CH A P T E R: The p-Block Elements

A. the boron group (p^1 elements)

• **group members**: boron (B), aluminum (Al), gallium (Ga), indium (In), thallium(Tl)
all, except for boron, are metals

• **properties:**

1. **boron**

• diagonal relationship with Si (tzv. diagonálna podobnosť): both are semiconductor
• metalloid, the compounds of boron are covalent
• Boron compounds are electron deficient (elektrónovo deficientná väzba); they are lack of an octet of electrons about the B atom (elektróny tvoriace väzbu sú delokalizované medzi viaceré atómy bóru).
• adduct of dimethyl ether and BH3
• **adduct (definition): a compound that results from the addition, through a coordinate covalent bond**, **of one structure to another**
• **diborane, B2H6,** the isolable (izolovateľný) simplest boron hydride
• **structure:** three-center two-electron: the H atoms are simultaneously bonded to two B atoms
the B-Hbridging bond lengths are greater than B-Hterminal.
- Boron oxide is acidic (it reacts readily with water to form boric acid)

2. **aluminium**

• **manufacture (Hall process)**: electrolysis of Al2O3 in molten cryolite (sodium hexafluoroaluminate-Na3AlF6) at the t = 950°C (main feedstock is bauxit)
• **aluminium compounds:** aluminium oxide is amphoteric
aluminum halides, e.g., AlCl3 dimer, an important catalyst in organic chemistry (have an incomplete octet, acts as Lewic acid by accepting lone pairs from Lewic bases, forming adduct
aluminum hydride, e.g., LiAlH4, a reducing agent

reactions: $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$
$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2NaAl(OH)_4(aq) + 3H_2$

B. the carbon group (p^2 elements)

• **group members**: carbon (C), silicon (Si), Germanium (Ge), Tin (Sn), lead (Pb).
Carbon is a **non-metal. Silicon** and **germanium** are **metalloids**. **Tin and lead** show typical **metallic** properties. As the atomic number rises the metallic (electropositive character increases and non-metallic (electronegative) character decreases.
Si and Ge crystallise in the same structure as diamond. Tin and lead have distorted **close-packed metal structures.**
Down the group: -change in bonding from covalent to metallic (ionic)
-decrease in melting point, boiling point, enthalpy change of atomisation, E_{i1}
-increase in density and conductivity
-the +2 oxidation state becomes more stable relative to the +4 ox.state
- the nature of monoxides changes from neutral to amphoteric
- the nature of dioxides changes from acidic to amphoteric

1. **carbon**

• organic chemistry,
• **carbon allotropes**: **1. graphite** (a layered giant covalent structure, hexagonal crystal structure), conductor
2. diamond (a layered giant covalent structure): each atom is linked to four other atoms by single covalent bonds, el. conductivity is very low (lack of delocalized electrones)
3. fullerite C_{60}, the solid form of buckminsterfullerene, nanotubes
• **coke (koks):** a high-carbon residue derived from heating coal in the absence of air to remove volatile substances
reducing iron oxide to iron
• **carbon black (technický uhlík, sadze):** a powdery soot (sadza) resulting from incomplete combustion and deposition on a surface
filler in rubber tires, pigment in printing inks, carbon paper, typewriter ribbons, photocopy
• **activated carbon (aktívne uhlie):** the form of carbon resulting from heating carbon black to 800-1000 °C in the presence of steam to remove all volatile matter
highly porous carbon, great capacity to adsorb substances from liquids and gases

gas masks, water filters, colored impurities removal (sugar recrystallization), odor control (air-conditioning), vapor recovery (industrial plants)
• **carbide**: the compounds derived from the reactions of carbon with metals, e.g., **lime** (CaO) and **coke** gives **calcium carbide (CaC2**).

2.• silicon
• diagonal relationship with boron
• differences from carbon:bond energy, • Si-Si = 226 kJ/mol, C-C = 347 kJ/mol
• Si-H = 318 kJ/mol, C-H = 414 kJ/mol
• Si-O = 464 kJ/mol, C-O = 360 kJ/mol
• spontaneous ignition on contact with oxygen: disilane (Si2H6) gives SiO2 and H2O
• few Si multiple bond
• **silica, SiO2 :** poor π3p(Si)–π2p(O) interaction: different structure from CO2
a network covalent solid: each Si atom forms bonds to four O atoms; each O atom forms bonds to two Si atoms.
high hardness (7 for quarts, compared to 10 of diamond), high melting point (quartz, kremeň, 1700 °C), insulator
• glass, ceramics, refractory materials
• ceramics: an inorganic solid produced at high temperatures and characterized by such physical properties as hardness, brittleness, stability at high temperatures and high melting point
• soda-lime (a mixture of solid NaOH and solid $Ca(OH)_2$) glass
• sodium and calcium silicate
• a product resulting from heating a mixture of sodium carbonate, calcium carbonate, and sand (silica) to about 1500 °C
• expansion and contraction with changes in temperature
• pyrex (ohňovzdorné sklo)
• borosilicate
• Boric oxide is used in the place of calcium carbonate in glass production.
• low thermal expansion and shock

