

GROUP (VI) ELEMENTS

- These are: carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).

Periodic Trends

- Carbon is typically a non-metal; silicon and germanium are metalloids while tin and lead are typically metals. Therefore, within the group, the nature of bonding in the lattices of the elements changes from covalent to metallic.

Ways in which carbon behaves as a non-metal

- It does not react with dilute acids to liberate hydrogen
- It forms covalent oxides and chlorides
- It reacts with oxygen to form carbon dioxide which is acidic
- It does not form cations in solution.

Ways in which lead behaves as a non-metal

Lead behaves as non-metal when it is in the +4 oxidation state. In this state lead;

- Forms a covalent chloride that is readily hydrolysed in water
- Forms a gaseous covalent hydride (plumbane)
- Forms an acidic oxide of lead(IV) oxide
- Does not form positive ions of lead(IV)

Ways in which lead behaves as metal

Lead behaves as metal when

- It reacts with dilute acids to liberate hydrogen
- Forms salts of lead(II) cations
- It forms ionic oxides in the +2 oxidation state.

The melting points of the elements generally decrease down the group.

Element	C	Si	Ge	Sn	Pb
Melting point (°C)	3730	1410	937	232	327

- Carbon, silicon and germanium have giant molecular structure with a three dimensional network of strong covalent bonds.
- The decrease in melting point is due to the decrease in the strength of the covalent bonds as the atomic radius increases and the nuclear attraction for the bonding electrons decreases.
- Tin and lead have giant metallic structures with lattices of cations in delocalized electron clouds. These metallic bonds are weaker compared to the covalent bonds in elements above in the group.
- The metallic bonds in lead are stronger than those in tin because of the difference in the arrangement of the cations. Lead has a face-centred cubic packing while tin has a tetragonal packing.

Electropositivity (metallic character) of the elements increases down the group.

- This is because, as the atomic radius increases down the group, the nuclear attraction for the outermost electrons decreases thus the tendency of the atoms to lose electrons increase.
- Note: A decrease in the ionization energies of the elements in the group illustrates an increase in the metallic character.

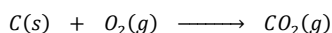
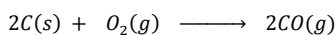
The elements form compounds in two oxidation states.

- i.e. +2 and +4 oxidation states. All the atoms of the elements have four electrons on the valence shell.
- The +4 oxidation state involves the use of all the four valence electrons in formation of a chemical bond. The +2 oxidation state involves the use of only two of the four electrons in formation of the chemical bond. Down the group, the stability of the +4 oxidation state decreases while that of the +2 oxidation state increases. For example tin(II) oxide is unstable and tin(IV) oxide is stable whereas lead(II) oxide is stable and lead(IV) oxide is unstable.
- Thus down the group, a pair of electrons in the s-orbital of the valence shell becomes less available to take part in chemical bonding, leaving only the pair in the p-orbital to bond.
- This is called the *inert pair effect*. And because of this, lead forms many of its compounds in +2 oxidation state.
- Inert pair effect results from the poor shielding effect of the electrons in the d-orbitals, so the electrons in the s-orbital of the valence shell experience increased nuclear attraction, decreasing their tendency to form bonds.

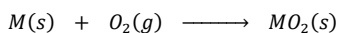
Reactions of group (IV) elements

Reaction with air

- Carbon burns when heated in limited air to form carbon monoxide and in excess air to form carbon dioxide.

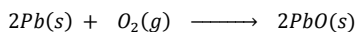


- Silicon, germanium and tin when heated react with air to form their corresponding dioxides



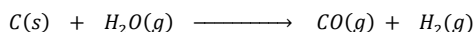
where M = Si, Ge or Sn

- Heated lead reacts with air to form lead(II) oxide

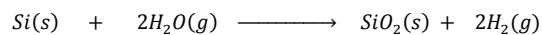


Reaction with water

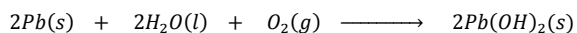
- Heated carbon reacts with steam to form carbon monoxide and hydrogen gas.



