

# THE CHEMISTRY OF GROUP IV ELEMENTS

## Electronic structures/ configurations

Element	Atomic number	Configuration
C	6	$1s^2 2s^2 2p^2$
Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$
Pb	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$

From the above electronic configurations, it can be concluded that the outermost electronic configuration of group IV elements is  $ns^2 np^2$ .

### The concept of inert pair effect

The general outermost configuration of group IV elements is  $ns^2 np^2$ .

As **atomic radius increases from carbon to lead**, the *two outermost ns-electrons* experience **increased nuclear attraction** due to **poor screening by the electrons in the d and f-orbitals**. This makes the ns- electrons less available for bonding.

**Inert pair effect is therefore the inability of the two outermost s- electrons of group IV atoms to participate in bonding.**

### Metallic character

Element	Character
Carbon	Non metal
Silicon	Metalloids
Germanium	
Tin	Metals
Lead	

Metallic character increases from carbon to lead. Carbon is a non-metal; silicon and germanium are semi-metals but silicon being more of a non-metal than a metal and germanium being more of a metal than a non-metal. Tin and lead are weakly electropositive metals.

## Bonding and structure

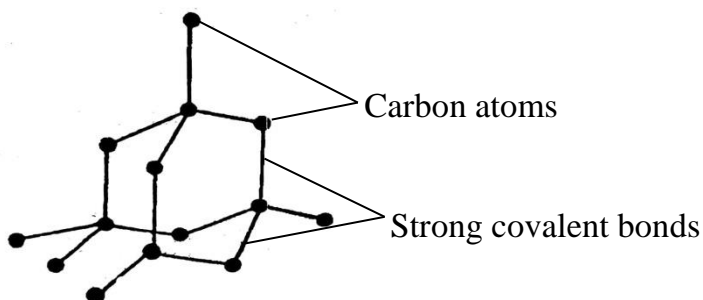
In diamond, each carbon atom is covalently bonded to four other carbon atoms to form a **tetrahedral structure** which is **continuous** to form a **giant molecular structure**.

In graphite, each carbon atom is covalently bonded to three other carbon atoms to form **hexagonal layers** of carbon atoms held together by **weak Van-der-Waals' forces of attraction**.

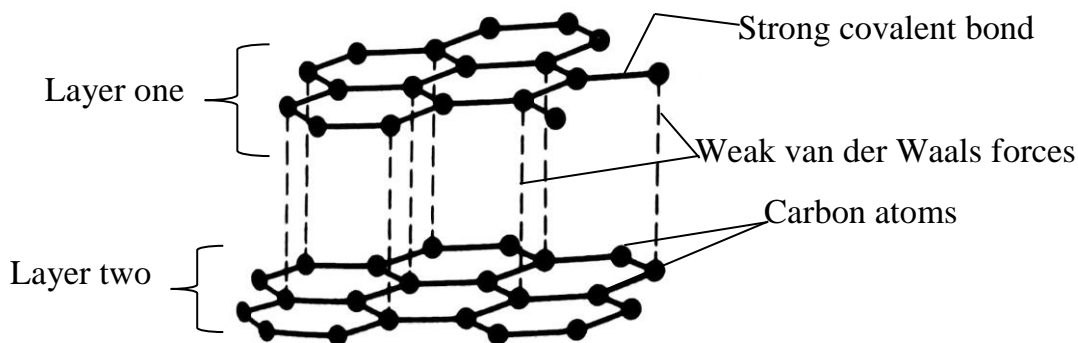
Silicon and germanium have a **giant molecular diamond like structure**. Each **silicon or germanium atom** is covalently bonded to four other atoms to form a **tetrahedral structure** which is **continuous** to form a **giant molecular structure**.

Tin and lead have a **giant metallic structure** in which the atoms are **held by strong metallic bonds**. However, the **metallic bonds in lead are stronger** than tin.