C. the nitrogen group (p^3 elements)

• **group members**: nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi)
the oxides of nitrogen and phosphorus are acidic (colourless NO and N_2O, the brown gas NO_2. **Remember** that NO_2 exists in equilibrium with its dimer N_2O_4, the position of the equilibrium depending on the temperature and pressure.
•1. **nitrogen:** the N2 molecule
• triple covalent bond, N≡N
• bond energy = 945.4 kJ, **one of the strongest chemical bonds known**
• fractional distillation of liquid air: Clean air is compressed and then cooled by refrigeration. Upon expanding, the air cools. Following a series of compressions and expansions, the air cools to a temperature at which it liquefies. The liquid air is filtered to removed $CO_2(s)$ and then distilled. Nitrogen is the most volatile component, with a normal boiling point of 77.4 K; it comes off as a gas. Argon, which boils at 87.5 K, is removed from the middle of the column, and liquid oxygen, the lease volatile component with a normal boiling point of 90.2 K, collects at the bottom of the column.
• synthesis of ammonia: the Haber process
• equilibrium; reaction does not go to completion.
• **conditions**: 3:1 mol ratio of H2 to N2
400-600 °C
140-340 atm
catalysts: Fe3O4 with small amounts of Al2O3, MgO, CaO, and K2O. (The Fe3O4 is reduced to metallic iron before use.)
• **NO, nitric oxide, a messenger molecule**
• a notorious air pollutant the whole time
• recent discovery by Louis Ignarro, Robert F. Furchgott, and Ferid Murad who won Nobel Prize in 1998
• carrying signals between cells (discovered in 1992)
• maintaining blood pressure
• establishing long-term memory

• aiding in the immune response to foreign invaders in the body
• mediating the relaxation phase of intestinal contractions in the digestion of food
Oxoacids: NO_2 (g) + H_2O → HNO_2 + HNO_3
nitric acid is a strong oxidizing agent

• 2. **phosphorus:** has several allotropes: **white phosphorus**, pyramidal shape with P-P-P bond angle of 60°
red phosphorus: obtained by heating white phosphorus to about 300 °C in the absence of air
• One P-P bond breaks in each P4 molecule (white phosphorus) and the P4 fragments join together in long chains.
• **oxoacids**: H3PO4, H3PO3, H3PO2
-is an essential element in nucleic acids and in ATP
Ammonia and phosphine (NH3 and PH3): ammonia readily forms solutions of salts with acids
Phosphine is a much weaker base than ammonia (**notice**: ammonia is not a base according Arrhenius acid-base theory)

D. the oxygen group (p^4 elements)

• **group members**: oxygen (O), sulfur (S), selenium (Se), tellurium (Te), polonium (Po)
oxygen and suphur are **non-metals**, **selenium and tellurium** are **metalloids**, **polonuim** is **metal**
Po is a radioactive element with a simple cubic structure (an unique)
• **oxygen, its allotropes: O**3 (trioxygen-systematic, ozone-comon) and O2 (dioxygen-systematic, oxygen)
• oxide, peroxide, superoxide
• combustion
• redox
• Oxygen forms compounds with all elements except light noble gases.
• ozone, O3: planar structure
powerful oxidizing agent
ozone holes: the seasonal deletions in stratospheric ozone levels over the polar regions

sulphur: Alltropes: a solid rhombic sulphur (below 96°C) and monoclinic sulphur (above 96°C), both are composed of ring-shaped S_8 molecules and differ only in the pattern in which these molecules pack
Biochemistry: Oxygen: for respiration,
Sulphur: disulphide bridges-links between S at diferent points in a protein chain. The shape of the hormone-insulin is partly controlled by disulphide bridges
SO2 is useful as an antioxidant in food
SO2 dissolves in rain water to form sulphurous acid
Selenium: a trace element in biological systems.