- Heated silicon reacts with steam to form silicon dioxide and hydrogen gas

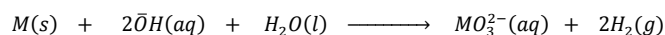


- Germanium and tin do not react with water at any condition
- Lead reacts with soft water in the presence of air to form lead(II) hydroxide

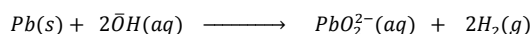


Reaction with caustic alkalis

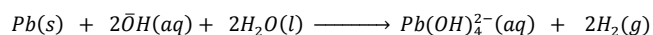
- Carbon does not react with alkalis at any condition.
- The rest of the compounds react with hot concentrated alkalis. Silicon forms silicates, germanium forms germanate(IV) and tin forms stannate(IV), Lead forms plumbate(II) and hydrogen gas respectively



where M = Si, Ge or Sn



Or



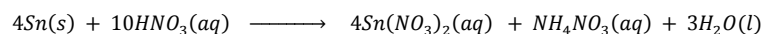
Reaction with acids

With dilute acids

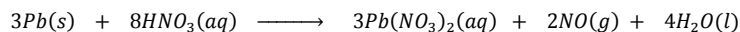
- Carbon, silicon and germanium do react with dilute acids. (Non-metals do not displace hydrogen from dilute acids)

Dilute nitric acid

- Tin is oxidised by cold dilute nitric acid to tin(II) nitrate and the acid reduced to ammonium nitrate and water

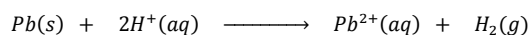


- Lead is oxidised by cold dilute nitric acid to lead(II) nitrate and the acid reduced to nitrogen monoxide and water



Dilute sulphuric and hydrochloric acids

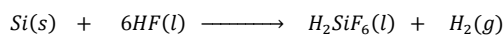
- Both metals react with cold dilute acids to form the corresponding salts and hydrogen



- The reaction of lead with these acids is very slow because of the insolubility of the lead(II) sulphate and lead(II) chloride in water which coat the metal and prevent much reaction

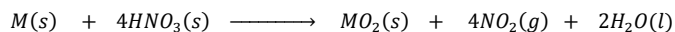
With concentrated acids

- Silicon has no reaction with mineral acids. However, it reacts with hydrofluoric acid to form hexafluorosilicic acid and hydrogen gas



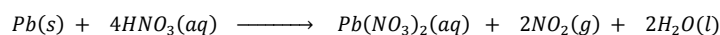
Concentrated nitric acid

- Carbon, germanium, and tin are oxidised by hot concentrated nitric acid to their corresponding dioxides and the acid reduced to nitrogen dioxide and water



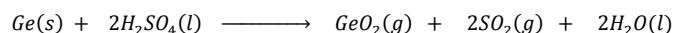
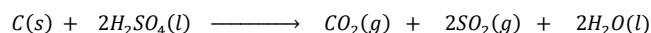
where M = C, Ge or Sn

- Lead is oxidised by cold concentrated nitric acid to lead(II) nitrate and the acid reduced to nitrogen dioxide and water

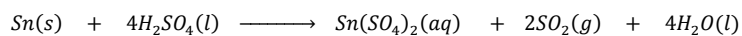


Concentrated sulphuric acid

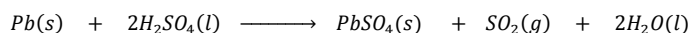
- Carbon and germanium are oxidised by hot concentrated sulphuric acid to their corresponding dioxides and the acid reduced to sulphur dioxide and water



- Tin is oxidised by hot concentrated sulphuric acid to tin(IV) sulphate and the acid reduced to sulphur dioxide and water



- Lead is oxidised by hot concentrated sulphuric acid to lead(II) sulphate and the acid reduced to sulphur dioxide and water



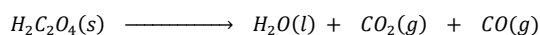
Compounds of group (IV) elements

Oxides

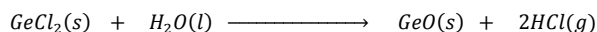
Monoxides (MO)

Preparation

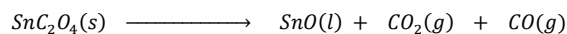
- Carbon monoxide: by dehydration of oxalic acid by concentrated sulphuric acid



