CHAPTER 24: Group IV

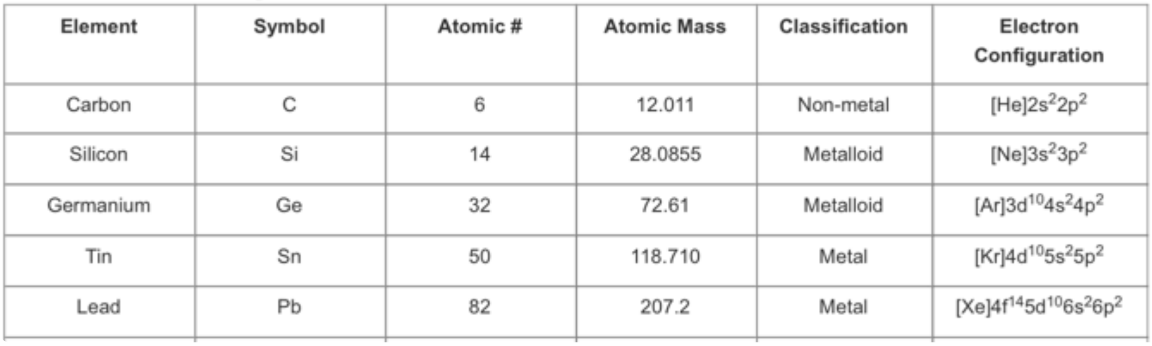
Learning outcomes:

(a) outline the variation in melting point and in electrical conductivity of the elements and interpret them in terms of structure and bonding.
(b) describe and explain the bonding in, molecular shape and volatility of the tetrachlorides.
(c) describe and explain the reactions of the tetrachlorides with water in terms of structure and bonding.
(d) describe and explain the bonding, acid-base nature and thermal stability of the oxides of oxidation states II and IV.
(e) describe and explain the relative stability of higher and lower oxidation states of the elements in their oxides and aqueous cations including, where relevant, E values.

24.1 Physical Properties of Group IV Elements

Introduction to Group IV elements

1) Group IV elements are p-block elements with a characteristic outer shell configuration of ns^2np^2.



Element	Symbol	Atomic #	Atomic Mass	Classification	Electron Configuration
Carbon	C	6	12.011	Non-metal	$[He]2s^22p^2$
Silicon	Si	14	28.0855	Metalloid	$[Ne]3s^23p^2$
Germanium	Ge	32	72.61	Metalloid	$[Ar]3d^{10}4s^24p^2$
Tin	Sn	50	118.710	Metal	$[Kr]4d^{10}5s^25p^2$
Lead	Pb	82	207.2	Metal	$[Xe]4f^{14}5d^{10}6s^26p^2$

2) Group IV elements exist in two different oxidation states, **+2 and +4 states**. The +2 state compounds become more stable going down the Group while the +4 state compounds become less stable going down the Group. The reasons will be explained later.

Variation in structure

1) Going down the Group, there is a trend of non-metal to semi-metal to metal.

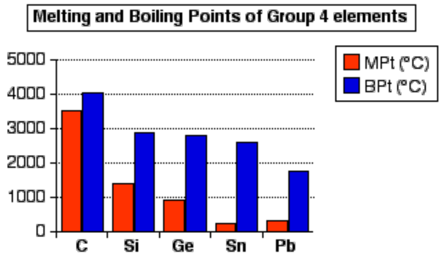
2) **Carbon** exists in two different allotropes, diamond and graphite(*for the structures, refer to Chapter 5*), they are both giant covalent compounds.

3) **Silicon** and **germanium** have the same type of structure as diamond. They are both giant covalent compounds.

4) There are two types of **tin**:
   i. Grey tin or alpha-tin has a giant covalent structure, same as the one diamond has.
   ii. White tin or beta-tin(the more common one) has a distorted 12-co-ordinated metallic structure with metallic bonds.

5) **Lead** is a metal and it has a simple 12-co-ordinated metallic structure.

Variation in melting and boiling point



1) From carbon to germanium, the melting point **decreases**. This is because going down the Group, the **covalent bond length increases**. Longer bonds have lower bond energies. Less energy is required to overcome the covalent bonds, therefore melting point is lower.