*Diamond*



*Graphite*



## VARIATION IN ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

### 1. Melting point

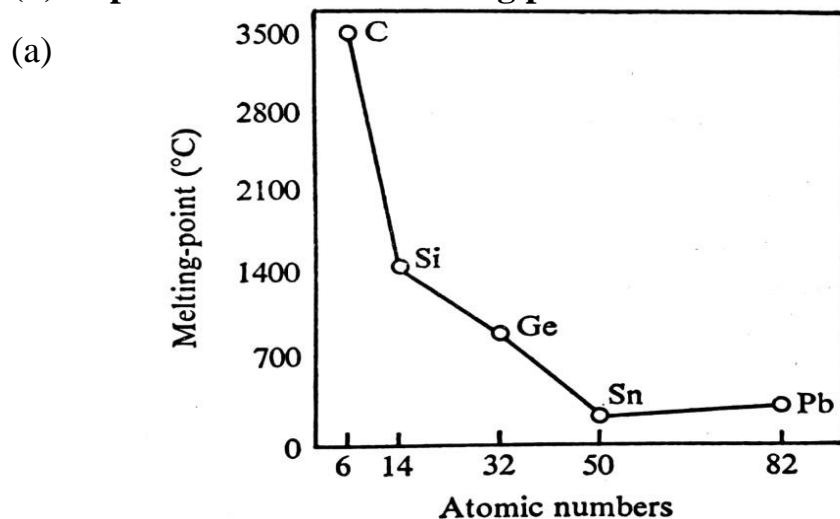
The table below shows the melting points of group II elements

Element	C(diamond)	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Melting points( $^{\circ}\text{C}$ )	3550	1410	937	232	327

(a) Plot a graph of melting point against atomic number

*(You are advised to plot own graph. The graph below is just a sketch and not on scale)*

(b) Explain the trend in melting points of the elements



*(b) Melting point decreases from carbon to tin and then increases slightly from tin to lead.*

*Carbon has the highest melting point because it has a large number of short and strong covalent bonds which require high amount of energy to break before it melts.*

*From carbon to germanium, atomic radius increases, bond length increases, bond strength decreases, and lower amount of energy is required to break the covalent bonds.*

*The further decrease in melting point from germanium to tin is because of weaker metallic bonds in tin.*

*Melting point increases slightly from tin to lead due to increase in metallic bond strength as a result of inert pair effect.*

## 2. Ionization energy

None of the group IV elements forms ions in the +1 oxidation state. This means that first ionisation energy alone is not helpful. However, some of the elements form ions in the +2 and +4 oxidation state.

Therefore total of first and second ionisation energies can be considered or the total of the first four ionisation energies which both a general trend.

### State and explain the trend in ionization energy of the elements

*Ionization energy generally decreases from carbon to lead.*

*This is because from carbon to lead, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases and outer most electrons are far and weakly attracted by the nucleus requiring a low amount of energy to be removed.*

## 3. Electropositivity

*The tendency of an atom of an element to lose its valence electrons to become positively charged.*

*Electropositivity generally increases from carbon to lead because metallic character increases, atomic radius increases and the valence electrons experience a lower nuclear attraction than repulsion hence easily lost.*

## 4. Electrical Conductivity

*Electrical conductivity increases from carbon to lead.*

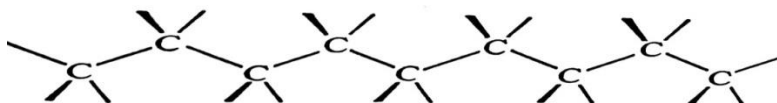
*Graphite is a conductor of electricity although diamond is a non-conductor. Silicon and germanium are semi-conductors. The electrical conductivity of graphite, silicon and germanium increases on heating.*

*Tin and lead are good conductors. The electrical conductivity of tin and lead decreases on heating.*

### The catenation of carbon

Catenation is the ability of an atom to form long chains of identical atoms. Carbon is one of the few elements which can catenate. Carbon atoms are able to link covalently to form stable chains which may contain from two up to very large numbers of carbon atoms. In these chains, only two valencies of carbon are used, leaving other two free to link with other elements or other carbon atoms (forming branched chains). The chains act as a backbone or skeleton on which an enormous number of organic compounds can be formed. For an element to be able to catenate, it must have a valency of at least two and be able to form relatively strong covalent bonds with itself.

