
p-Block chemistry

27.1 General aspects and trends in the *p* block

- Most *p*-block elements can adopt more than one oxidation state, and they normally vary in units of 2.
- Group 13 compounds act as Lewis acids, as can compounds of Group 14 and 15 if they contain elements of the third period or lower.
- Group 15, 16, and 17 compounds have lone pairs, so they can act as Lewis bases, but the strength of the base depends on the type of orbital the electron pair is in.

Trends across the periods of the *p* block

- The metallic character of an element decreases from left to right across a period of the *p* block due to increasing ionization enthalpies.
- The maximum oxidation state increases across a period, though expansion of the octet is not possible for the second period elements.
- The ionic character of the oxides and halides decreases across each period.
- The acidic character of the oxides increases across each period.

Trends down the groups of the *p* block

- The metallic character of an element decreases down each group of the Periodic Table due to decreasing ionization enthalpies.
- The '*Group -2*' oxidation state increases in importance down Groups 13–15. This known as the inert pair effect.
- Bond enthalpies generally decrease down each group, but when the atoms have lone pairs the bond enthalpy is low for the second period element due to high electron–electron repulsion.

- The ionic character of the oxides and halides increases down the groups and the oxides become more basic.
- π bonding becomes less important going down each group.

27.2 Group 13: boron, aluminium, gallium, indium, and thallium

The Group 13 elements

- Boron is a non-metal, whereas the other Group 13 elements are metals.
- The most common oxidation state for Group 13 is +3, but the +1 oxidation state becomes increasingly important going down the group.
- Aluminium and gallium are amphoteric, but indium and thallium show more metallic character and do not dissolve in alkalis.

The Group 13 oxides, hydroxides, and oxoanions

- Boron forms the oxide B_2O_3 and a large number of borate anions containing trigonal planar BO_3 units and/or tetrahedral BO_4 units.
- Boric acid ($B(OH)_3$) is a monobasic acid. It acts as a Lewis acid, interacting with water to form $B(OH)_3(OH_2)$, which loses a proton to form $[B(OH)_4]^-$.
- Al_2O_3 and Ga_2O_3 are amphoteric, but In_2O_3 and Tl_2O_3 are basic.
- $[M(H_2O)_6]^{3+}$ salts are acidic in aqueous solution due to hydrolysis.

The Group 13 halides

- The boron halides are monomeric and do not form dimers. $p\pi-p\pi$ bonding in BX_3 would be lost on dimerization and it is sterically unfavourable to put four large halogen atoms around a boron atom.
- The Lewis acidity of the boron halides increases in the order $BF_3 < BCl_3 < BBr_3 < BI_3$. This is because it takes less energy to distort the trigonal planar geometry with larger halides. This trend can be explained by weaker $p\pi-p\pi$ bonding.
- Aluminium fluoride is a solid with high ionic character, but the other aluminium halides have structures containing covalent bonds. Al_2X_6 dimers with 3-centre 4-electron bonds are present in the gas phase or when the compounds are dissolved in nonpolar solvents.

27.3 Group 14: Carbon, silicon, germanium, tin, and lead

The Group 14 oxides

- The carbon oxides, CO₂ and CO, exist as discrete molecules containing multiple bonding.
- Silicon dioxide forms covalent network structures that contain Si–O single bonds. A wide range of silicate anions is known.
- CO₂ and SiO₂ are weakly acidic.

The Group 14 halides

- CF₄ and CCl₄ are very unreactive compounds, but as the halogen increases in size the stability of the carbon tetrahalide towards thermal decomposition decreases.
- With the exception of the carbon compounds, the Group 14 tetrahalides are hydrolysed by water. The reaction is thermally favoured for CX₄, but the carbon atom is sterically shielded by the halogen atoms.
- With the exception of the carbon compounds, the Group 14 tetrahalides are Lewis acids, and able to form hexahalide anions.
- The dihalides become increasingly more important going down the group, and for lead these are more stable than the tetrahalides.

Other Group 14 compounds

- Most elements form binary compounds with carbon. These carbides can be ionic solids, covalent network structures, or the carbon atoms can occupy interstitial sites in metal lattices.
- Multiple bonds (C=C, C_αC, C=O, C=N, C_αN, C=S) are important for carbon, but less so for the other Group 14 elements.

27.4 Group 15: nitrogen, phosphorus, arsenic, antimony, and

The Group 15 elements

- Of the Group 15 elements, nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids, and bismuth is a metal.
- Oxidation states vary from –3 to +5, with +3 and +5 the most common.
- Nitrogen occurs naturally as N₂ molecules in the atmosphere.

- Phosphorus forms several allotropes. White phosphorus is very reactive, igniting in air, but the reactivity of the allotropes decreases with increasing connectivity within the structure.

The Group 15 oxides and oxoacids

- Nitrogen forms a range of oxides including N_2O , NO , and NO_2 . These compounds all contain multiple bonds between nitrogen and oxygen.
- The phosphorus oxides have structures based on the P_4 tetrahedron with bridging oxygen atoms between the phosphorus atoms. For phosphorus(V) oxide, the phosphorus atoms are also bonded to terminal oxygen atoms.
- Nitrogen and phosphorus form many oxoacids, including HNO_3 , HNO_2 , and H_3PO_4 .