2) i. Tin has a **lower melting point** than lead. This is because in the solid state, metallic tin has a distorted structure, resulting the **metallic bonds being less effective**. This factor outweighs the larger atomic size of lead. Therefore, less energy is required to overcome the metallic bond in tin.
   ii. Tin has a **higher boiling point** than lead, this is because in the liquid state, there is no ordered arrangement between the atoms. The **larger atomic size** of lead resulting the metallic bond being **longer and weaker**. Therefore, less energy is required to overcome the metallic bond in lead.

Variation in electrical conductivity

1) The electrical conductivity increases down the Group as the nature of the elements changes from non-metal to semi-metal to metal.

2) i. **Carbon(diamond form)** **does not conduct electricity**. This is because all the outer electrons are used in covalent bonding. Therefore there are no free and moving electrons to conduct the electricity.
   ii. However, **carbon(graphite form)** **conducts electricity**. This is because in the graphite structure each atom donates one electron to a delocalised system of electrons(*for more details, refer to Chapter 5*). Therefore there are free electrons present to conduct the electricity.

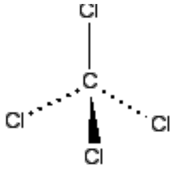
3) **Silicon** and **germanium** are **semi-conductors**, whose conductivity is between that of metals and non-metals.

4) **Tin** and **lead** are metals, hence they are **good conductors of electricity**. This is because each atom involved in metallic bonding donates electrons into the sea of delocalised electrons. Therefore free electrons are present to conduct electricity.

24.2 Group IV Chlorides

Introduction to Group IV chlorides

1) All Group IV chlorides are simple covalent molecules which exist as liquid at room temperature with the general formula of $X\text{Cl}_4$, where X = A Group IV element.



2) All of them have a tetrahedral shape with a bond angle of 109.5°. A typical example is carbon tetrachloride:

3) The boiling point of Group IV tetrachlorides **increases** down the Group. This is because as the number of electrons increases, more temporary dipoles can be set up between the molecules. Hence the van der Waals' forces of attraction are stronger.

   Note: Carbon tetrachloride, CCl_4 is an exception.

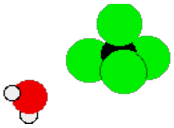
	B Pt (°C)
CCl_4	76
SiCl_4	57
GeCl_4	87
SnCl_4	114
PbCl_4	decomposes at 105

Reaction with water, H_2O(Hydrolysis)

1) i. **Carbon tetrachloride** does not react with water. If carbon tetrachloride is added to water, two immiscible layers are formed.

   ii. There are two reasons for this:

   - Carbon is a small atom cluttered with big chlorine atoms. This causes the water molecule to have **difficulty approaching the bulky molecule**. Even if the water molecule successfully gets in, the transition state is very cluttered and unstable, the activation energy is very high.
   - Also, there **isn't any convenient orbital** on the carbon that the lone pair of the water molecule can attaches itself to.



2) i. **Silicon**, **germanium** and **tin tetrachlorides**(also called silicon(IV) chloride, germanium(IV) chloride and tin(IV) chloride) hydrolyses in water to form an oxide and steamy fumes of hydrogen chloride.

$$X\text{Cl}_4 + 2\text{H}_2\text{O} \rightarrow X\text{O}_2 + 4\text{HCl} \quad ; \text{where } X = \text{Si/Ge/Sn/Pb}$$

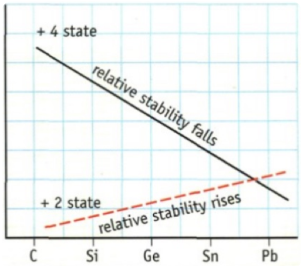
   ii. Unlike carbon tetrachloride, this is possible because the Group IV atoms are bigger, the molecules are less bulky.

3) **Lead(IV) chloride** behaves similarly as silicon, germanium and tin tetrachlorides. However, the heat released during the reaction would tend to decompose lead(IV) chloride, $PbCl_4$ to lead(II) chloride, $PbCl_2$.

$$PbCl_4 \rightarrow PbCl_2 + Cl_2$$

4) The hydrolysis reactions become **more vigorous** going down the Group. This is because going down the Group, the ***X*-Cl bond becomes longer**. A longer bond has a lower bond energy and it is more easy to be broken.

