Unique properties of some selected p block elements (Reading material for CML 514)

Unique properties of Aluminium and its compounds

- Aluminium is the third most abundant metal on the earth's crust and it is found to be present in as many as 270 minerals.
- Aluminosilicates form a major component of the earth's crust.
- Aluminium is one of the lightest metals with low density and resists reactivity by forming a thin passivation layer of aluminium oxide (about 4 nm thickness) on any exposed aluminium surface.
- Although pure aluminium has a very low yield strength (*the stress at which a material begins to deform plastically*) its alloys with metals such as copper, magnesium and zinc have very high yield strength comparable to that of steel. Many of its alloys have very good *strength to weight ratio* and therefore find applications where a strong light metal is required such as aeroplanes, modern trains and racing cars.
- It is a good thermal and electrical conductor, possessing 59% of the electrical conductivity of copper, while its density is only 30% that of copper.
- $AlCl_3$ is a very good Lewis acid and a reagent suited specifically for alkylation and acylation reactions of aromatics (Friedel–Crafts reaction). Sodium salts of long chain aryl sulphonates (for example, dodecyl benzenesulphonate), whose aryl–alkyl unit is made using $AlCl_3$ catalyst, are used as surfactants in laundry detergents.
- Aluminium sulfate is an important flocculating agent in the purification of water and a sizing agent of paper replacing potassium alum. Positively charged aluminium cations neutralise the negative charge on colloidal particles in water leading to mutual adsorption and flocculation.
- Triethylaluminium and trimethylaluminium and a partially hydrolysed form of Me_3Al – methylalumoxane (MAO) – are important alkylation reagents and cocatalysts especially in olefin polymerisation (for example, Ziegler–Natta and Kaminsky catalysts).
- Aluminium oxide (alumina, α-Al_2O_3) constitutes the mineral corundum, varieties of which form the precious gemstones ruby and sapphire. Claus process (recovery of sulfur from H_2S) and alcohol dehydrogenation are industrial processes using alumina as a sole catalyst. Aluminium oxide is an amphoteric substance as it reacts with both acids and bases, such as hydrofluoric acid and sodium hydroxide, acting as an acid with a base and as a base with an acid, neutralising the other and producing a salt.
- $LiAlH_4$ is a strong reducing agent which is extremely effective in the reduction of acids, esters and amides to alcohols.
- Red-Al is a reducing agent comparable to lithium aluminium hydride in activity but not as sensitive to oxygen, nor pyrophoric and has good solubility in organic solvents.
- Partial reduction of esters and nitriles to aldehydes is achieved using DIBAL-H, an aluminium hydride reagent. DIBAL-H is also an excellent reagent for hydroalumination reactions.
- The stepwise growth of aluminium alkyls through alkene insertion (Aufbau reaction) is a very important step in the use of aluminium alkyls in Ziegler–Natta and metallocene catalysed polymerisation of alkenes.
- The thermite process, in which aluminium powder reacts with Fe_3O_4, releases very high temperatures (2500°C) and generates molten iron which has been used for spot welding, especially of railway tracks.

Unique properties of Germanium and its compounds

- The unique optical properties of germanium are, highest refractive index (4.003) for any glass forming material and low optical dispersion. These properties make it useful as an additive to reduce attenuation (reduction in power of light signal) of fibreoptic cables used in telecommunication.
- Germanium is the material from which the first transistors were made. A tin-doped germanium rectifier diode for solid state signal processing was found to be highly resistant to burnout by stray voltages during the second world war. It was extensively used as a semiconductor material (band gap 0.67 eV at 273 K) from 1940–1960.
- Modern day germanium-containing semiconductors find use in mobile phones and hand held devices as they consume much less power and are much faster than conventional semiconductors.
- Its use as a semiconductor declined considerably after the advent of silicon-based semiconductors as silicon was inexpensive; large scale and very large scale integrated circuits (VLSI) were made readily from silicon.
- Germanium and germanium-based glasses transmit near IR radiation more effectively than silicon. This property made it useful in the making of passive night vision lenses which use heat radiated by objects to view them in the dark.
- GeO_2 is extensively used as a catalyst for the manufacture of polyethylene terephthalate (PET) as unlike PET made using antimony-based catalysts, the mineral water bottles made out of PET polymerised using GeO_2 retain transparency and do not turn yellow with time.
- Germanium (II) compounds, often prepared from $GeCl_2$.dioxane are more stable compared to Si(II) compounds.
- The first stable germanone (heavier analogue of a ketone), $(Eind)_2Ge=O$ with a tri-coordinate germanium was prepared in 2012 using sterically hindered substituents on the germanium.