E. the halogen group p^5

• **group members**: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At)
properties: **non-metals**, form **ionic** compounds with **metals**, and **covalent** compounds with **non-metals**
as atomic number increases from fluorine to iodine: M.P., B.P., and atomic radius increase; ionization energy and electronegativity decrease
Manufacture: Chlorine (and sodium hydroxide) is manufactured by the electrolysis of saturated NaCL(aq) **brine (soľný roztok)** (the key problem is that the products of the electrolysis, Cl_2 and OH^- react with each other, the uses of **diaphragm cell** keeps the products separate or uses of **membrane cell** allows only cations passes through it).
Laboratory preparation of Cl2: **$2KMNO_4(s) + 16HCl(aq) \rightarrow 2KCl(aq) + 2MnCl_2(aq) + 5Cl_2 + 8H_2O(l)$**
Uses of chlorine: -sterilizing water, recovery of tinplate from cans, making HCl(**$Cl_2 + H_2O \rightarrow HCl + HClO$ (hypochlorous acid, disproportionation reaction-dismutácia**), PVC-plastic, halothane-anaesthetics)
Manufacture: Bromine and iodine: by using chlorine to displace the halogen from aqueous solution of the halide
Fluorine by the electrolysis of a molten mixture of HF and KHF_2 at about 100°C.

- **Trends:** The oxidizing power of the halogens decreases in the order $F_2 > Cl_2 > Br_2 > I_2$
  - The general chemical reactivity follows the order of their oxidizing power.
  - Iodine reacts quantitatively with thiosulphate ion: **$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ (tetrathionate, ox. number is 2,5!!!)**
  - A halogen will displace a halide that has a greater atomic number than itself
  - Halide ions may act as reductants; the order of reactivity is $I^- > Br^- > Cl^- > F^-$
  - Iodide ion is the most commonly used halide reductant

- Hydrogen halides are produced by the action of conc. sulphuric acid or conc. phosp. acid on a metal halide salt.
- **HF (aq) is weakly acidic** (the H-F bond is particluraly strong and hydrogen bonding between HF molecules and water molecules inhibits the ionization of HF.) ; HCl, HBr, HI are all strong acids in aq. solution (do not show hydrogen bonding)
- The hypohalous acids are weak acids with stabilities in the orderHClO> HBrO> HIO

Test for halide ions: a solution of **$AgNO_3$ acidified with dilute HNO_3**, the precipitates that form are **white (AgCl), cream (AgBr), yellow (AgI),** AgF is soluble and its solution is colourless. Aqueous ammonia is used to confirm the result of precipitation (a complex ion is formed $[Ag(NH_3)_2]^+$): AgCl and AgBr dissolve in dil .(conc., resp.) aq. ammonia; AgI remains as a precipitate

• **interhalogen compound**: a compound of two (or three, but rare) different halogen elements e.g., ClF3, BrF3, etc.

• standard electrode potential,

• hydrogen halides

• oxoacids,

• **fluorine:** high electronegativity

Fluorine forms compounds with all elements (e.g., XeF4) except light noble gases.

HF, glass etching

• **chlorine:** permanent hard water

• **CFCs: chlorofluorocarbons** that have F and Cl atoms bonded to one carbon atom

volatile liquids or easily condensable gases, worked as refrigerants and as lowing agents to form pores in foam plastics

a substance that causes the destruction of stratospheric ozone

F. nobel gas group (p^6)

• **group members:** helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Rn)

• Some compounds of Kr, Xe, Rn exist, but no compounds of He, Ne, or Ar are known; e.g., XeF2, XeF4, XeF6, etc. review VSEPR notation and molecular structures

• **helium:** filling balloons and airships

non-flammable

providing an inert atmosphere

helium-oxygen breathing mixtures for deep-sea divers

• Helium is considerably less soluble than is N_2. Its absorption into the bloodstream is quite limited, and it has no *narcotic effect*.

narcotic, illegal drug, like morphine

• Helium diffuses into partially obstructed areas of lungs more rapidly than N_2 does. It causes less d*ecompression sickness* (kesónova choroba)

• **liquid helium**: boiling point = 4.2 K (-268.9 °C)

a medium to reach extremely low temperatures

Some metals become superconductor at liquid helium temperatures, that is, they essentially lose their resistance to the flow of electric current.

powerful magnets for NMR (nuclear magnetic resonance) and MRI (magnetic resonance imaging)

• **neon:** lighted advertising signs

cathode ray tube

• **argon:** the most plentiful noble gas

obtained from liquefied air