Briefly, carbon is able to catenate due to its small atomic radius that enables it to form stable and strong carbon-carbon bonds



### OXIDATION STATES

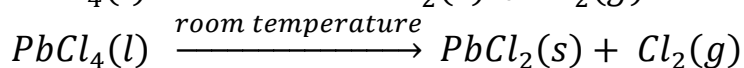
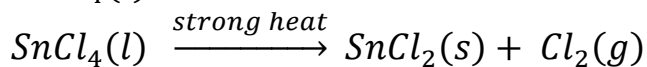
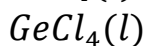
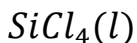
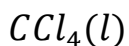
**Qn. (a) State the common oxidation states exhibited by elements in group IV of the Periodic Table.**

**(b) Discuss the stability of the oxidation states in (a) from carbon to lead using the;**

- (i) Chlorides**
- (ii) Oxides**

*(a) Group IV elements exhibit the +2 and +4 oxidation states*

**(b)(i) Considering the tetrachlorides;**



*Carbon tetrachloride, silicon tetrachloride and germanium tetrachloride exist and are stable to heat.*

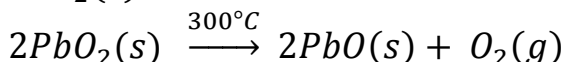
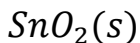
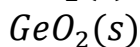
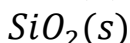
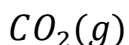
*Tin(IV) chloride on strong heating decomposes to form tin(II) chloride and chlorine.*

*Lead(IV) chloride is unstable. It decomposes on simple warming or even at room temperature to form lead(II) chloride and chlorine. This means that the +2 oxidation state is more stable than the +4 oxidation state for compounds of lead.*

*Carbon(II) chloride and silicon(II) chloride do not exist but tin(II) chloride and lead(II) chloride exist with increasing stability down the group*

***Therefore stability of +2 oxidation state increases from carbon to lead whereas stability of +4 oxidation state decreases from carbon to lead.***

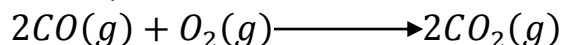
**(ii) Considering the dioxides**



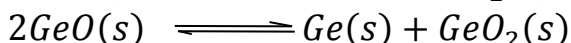
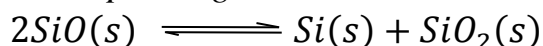
*Carbon dioxide, silicon(IV) oxide, Germanium(IV) oxide and tin(IV) oxide exist and are stable to heat.*

*Lead(IV) oxide exists but decomposes on heating to form lead(II) oxide and oxygen implying that the +2 oxidation state is more stable in lead.*

*Carbon monoxide exists but easily oxidise to more stable carbon dioxide*



*Silicon(II) oxide and germanium(II) oxide are unstable and undergo disproportionation to form corresponding stable dioxides and the elements.*



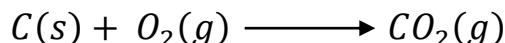
***Therefore stability of +2 oxidation state increases from carbon to lead whereas stability of +4 oxidation state decreases from carbon to lead***

***This variation in stability of the two oxidation states is due to inert pair effect.***

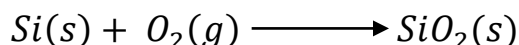
## CHEMICAL PROPERTIES OF THE ELEMENTS

### 2. Describe the reactions of group IV elements with air.

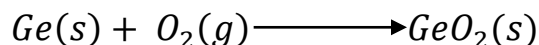
**Strongly heated carbon** reacts with air to form **carbon dioxide**.