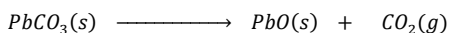
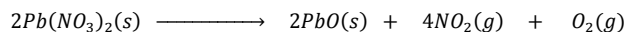
- Germanium monoxide (germanium(II) oxide): by hydrolysis of germanium(II) chloride



- Tin(II) oxide: by heating tin(II) oxalate in the absence of air



- Lead(II) oxide: by heating lead(II) nitrate or carbonate



Reactions of monoxides

With alkalis

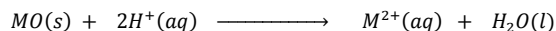
- Carbon monoxide reacts with hot concentrated alkalis to form methanoates
- Germanium(II) oxide, tin(II) oxide and lead(II) oxide react with hot concentrated alkalis to form germanate(II), stannate(II) and plumbate(II) salts respectively



where M = Ge Sn or Pb

With acids

- Carbon monoxide does not react with acids
- Germanium(II) oxide, tin(II) oxide and lead(II) oxide react warm with dilute mineral acids to form their corresponding salts and water



where M = Ge Sn or Pb

- The reaction of lead(II) oxide with dilute hydrochloric acid and sulphuric acid is slow due to formation of the insoluble lead(II) chloride and sulphate that prevent further reaction. When warm hydrochloric acid is used, the reaction occurs faster due to the solubility of lead(II) chloride in hot water.

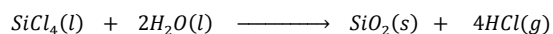
Dioxides (MO₂)

Preparation

- Carbon dioxide: by the action of dilute acids on carbonates



- Silicon dioxide: by hydrolysis of silicon tetrachloride



- Germanium dioxide: by hydrolysis of germanium tetrachloride



- Tin(IV) oxide: by hydrolysis of tin(IV) chloride



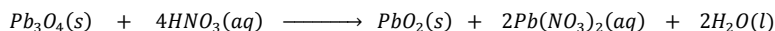
- Or: action of hot concentrated nitric acid on tin



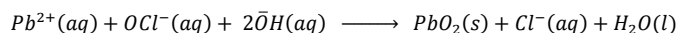
- Lead(IV) oxide: by hydrolysis of lead(IV) chloride



- Or: action of hot dilute nitric acid on trilead tetraoxide



- Or: oxidation of lead(II) ions by calcium hypochlorite in the presence of calcium hydroxide and heat. (Sodium hypochlorite and sodium hydroxide can do)



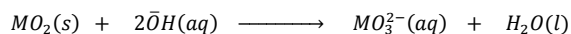
Properties of dioxides

- Carbon dioxide is the only gaseous dioxide and the rest are solids. Due to its low molecular mass and simple molecular structure with discrete molecules, the carbon dioxide molecules are held by weaker Van der Waals forces that required little energy to break.
- Silicon dioxide is a solid with a high melting point. This is because it has a giant molecular/ covalent structure in which each silicon atom is bonded to four oxygen atoms by strong covalent bonds in a three dimensional network. These many strong covalent bonds need a lot of energy to break

Reactions of dioxides

With alkalis

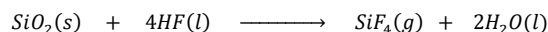
- All dioxides react with hot concentrated alkalis. Carbon dioxide forms carbonates, silicon dioxide forms silicates, germanium(IV) oxide forms germanate(IV), tin(IV) oxide forms stannate(IV) and lead(IV) oxide forms plumbate(IV)



where M = C, Ge, Si, Sn or Pb

Reaction with acids

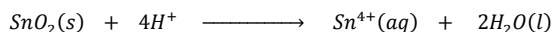
- Carbon dioxide and germanium dioxide do not react with acids
- Silicon dioxide does not react with the sulphuric, nitric or hydrochloric acids but reacts with hydrofluoric acid to form silicon tetrafluoride and water



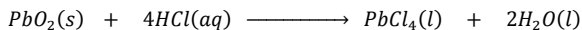
- In the presence of excess acids, silicon tetrafluoride reacts with it to form hexafluorosilicic acid



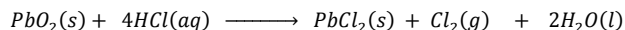
- Tin(IV) oxide reacts with hot dilute mineral acids to form tin(IV) salts and water