Unique properties of tin and its compounds

- Bronze, an alloy of tin and copper was the first alloy to be used on a large scale since 3000 BC. After 600 BC, pure metallic tin was produced.
- An important application for tin is corrosion-resistant tin plating of steel especially for making cans for storing food without decomposition.
- Tin has the second lowest melting point (232°C) among air- and moisture-stable solid metals (comparable melting points: aluminium 660°C, zinc 419.5°C, lead 327.5°C, cadmium 321°C and indium 156.6°C). Lower melting points than tin are only for alkali metals which are moisture sensitive also mercury, gallium and indium. Indium has a very low natural abundance and is an expensive metal.
- The low melting point, good natural abundance, air and moisture stability and ease of forming flexible alloys makes tin a sought after metal for making low melting alloys especially solders. All well known lead-containing and lead-free soldering alloys have tin as a major component, most notably tin/lead soft solders, which are typically 60% or more tin.

- In 1810 Peter Durand, a British merchant, received the first patent for preserving food using tin cans. Durand made containers out of tinplate which was made out of wrought iron sheets coated with tin to prevent rusting.
- Stannous chloride, easily prepared by the reaction of tin and HCl is a well known reducing agent for organic transformations such as, nitro to amino groups and nitrile to aldehyde groups.
- While tin and its inorganic salts are generally found to be nontoxic, organic tin compounds have a high level of toxicity. Some of the organotin compounds have been used as biocides especially bis-tributyltin oxide (TBT).
- Tributyltin hydride, n-Bu_3SnH with a weak Sn–H bond (74 kcal/mol) is a very useful reagent in organic synthesis for the conversion of C–X bonds to C–H bonds by a free radical mechanism.
- Niobium–tin is a superconductor with a critical temperature of 18 K and critical magnetic field of 24.5 tesla. This is useful for constructing superconducting magnets which can withstand high current densities (200,000 A/cm^2) at the highest working magnetic field of 15 T. Although it is brittle, magnetic coils are made by wrapping separate strands of niobium in tin and then fusing them to make the alloy. Another well-known intermetallic compound of tin is indium tin oxide (ITO) which is the most widely used transparent conducting oxide.

Unique properties of oxygen, sulfur and their compounds

Oxygen

- While oxygen constitutes 20.94% of the earth's atmosphere, its only allotrope, ozone, constitutes 0.6 ppm of the atmosphere.
- More than 50% of the commercially produced oxygen is used in the smelting of iron ore to steel. Oxygen injected into molten iron removes sulfur as SO_2 and carbon as CO.
- 25% of the commercially produced oxygen is used by the chemical industry for the synthesis of ethylene oxide which is further converted to ethylene glycol.
- Other industrial uses of oxygen include, medical use, for making oxyacetylene flames for welding and as liquid rocket fuel.
- The importance of breathing oxygen is reflected in the fact that glucose upon oxidation in the presence of O_2 produces 18 times more energy than in the absence of O_2.
- Plants produce oxygen during photosynthesis by splitting of water molecules.
- Oxygen molecule is reversibly bound to the iron centres of hemoglobin which are carried by the red blood cells from lungs to the muscles where it is transferred to the myoglobin.
- Ozone strongly absorbs ultraviolet radiation (UV-B) and the stratospheric ozone layer helps to protect the earth from harmful UV radiation.
- Ozone with an oxidation potential of 2.07 V, is a stronger oxidising agent than H_2O_2, O_2 and $KMnO_4$.
- Robert H Goddard developed a rocket engine that used a liquid fuel with liquid oxygen as the oxidiser. He successfully flew a small rocket to a height of 56 m in 1926 with this fuel.
- Oxygen is composed of three stable isotopes, ^{16}O, ^{17}O and ^{18}O, with ^{16}O being the most abundant (99.762% natural abundance).
- Oxygen constitutes 49.2% of the earth's crust by mass as part of oxide compounds such as iron oxides, silicates and alumino silicates. It is also the major element of the world's oceans (88.8% by mass).

- 65% of the human body consists of oxygen where it is the largest constituent. Sulfur is present in 0.3%.
- O_2 accumulation in the earth's atmosphere is believed to have begun 2.5 billion years ago during the Great Oxygenation Event (GOE). Oceanic cyanobacteria, which evolved into multicellular forms more than 2.3 billion years ago are believed to be the first microbes to produce oxygen by photosynthesis.
- In acidic solutions, H_2O_2 (1.78 V) is one of the most powerful oxidisers known—stronger than $KMnO_4$ and gets reduced to water. In basic solutions, H_2O_2 (–0.68 V) acts as a reducing agent, while it gets oxidised to O_2 gas.
- Fenton's reagent, a solution of hydrogen peroxide with ferrous iron as a catalyst is used to oxidise many unreactive organic compounds. For example, hydroxylation of arenes.