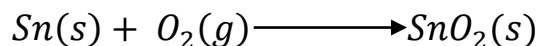
**Strongly heated silicon** reacts with air to form **silicon(IV) oxide**.



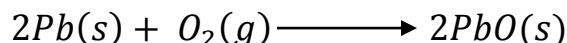
**Strongly heated germanium** reacts with air to form **germanium(IV) oxide**.



**Strongly heated tin** reacts with air to form **tin(IV) oxide**.

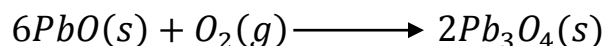


**Heated lead** burns in air to form **lead(II) oxide**



*Note; Lead does not form lead(IV) oxide because its compounds are more stable in the +2 oxidation state.*

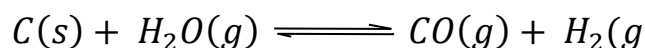
However when heated up to 470°C, the lead(II) oxide is oxidised further to dilead(II) lead(IV) oxide.



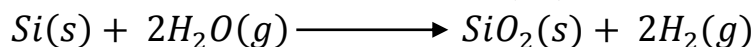
### 3. Describe the reactions and conditions under which group IV elements react with water

Carbon, silicon, germanium and tin **do not react with cold water**

**Red hot carbon** reacts **slowly and reversibly** with **steam** to form **carbon monoxide** and **hydrogen**. *The gaseous mixture of carbon monoxide and hydrogen is called water gas*

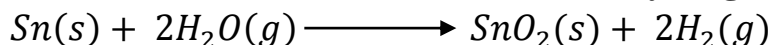


**Red hot silicon** reacts with **steam** to form **silicon(IV) oxide** and **hydrogen**.

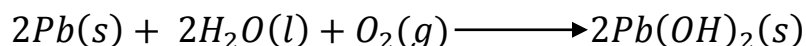


Germanium **does not react** with water under any condition.

**Red hot tin** reacts with **steam** to form **tin(IV) oxide** and **hydrogen**.



Lead reacts with **soft water containing dissolved oxygen** to form **lead(II) hydroxide**.



### 4. Describe how group IV elements react with;

(a) **dilute acids**

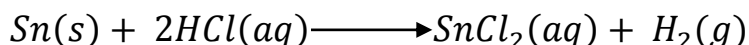
(b) **concentrated acids**

(a) **dilute acids**

(i) *Dilute hydrochloric acid.*

Carbon, silicon and germanium **do not react** with dilute hydrochloric acid.

Tin reacts with **cold dilute hydrochloric acid** to form **tin(II) chloride** and **hydrogen** gas.



Lead also reacts **slowly with dilute hydrochloric acid** and the **reaction stops** due to **formation of insoluble lead(II) chloride**.



**(ii) Dilute sulphuric acid**

Carbon, silicon and germanium **do not react** with dilute sulphuric acid.

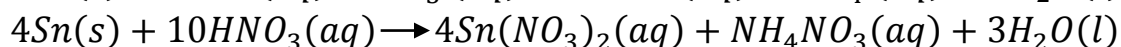
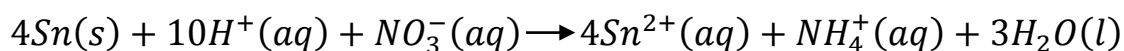
Tin **does not react** with sulphuric acid.

Lead reacts **slowly with dilute sulphuric acid** and the **reaction stops** due to **formation of insoluble lead(II) sulphate**.