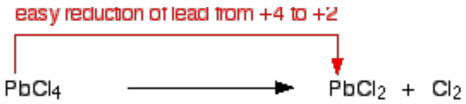
Relative stability of the oxidation states of Group IV chlorides



1) A fact about Group IV elements is as such:
   - i. Going down the Group, compounds with a **+2** oxidation state Group IV element become more stable.
   - ii. Going up the Group, compounds with a **+4** oxidation state Group IV element become more stable.

2) This means that the +4 oxidation is less favourable down the Group while the +2 oxidation state is more favourable down the Group.

3) From carbon to tin, the +4 oxidation state is more stable than +2 oxidation state. However, for lead, the +2 oxidation is more stable. This is why lead(IV) chloride decomposes to lead(II) chloride on heating.



24.3 Group IV Oxides

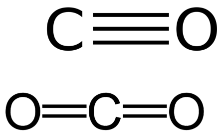
Introduction to Group IV oxides

1) Group IV elements form two types of oxides: **monoxide and dioxide**. This is because the elements have two possible oxidation states, +2 and +4.

2) Monoxides include:
   - i. carbon monoxide, CO
   - ii. silicon monoxide/silicon(II) oxide, SiO
   - iii. germanium monoxide, GeO

  iv. tin(II) oxide, SnO
  v. lead(II) oxide, PbO

3) Dioxides include:
  i. carbon dioxide, CO_2
  ii. silicon dioxide/silicon(IV) oxide, SiO_2
  iii. germanium dioxide, GeO_2
  iv. tin(IV) oxide, SnO_2
  v. lead(IV) oxide, PbO_2



4) i. **Carbon monoxide** and **carbon dioxide** is a simple covalent molecule which exists as a gas at room temperature.

5) i. **Silicon monoxide** and **silicon dioxide** has a giant covalent structure(*for more details, refer to Chapter 5*).
  ii. The difference in structure between carbon dioxide and silicon dioxide is due to silicon atom being larger. When the atom is larger, the overlapping of p orbitals to form a π bond is less complete and a π bond as such is very unstable. So, silicon bonded with the oxygen atoms in such a way that π bonds are not formed.

6) **Germanium monoxide** and **germanium dioxide** have the same structure as silicon monoxide and silicon dioxide respectively.

7) **Tin(II) oxide** and **tin(IV) oxide** have a giant ionic lattice structure with ionic bonds between the Sn^{2+}/Sn^{4+} and O^{2-}.

8) **Lead(II) oxide** and **lead(IV) oxide** have a giant ionic lattice structure with ionic bonds between the Pb^{2+}/Pb^{4+} and O^{2-}.

Group IV monoxides

1) **Carbon monoxide** is a **slightly acidic oxide** which is only slightly soluble in water. It reacts with hot and concentrated sodium hydroxide, NaOH to give a solution of sodium methanoate.

$$CO + NaOH \rightarrow HCOONa$$

2) i. **Germanium**, **tin** and **lead monoxides** are **amphoteric oxides**. They can act as an acid as well as a base.

ii. *<u>As a base</u>* : $XO + 2HCl \rightarrow XCl_2 + H_2O$; where X = Ge/Sn/Pb
iii. *<u>As an acid</u>* : $XO + 2NaOH \rightarrow Na_2XO_2 + H_2O$; where X = Ge/Sn/Pb

Group IV dioxides

1) **Carbon dioxide** is a **slight acidic oxide** which is only slightly soluble in water. It reacts with cold sodium hydroxide, NaOH to give either sodium carbonate or sodium hydrogencarbonate solution, depending on the proportion.

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \quad \text{or}$$
$$CO_2 + NaOH \rightarrow NaHCO_3$$

2) **Silicon dioxide** is **weakly acidic**. It reacts with hot and concentrated sodium hydroxide to give sodium silicate. However, it does not react with water due to the strong covalent bonds need to be broken.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

3) i. **Germanium**, **tin** and **lead dioxides** are **amphoteric oxides**. They can act as an acid as well as a base.
ii. *<u>As a base</u>* : $XO_2 + 4HCl \rightarrow XCl_4 + 2H_2O$; where X = Ge/Sn/Pb
For germanium and tin dioxides, hot and concentrated hydrochloric acid is used. However, for lead dioxide, cold hydrochloric acid is used. This is because lead dioxide will decompose if the temperature increases.
iii. *<u>As an acid</u>* : $XO_2 + 2NaOH \rightarrow Na_2XO_3 + H_2O$; where X = Ge/Sn/Pb
For all reactions, hot and concentrated sodium hydroxide is used.

