulfuric acid and the treatment of fruits, vegetables and wines with SO_2 as a preservative.
Sulfuric acid production:
$S + O_2 \rightarrow SO_2$
$SO_2 + O_2 \rightarrow 2SO_3$
$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$
$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$
Selenium is refined from flue dusts from the roasting of sulfide ores and from anode mud from the purification of copper. These materials are treated with oxidizing agents such as nitric acid or chromic acid, which oxidizes the selenium to selenous acid and selenic acid. Selenium is used to make semiconductor devices.

Important Compounds

Hydrogen compounds exist for all group VI elements. H_2O is a liquid, H_2S is a gas, H_2Se is a gas and H_2Te is a liquid.
Problem 5: Explain the differences in boiling points for the group VI hydrogen compounds in terms of intermolecular forces.
Problem 6: Explain how sulfuric acid is made from sulfur.
Problem 7: When S and O form single bonds together, their bond length is 1.70 Å. In the sulfate ion, the bond length is 1.51 Å. Explain why in terms of bonding and using VBT.

Problem 8: What is the formula for sodium thiosulfate and what is it used for?

Problem 9: How is selenic acid prepared? It is a strong or weak acid.

Problem 10: How is teluric acid prepared? It is a strong or weak acid. Why?

Group VIIA: The Halogens

All halogens are diatomic elements. When combined with other elements the halogens exhibit oxidation states from -1 to +7 with the exception of fluorine, which only exits in the -1 charge state.
Problem 11: Why does fluorine only exist in the -1 charge state when combined?

Problem 12: Fluorine and chlorine are gaseous elements, bromine is a liquid and iodine is a solid. Explain why in terms of intermolecular forces.

Demo: Colors and properties of halogens.
Fluorine reacts directly with water to form HF and O_2. Chlorine and bromine react directly with water to form the hypochlorite and the acid.
Problem 12: What is the relative strength of the halogen acids?

The relative oxidizing strength of the halogens increases as you go up the periodic table.
Problem 13: Write all single replacement reactions for the halogens.

Preparation and Uses of the Halogens

Fluorine is the most powerful oxidizing agent and can only be prepared by electrolysis of molten salts. Fluorine is used extensively in the purification and isotope separation of uranium.
Problem 14: Fissionable ^{235}U is a minor isotope of naturally occurring uranium, and must be separated from the nonfissionable ^{238}U before use in nuclear power plants or atomic bombs. UF_6 is a gas. Determine the relative rate of diffusion for the major isotopes of uranium and devise a method for separating the isotopes.
Chlorine is prepared by electrolysis of salt water and is used extensively in the water treatment, bleaching and in the production of solvents, and freons.
Bromine is obtained from seawater where it exists as Br^-. The chlorine is used to oxidize bromide to bromine. Bromine is used as an oxidizing agent and in the production of methyl bromide (for termites), and silver bromide for photographic films.
Iodine is prepared in a similar manner as bromine however; it shows up as a precipitate after oxidation. It is also present in seaweed in large amounts. Burning the seaweed releases $I_{2(g)}$ which can be cooled yielding iodine crystals. Iodine is used as an antiseptic and to make silver bromide for photographic film and potassium iodide, a nutritional supplement.
The hydrohalic acids are all soluble in water and, with the exception of HF, are strong acids.
Problem 15: Why is HF weak while the other hydrohalic acids are strong?
Problem 16: Define disproprotionation. Show the disproportionation reaction for Cl_2 in water.

Group VIII: The Noble Gases

Helium is found in small quantities in natural gas wells, the other noble gases are collected by fractional distillation of air with the exception of Rn, which is a decomposition product of Ra. The lowest boiling point substance is He (-268.9°C) and is used in low temperature research. Argon is used as a blanketing gas in welding. Neon is used to make neon signs and He-Ne lasers.

Compounds

Not much to say here. He Ne and Ar have no known compounds. Few Kr, Xe and Rn compounds have been made with fluorine and oxygen.

Problem 17: Give the structure for all fluorine and oxygen compounds of Xe.

Problem 18: Noble gases are extremely unreactive since all electrons are paired in filled s and p-orbitals. Explain why noble gas compounds can be made in lieu of this fact.

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