Sulfur

- Sulfur is known from very ancient times, is mentioned in the Bible and Greek mythology as brimstone and was used by alchemists.
- Sulfur and mercury were called philosophical elements (along with the Aristotelian elements air, water, earth and fire) during the time of alchemy and it represented the principle of combustibility.
- Sulfur mostly forms divalent, tetravalent and hexavalent compounds and the latter in its tetracoordinate form is the most stable geometry and oxidation state of sulfur.
- Sulfur is stable in its elemental state and was mined directly from the earth for a long time.
- The most industrially important compound of sulfur is sulfuric acid which is used for making sulfate- and phosphate-based fertilisers. 93% of sulfur produced is used for making sulfuric acid.
- Sulfur forms the maximum number of allotropes (over 30) and many of them are cyclic compounds with ring sizes varying from 6–20.
- Sulfur was extracted earlier from sulfur deposits, but this method has been obsolete since the late 20^{th} century. Today, almost all of the elemental sulfur (~97%) is produced from natural gas and petroleum as a byproduct from its sulfur-containing contaminants. Another 2% is obtained from coal gassification processes.
- Sulfur is the fourth major plant nutrient after N, P and K. About 12.5 million tons of sulfur was applied as fertilisers worldwide in 2015.
- Sulfur is a component of almost all proteins, present in the amino acids, cysteine (having SH group) and methionine (having $S–CH_3$ group). Disulfide bonds are very important for building the tertiary structure of many proteins and are largely responsible for the mechanical strength and insolubility of proteins such as keratin, found in the hair.
- Sulfur in the organic form is present in the vitamins biotin (B_7) and thiamine (B_1). Sulfur is also an important part of many enzymes and in antioxidant molecules such as glutathione peroxidase and thioredoxin.
- Sulfonamides which are structural analogues of *para*-aminobenzoic acid are a class of bacteriostatic drugs (which stops bacteria multiplication).
- Thionyl chloride is a chlorinating and dehydrating agent while sulfuryl chloride is a chlorinating agent similar in reactivity to Cl_2.
- Sulfur tetrafluoride and related compounds are useful as reagents for selective conversion of C=O to CF_2 groups.

- In the early literature the spelling ‘sulphur’ was dominant, especially in Europe and Asia over the spelling ‘sulfur’. The IUPAC and the nomenclature committee of the Royal Society of Chemistry, UK adopted the spelling ‘sulfur’ in 1990 and 1992 respectively.

Unique properties of selenium and its compounds

- Selenium is a photoconductor, a material that changes light energy into electrical energy. Furthermore, it becomes better at this conversion as the intensity of light increases. Once an essential material present in photocopiers, it has largely been replaced by organic photoconductors.
- Although selenic acid (H_2SeO_4) resembles sulfuric acid, it is a more powerful oxidant, capable of releasing Cl_2 from concentrated HCl and of dissolving gold to form gold (III) selenite.
- Selenium is incorporated in proteins through the amino acids selenocysteine and selenomethionine in which it replaces the sulfur atom of cysteine and methionine, respectively.
- Selenocystiene which is the 21st amino acid found in living systems, is present in at least 54 human proteins. Selenoproteins are essential components of metabolic pathways, including thyroid hormone metabolism, antioxidant defense systems or immune functions.
- Red selenium is a Se_8 macrocycle similar to the sulfur allotrope S_8.
- Grey selenium, the most stable form, is a semiconductor that conducts electricity better in the light than in the dark, and is used in photovoltaic cells.
- Most of the selenium produced worldwide is isolated from the mud that forms at the anode during the electrolytic refining of copper.
- Combined with bismuth, it has replaced lead in plumbing brasses since the 1990s to meet lead-free environmental standards. EnviroBrass, a type of modern brass for making brass drinking water faucets and shower heads is made of a lead free alloy (SeBiLOY) which contains 2% Bi and 1% Se along with Cu (86%–88%), tin (4%–6%) and zinc (4%–6%). A combination of bismuth and selenium provides the same beneficial effect on machinability as does lead in addition to safety from lead poisoning.
- The grey form of selenium also converts electric current from AC to DC, because of which it is a component in rectifiers.
- The largest worldwide use of selenium, especially as selenium dioxide is in manufacturing of red and pink coloured glass, where it is used as a dopant. The ubiquitous red traffic light owes its colour to selenium additives, sometimes along with CdS.
- SeO_2 is a well known oxidising agent by itself or along with other oxidants as catalyst. During oxidation, SeO_2 gets reduced to red elemental selenium and gets precipitated due to the poor solubility of selenium.
- Selenium is a well established essential trace element with a recommended dietary intake of 55 μg per day for adults (in both USA and Europe). This amount can be supplied by a single dried Brazil-nut. The upper limit for the intake of selenium has been fixed by FDA as 400 μg per day.
- Although selenium is not toxic and is considered a micronutrient, many of its compounds, such as hydrogen selenide (H_2Se) are quite toxic.
- Woolins’ reagent, $[PhPSe_2]_2$, is a useful selenating agent that converts certain carbonyl groups (C=O) to the selenocarbonyl group (C=Se).