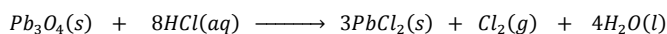
- Lead(IV) oxide reacts with cold concentrated hydrochloric acid to form lead(IV) chloride and water



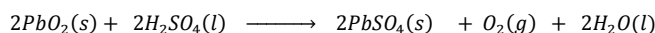
- Lead(IV) oxide reacts with hot concentrated hydrochloric acid to form lead(II) chloride, chlorine gas and water



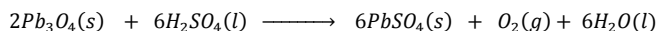
- Trilead tetraoxide also reacts correspondingly



- Lead(IV) oxide reacts with hot concentrated sulphuric acid to form lead(II) sulphate, oxygen and water

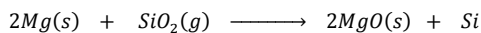
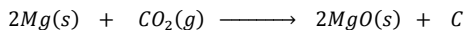


- Trilead tetraoxide also reacts in a similar way

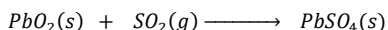


Others reactions

- Burning magnesium reduces both carbon dioxide and silicon dioxide to carbon and silicon respectively and itself oxidised to magnesium oxide



- When sulphur dioxide is passed over heated lead(IV) oxide, lead(II) sulphate is formed.



Acidic nature of the oxides

- The dioxides are more acidic than the monoxides (monoxides are more basic than dioxides). For example

Carbon monoxide is neutral but carbon dioxide is acidic and it reacts with alkalis to form carbonates. Germanium(II) oxide is amphoteric and reacts with both acids and alkalis to form salts while germanium(IV) oxide is acidic, only reacting with alkalis to form salts and not acids.

- The acidity of the oxides decreases down the group as the metallic nature of the elements increases. For example

Carbon dioxide, silicon dioxide and germanium dioxide are acidic and react with alkalis to form the corresponding salts

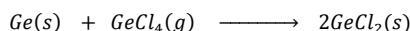
Tin(IV) oxide and lead(IV) oxide are amphoteric, and react with both acids and alkalis to form salts

Chlorides

Dichlorides (MX₂)

Preparation

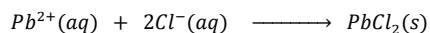
- Carbon and silicon do not form dichlorides. They would be very unstable
- Germanium dichloride: By passing germanium vapour over heated germanium.



- Tin(II) chloride: By heating tin in a stream of dry hydrogen chloride

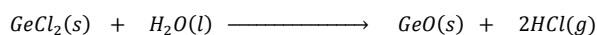


- Lead(II) chloride: By reacting sodium chloride solution and lead(II) nitrate solution



- Reactions with water (hydrolysis)

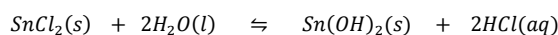
- Germanium dichloride is readily hydrolysed in water to form germanium(II) oxide and hydrogen chloride gas. (fumes in moist air)



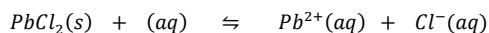
- Tin(II) chloride undergoes slight hydrolysis to form a basic chloride.



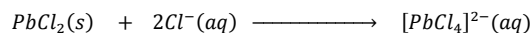
- In excess hot water, tin(II) hydroxide is formed



- Lead(II) chloride is not hydrolysed in water because it is ionic. It is only sparingly soluble



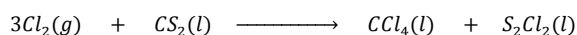
- Lead(II) chloride is however soluble in concentrated hydrochloric acid due to formation of a soluble tetrachloroplumbate(II) complex ion.



Tetrachlorides (MX₄)

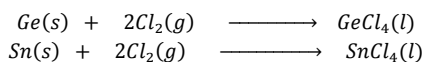
Preparation

- Carbon tetrachloride: By heating a mixture of carbon disulphide and dry chlorine

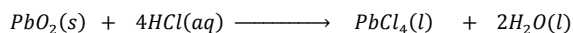


- Germanium, silicon, and tin tetrachlorides are prepared by heating the elements in a stream of dry chlorine





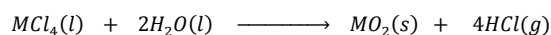
- Lead(IV) chloride (yellow liquid) is obtained by reacting lead(IV) oxide with cold concentrated hydrochloric.