**(iii) Dilute nitric acid**

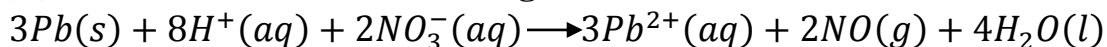
Carbon, silicon and germanium **do not react** with dilute nitric acid

**Cold dilute nitric acid** oxidises tin to **tin(II) nitrate**, itself reduced to **ammonium nitrate** and **water**.



*C.f Fe and Zn*

**Dilute/ moderately concentrated/ half concentrated nitric acid** oxidises lead to **lead(II) nitrate**, itself reduced to **nitrogen monoxide** and **water**.

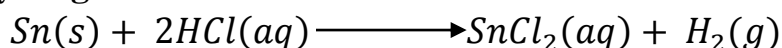


**(b) concentrated acids**

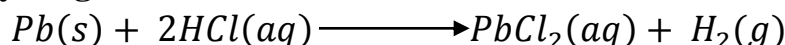
**(i) concentrated hydrochloric acid.**

Carbon, silicon and germanium **do not react** with concentrated hydrochloric acid.

Tin reacts vigorously with **hot concentrated hydrochloric acid** to form **tin(II) chloride** and **hydrogen**.

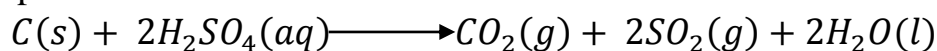


Lead also reacts with **boiling concentrated hydrochloric acid** to form **lead(II) chloride** and **hydrogen**.



**(ii) concentrated sulphuric acid**

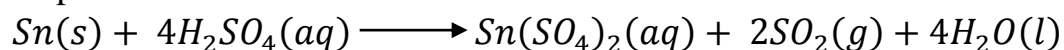
**Hot concentrated sulphuric acid** oxidises carbon to carbon dioxide and itself reduced to Sulphur dioxide and water.



Silicon **does not react** with concentrated sulphuric acid

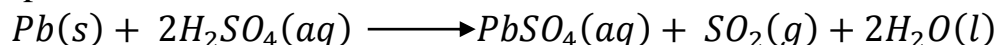
Germanium **does not react** with concentrated sulphuric acid.

**Hot concentrated sulphuric acid** oxidises tin to **tin(IV) sulphate** and itself reduced to Sulphur dioxide and water.





**Hot concentrated sulphuric acid** oxidises lead to **lead(II) sulphate** and itself reduced to Sulphur dioxide and water.



(iii) **concentrated nitric acid**

**Hot concentrated nitric acid** oxidises carbon to **carbon dioxide** and itself reduced to **nitrogen dioxide** and water

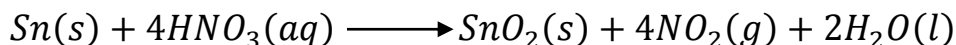


Silicon **does not react** with concentrated nitric acid

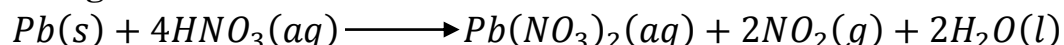
Germanium is oxidised by **hot concentrated nitric acid** to **germanium(IV) oxide** and itself reduced to **nitrogen dioxide** and water.



Tin is oxidised by **hot concentrated nitric acid** to **tin(IV) oxide** and itself reduced to **nitrogen dioxide** and water.



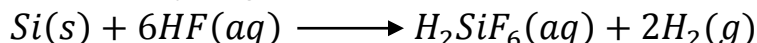
Lead is oxidised by **hot concentrated nitric acid** to **lead(II) nitrate** and itself reduced to **nitrogen dioxide** and water.



**Other acids.**

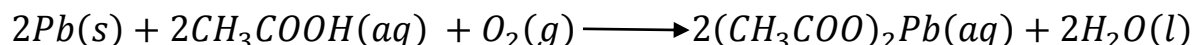
(i) **hydrofluoric acid**

Silicon is the only element that reacts with hydrofluoric acid to form hexafluorosilicic acid and hydrogen.