The Group 15 halides

- Nitrogen trifluoride is a stable, unreactive compound, but the other nitrogen trihalides are very reactive and the solids are explosive.
- Phosphorus forms trihalides, the molecules of which are trigonal pyramidal, and pentahalides, which are trigonal bipyramidal in the gas phase.
- NCl_3 and PCl_3 both react with water to give acidic solutions, but the reactions occur in different ways. Water attacks the chlorine atoms in NCl_3 to give HOCl and the phosphorus atom in PCl_3 to give H_3PO_3 .

27.5 Group 16: oxygen, sulfur, selenium, tellurium, and polonium

The Group 16 elements

- Of the Group 16 elements, oxygen and sulfur are non-metals, selenium and tellurium are metalloids, and polonium is a metal.
- The group oxidation state of +6 is not possible for oxygen, which has a maximum oxidation state of +2 but is most commonly seen in the -2 oxidation state. The +4 and +6 oxidation states are observed for the other Group 16 elements.
- Oxygen forms two allotropes, O_2 and ozone (O_3). Sulfur forms a wide range of allotropes containing S-S single bonds.

The Group 16 oxides and oxoacids

- The two most common sulfur oxides are sulfur dioxide (SO₂) and sulfur trioxide (SO₃). SO₃ dissolves in water to form sulfuric acid.
- Sulfurous acid (H₂SO₃) cannot be isolated, but its anions SO₃²⁻ and HSO₃⁻ are present in many salts.

The Group 16 halides

- Oxygen forms halides OF₂ and Cl₂O, which differ with respect to the polarization of the oxygen–halogen bond.
- The most common sulfur fluorides are S₂F₂, SF₄, and SF₆. Sulfur hexafluoride is very unreactive as the six fluorine atoms shield the central sulfur atom from attack.
- Chlorine is not oxidizing enough to stabilize the sulfur(VI) oxidation state, so sulfur tetrachloride is known, but not sulfur hexachloride.

27.6 Group 17: fluorine, chlorine, bromine, iodine, and astatine

The Group 17 elements

- The Group 17 elements are known as the halogens. All are non-metals.
- The elements exist as diatomic molecules, X₂. Fluorine and chlorine are gases at room temperature, bromine is a liquid, and iodine is a solid.
- Fluorine is the most electronegative element, and forms compounds only in the –1 oxidation state. For the other halogens the oxidation states up to +7 are also observed.
- Going down the group, the elements become less oxidizing.
- Astatine is radioactive, with the longest lived isotope having a half life of only several hours.
- The X₂ bond dissociation enthalpies generally decrease going down the group, but the value for F₂ is anomalously low due to a high degree of electron–electron repulsion.

The Group 17 oxides

- Chlorine oxides include ClO₂, which is paramagnetic, and Cl₂O₇. All of the halogen oxides are acidic.

- Chlorine forms oxoacids in the +1 (HOCl), +3 (HClO₂), +5 (HClO₃), and +7 (HClO₄) oxidation states.

The Group 17 halides

- The stability of a non-metal halide AX_n, where A is a *p*-block element and X is a halogen, decreases with increasing size of X. The weakness of the F–F bond and the decreasing bond enthalpies of the A–X bonds with increasing size of X are the major factors behind this.
- Fluorine stabilizes high oxidation states. The A–F bond enthalpies decrease less with increasing coordination number than A–Cl bond enthalpies.
- Interhalogen compounds can be neutral, cationic, or anionic. The shapes of the molecules and ions can be predicted using VSEPR theory.

27.7 Group 18: helium, neon, argon, krypton, xenon, and radon

- The Group 18 elements exist as monatomic gases. Radon is radioactive.
- Until the 1960s it was believed that compounds of the Group 18 elements were not possible, but compounds are now known for argon, krypton, and xenon, with xenon chemistry the most well developed.
- The xenon fluorides XeF₂, XeF₄, and XeF₆ are all known, and act as strong fluorinating agents.

27.8 *p*-Block organometallic chemistry

- Trialkylaluminium compounds generally exist as electron-deficient dimers, in contrast to monomeric trialkylboron compounds.
- The thermal stability of Group 14 organometallics decreases with increasing size of the Group 14 element.
- As the electronegativity of the metal or metalloid increases, the bonding in its organometallic compounds becomes more covalent and the compounds become less reactive.

Learning outcomes

By the end of this chapter you should be able to do the following.

- Describe the preparation, uses and reactivity of the more important *p*-block elements.
- Describe the common oxidation states for the *p*-block elements.
- Describe the structures and key reactions of the *p*-block oxides, hydroxides, oxoacids, and halides.
- Describe and rationalize trends in behaviour across the rows and down the groups of the *p* block.
- Understand why the metal/non-metal divide runs diagonally through the *p* block.
- Explain the basis of the inert pair effect and predict when it occurs.
- Explain the consequences of only having 6 valence electrons on the structures and reactions of Group 13 compounds.
- Use enthalpy cycles together with bond enthalpies to explain the differences in stabilities of compounds going down a group.
- Explain why fluorine is better at stabilizing high oxidation states than chlorine.
- Predict the shapes of simple *p*-block compounds using VSEPR theory.
- Understand the differences in structure and reactivity of organometallic compounds of Groups 13 and 14.