Thermal stability of Group IV oxides

1) **Carbon**, **silicon** and **germanium oxides** will **disproportionate on heating**.

$$2XO \rightarrow X + XO_2 \qquad ; \text{where } X = \text{C/Si/Ge}$$

2) **Tin** and **lead monoxide** are **stable on heating**.

3) This reflects the stability of +2 oxidation state of Group IV elements increases down the Group.

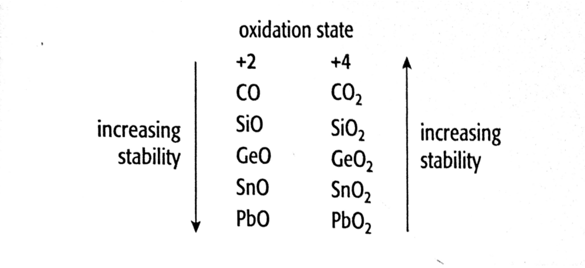
4) All dioxides are stable on heating **except lead dioxide(lead(IV) oxide)**. This decomposes on heating to give lead(II) oxide and oxygen.

$$2PbO_2 \rightarrow 2PbO + O_2$$

5) This shows the stability of +4 oxidation state of Group IV elements decreases down the Group.

24.3 Relative Stability of +2 and +4 Oxidation States

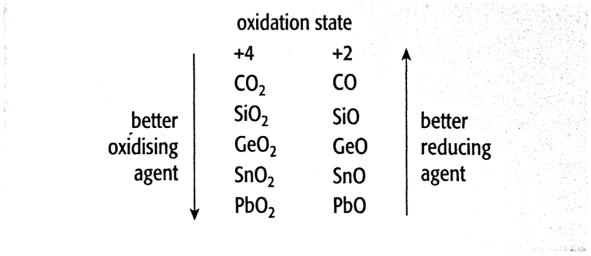
The stability of +2 and +4 oxidation states



increasing stability ↓

+2	+4
CO	CO_2
SiO	SiO_2
GeO	GeO_2
SnO	SnO_2
PbO	PbO_2

↑ increasing stability



better oxidising agent ↓

+4	+2
CO_2	CO
SiO_2	SiO
GeO_2	GeO
SnO_2	SnO
PbO_2	PbO

↑ better reducing agent

1) i. +4 compounds at the top of the Group is more stable than at the bottom.
   ii. +2 compounds at the bottom of the Group is more stable than at the top.

2) For carbon, carbon dioxide(+4) is more stable than carbon monoxide(+2). Therefore, carbon monoxide is **readily oxidised** to carbon dioxide, it is a **good reducing agent**. For example, it reduces iron(III) ions to iron.

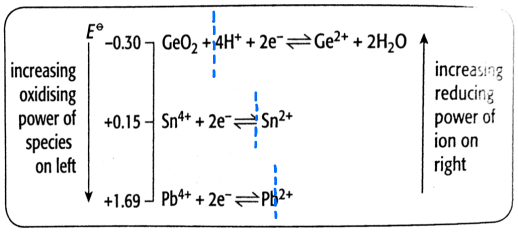
$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

3) For lead, lead(II) oxide(+2) is more stable than lead(IV) oxide(+4). Therefore, lead(IV) oxide is **readily reduced** to lead(II) oxide, it is a **good oxidising agent**. For example, lead(II) oxide oxidises hydrochloric acid to chlorine.

$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$$

4) Between these extremes, there is a gradual change in stability of the +2 compared with the +4 state.
   i. The +4 state of germanium compounds is more stable than the +2 state. Therefore, germanium(II) compounds are good reducing agents.
   ii. The +4 state of tin compounds is slightly more stable than the +2 state. Therefore, tin(II) compounds are weak reducing agents.

5) This can be interpreted from the E° values of the ions of Group IV elements in aqueous solutions.



6) i. The more positive the value of E°, the easier it is to reduce the species on the left of the half-equation.
ii. The less positive the value of E°, the easier it is to oxidise the species on the right of the half-equation.