Note: All tetrachlorides of group (IV) elements are: covalent liquids and non-electrolytes

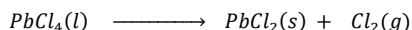
Reaction of the dichlorides with water (hydrolysis)

- Carbon tetrachloride is not hydrolysed by water.
- The rest of the oxides are hydrolysed by water forming hydrogen chloride gas (misty fumes) and the respective dioxides of the elements (precipitates)



where M = Si, Ge, Sn or Pb

- Carbon tetrachloride is not hydrolysed by water while silicon tetrachloride is hydrolysed. The difference in reaction is explained by the lack of empty orbitals in the carbon atom ($1s^2 2s^2 2p^2$) hence cannot accommodate the lone pairs of electrons from the water molecules to cause hydrolysis. The silicon atoms $1s^2 2s^2 2p^6 3s^2 3p^2$ have empty 3d-orbitals that can accept lone pairs of electrons from water molecules to cause hydrolysis
- Note: Due to inert pair effect, the tetrachlorides of tin and lead are less stable compared to their corresponding dichlorides. Hence, lead(IV) chloride will easily decompose on heating to form lead(II) chloride and chlorine gas.

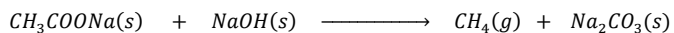


Hydrides

- All the elements form tetrahydrides, (MH_4) which are all gases at room temperature.

Preparation

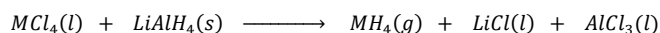
- Methane: By heating sodium ethanoate with soda lime



- Silane: By reacting magnesium silicide with dilute hydrochloric acid



- Germane, stannane and plumbane are prepared by reacting the corresponding tetrachloride with lithium aluminium hydride in dry ether at 0°C .



where M = Ge, Sn or Pb

Reactions

- Silane is decomposed by caustic alkalis solutions (alkaline hydrolysis) to form silicates and hydrogen gas
- $\text{SiH}_4(\text{g}) + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{SiO}_3^{2-}(\text{aq}) + 4\text{H}_2(\text{g})$

Thermal stability

- The thermal stability of the hydrides decrease from methane to plumbane. This is due to a decrease in bond strength. As atomic radius increases from carbon to lead within group(IV), the nuclear attraction for the bonding electrons decreases. This reduces the effective overlap of the orbitals leading to weaker bonds.

The anomalous behaviour of carbon

- Carbon shows many properties in which it differs from the rest of the elements of group (IV).

Why carbon differs from other elements of group (IV)

- Has the smallest atomic radius in the group
- Has the highest electronegativity in the group
- Lacks vacant d-orbitals while other members of the group have them

Ways in which carbon differs from other elements of group (IV)

- It can form multiple bonds between itself and also with atoms of other elements
- Carbon can form long chains while others cannot
- Carbon does not form complexes
- Carbon is the only group(IV) element that forms gaseous oxides, others form solid oxides
- Carbon forms carbon tetrachloride which is not hydrolysed by water while the tetrachlorides of other elements are readily hydrolysed.
- Carbon forms all its stable compounds in the +4 oxidation state

Analysis of lead(II) (Pb^{2+}) ions in solution

Reagent and test	Observation
Sodium hydroxide solution drop wise until in excess	White precipitate soluble in excess
Aqueous ammonia drop wise until in excess	White precipitate insoluble in excess
Dilute hydrochloric/ sodium chloride and heat	White precipitate soluble on heating and re-crystallises on cooling
Dilute sulphuric acid (sodium sulphate) solution	White precipitate (insoluble on heating)
Potassium iodide solution	Yellow precipitate
Dilute potassium chromate by dilute sodium hydroxide	A yellow precipitate soluble in the alkali