(ii) **ethanoic acid**

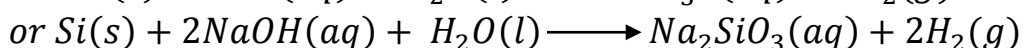
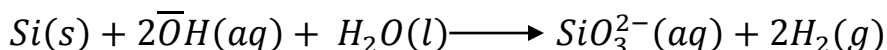
Lead reacts with ethanoic acid in **presence of air** to form lead(II) ethanoate and water.



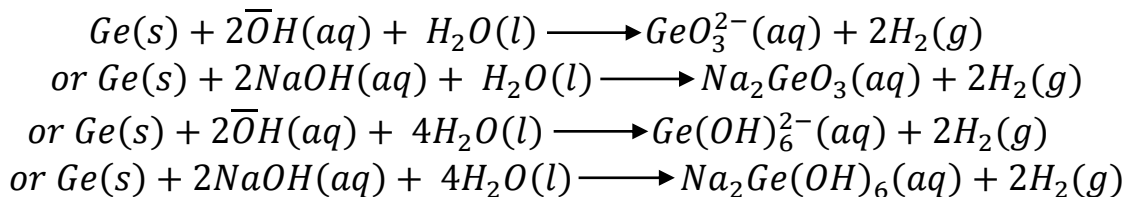
## 5. Describe the reaction of group IV elements with dilute and concentrated sodium hydroxide.

Carbon **does not react** with dilute or concentrated sodium hydroxide solution.

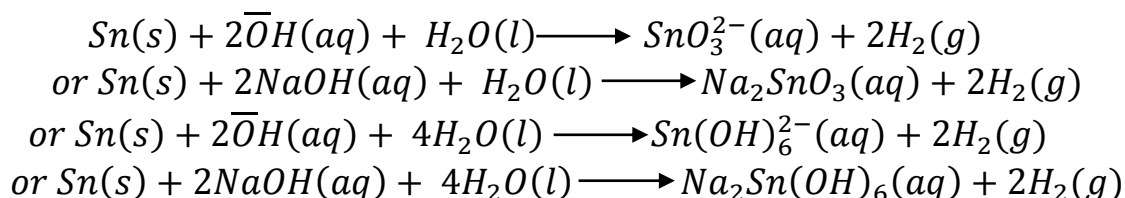
Silicon reacts with **both dilute and hot concentrated sodium hydroxide** to form **sodium silicate** and **hydrogen gas**



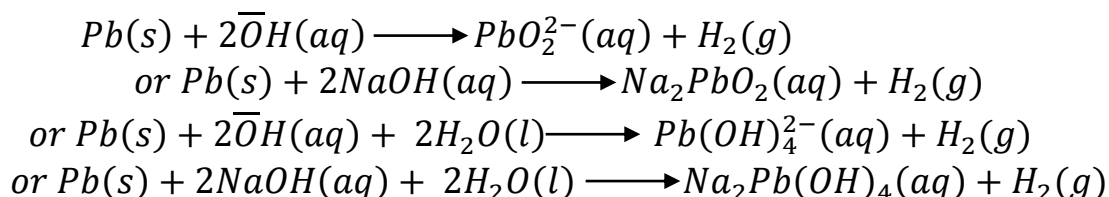
Germanium reacts with **hot concentrated sodium hydroxide** to form **sodium germate(IV)** and **hydrogen gas**



Tin reacts with **hot concentrated sodium hydroxide** to form **sodium stannate(IV)** and **hydrogen gas**



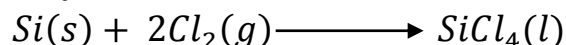
Lead reacts with **hot concentrated sodium hydroxide** to form **sodium plumbate(II)** and **hydrogen gas**



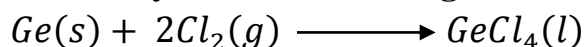
## 6. Describe the reactions of group IV elements with chlorine

Carbon **does not react with** chlorine.