GROUP (IV) QUESTIONS

1. Carbon, silicon, tin and lead are elements of group (IV) of the periodic table
 - a. Explain how each of the following properties vary within the group
 - i. Atomic radius
 - ii. Electronegativity
 - iii. Melting point
 - iv. Metallic character
 - b. Carbon as a group (IV) element shows many properties in which it differs from others
 - i. Explain why carbon differs from others
 - ii. State ways in which carbon differs from others
2. C, Si, Ge, Sn and Pb, are elements of group (IV) of the periodic table.
 - a. State
 - i. The two common oxidation states shown by the elements
 - ii. How the stability of the oxidation states vary within the group. Use the oxides of carbon and lead to illustrate your answer
 - b. Explain your answer in a (ii) above
 - c. Discuss the reactions of the chlorides of each element with water
 - d. Write equations for the reactions between
 - i. Lead (IV) oxide and conc. Hydrochloric acid
 - ii. Lead (IV) oxide and warm conc. Hydrochloric acid
3. Explain the following observations
 - a. The melting point of carbon is higher than that of lead
 - b. Carbon dioxide is a gas at room temperature while silicon dioxide is a solid
 - c. Carbon tetrachloride does not react with water while silicon tetrachloride does.
 - d. Lead (II) chloride is sparingly soluble in water but readily dissolves in conc. Hydrochloric acid
 - e. Lead (II) chloride is ionic while lead (IV) chloride is covalent
 - f. Lead (II) bromide exists while lead (IV) bromide does not
4.
 - (a) Briefly describe how carbon dioxide and silicon dioxide can be obtained in the laboratory
 - (b) Compare the behavior of silicon and carbon with
 - i. Oxygen
 - ii. Chlorine
 - iii. Hydrogen chloride
 - iv. Caustic alkali
 - v. Acids
 - (c) Compare the properties of lead(II) chloride and lead(IV) chloride. Explain any differences
 - (d) State what is observed and write equation for the reaction that takes place when a solution of tin(II) chloride in concentrated hydrochloric is added to

- (i) Iron(III) sulphate
 - (ii) Iodine solution
 - (iii) Acidified potassium dichromate(IV)
 - (iv) Acidified potassium manganate(VII)
5. C, Ge, Si, Sn, and Pb are elements of group (IV) of the periodic table. Describe the reactivity of the elements with
- a. Water
 - b. Sodium hydroxide
 - c. Air
 - d. Acids
6. (a) Describe how the oxides of group (IV) elements can be obtained in the laboratory.
- (b) Discuss the reaction of the oxides with
- i. Acids
 - ii. Alkalies
- (c) Using the oxides of group (IV), explain how the
- (i) Acidity of the oxides vary within the group
 - (ii) Stability of the oxidation states of the elements vary within the group
7. (a) Explain ways in which
- (i) Carbon behaves as non-metal
 - (ii) Lead behaves as a non-metal
 - (iii) Lead behaves as metal
- (b) Compare the reaction of carbon and lead with
- (i) Acids
 - (ii) Water
 - (iii) Alkalies
8. (a) State what is observed and write equation for the reaction that takes place when water is added separately to
- (i) Carbon tetrachloride
 - (ii) Silicon tetrachloride
 - (iii) Tin(II) chloride
 - (iv) Tin(IV) chloride
 - (v) Lead(II) chloride
 - (vi) Lead(IV) chloride
- (b) Explain the difference in the observations made in
- (i) (c) (i) and (ii)
 - (ii) (c) (iii) and (iv)

9. State what was observed and write the equations for the reaction when
- (a) Burning magnesium ribbon is lowered in a gas jar of carbon dioxide
 - (b) Lead (II) carbonate is strongly heated
 - (c) Conc. Hydrochloric acid is warmed with lead (IV) oxide
 - (d) A mixture of red lead and conc. Sulphuric acid is heated
 - (e) An aqueous mixture of lead (II) nitrate, calcium hypochlorite and calcium hydroxide is heated
 - (f) Tin is boiled with conc. Nitric acid
 - (g) A mixture of red lead and dilute nitric acid is heated
10. (a) Cold concentrated hydrochloric acid was slowly added to lead(IV) oxide and the mixture stirred
- (i) State what was observed
 - (ii) Write equations for the reaction that took place
- (b) To the product in (a) was added a concentrated solution of ammonium chloride.
- (i) State what is observed
 - (ii) Write equation for the reaction that took place
- (c) Concentrated sulphuric acid was added to the product in (b)
- (i) State what was observed
 - (ii) Write equation for the reaction that took place