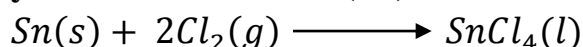
**Heated silicon** reacts with **dry chlorine** to form **silicon tetrachloride**.



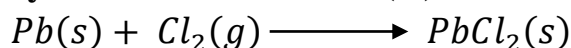
**Heated germanium** reacts with **dry chlorine** to form **germanium(IV) chloride**.



**Heated tin** reacts with **dry chlorine** to form **tin(IV) chloride**.

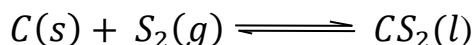


**Heated lead** reacts with **dry chlorine** to form **lead(II) chloride**.

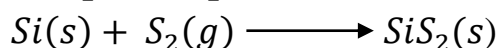


## 7. Discuss the reactions of group IV elements with sulphur

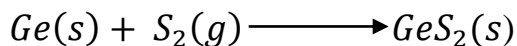
**Heated carbon** reacts with **sulphur vapour** to form **carbon disulphide**



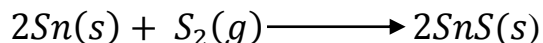
**Heated silicon** reacts with **sulphur vapour** to form **silicon(IV) sulphide**



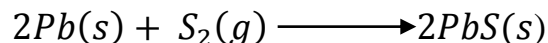
**Heated germanium** reacts with **sulphur vapour** to form **germanium(IV) sulphide**



**Heated tin** reacts with **sulphur vapour** to form **tin(II) sulphide**



**Heated lead** reacts with **sulphur vapour** to form **lead(II) sulphide**



## COMPOUNDS OF GROUP IV ELEMENTS

### THE DIOXIDES

Formula of the oxide	$\text{CO}_2$	$\text{SiO}_2$	$\text{GeO}_2$	$\text{SnO}_2$	$\text{PbO}_2$
Physical state	Gas	Solids			
Bonding and structure	Simple molecular	Giant covalent	Giant covalent	Giant ionic	Giant ionic

#### (a) Structure and bonding

Carbon dioxide has a simple molecular structure with discrete molecules held by weak Van der Waals' forces.

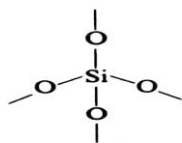
Silicon dioxide and germanium dioxide have giant covalent structures with a 3-dimensional network of strong covalent bonds.

Tin(IV) oxide and lead(IV) oxide have giant ionic structures held by strong ionic bonds.

**Qn. Briefly explain why carbon dioxide is a gas whereas silicon(IV) oxide is a solid at room temperature.**

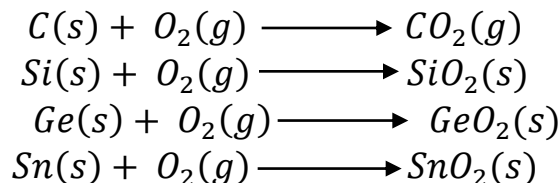
*Carbon dioxide is non-polar. It has discrete molecules with a simple molecular structure held by weak van der Waals forces of attraction which are easily overcome at room temperature keeping them far apart from each other.*

*However, in silicon(IV) oxide, each silicon atom is covalently bonded to four oxygen atoms to form a tetrahedral structure which is continuous to form a giant molecular structure with very many strong covalent bonds that keep its molecules very close to each other.*

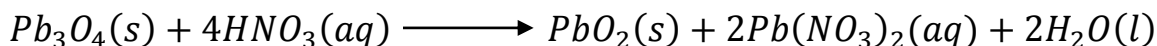


**(b) With relevant equations, describe how the dioxides of Group IV elements can be formed.**

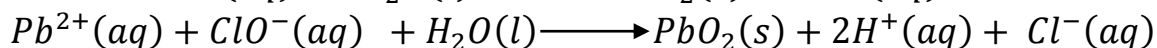
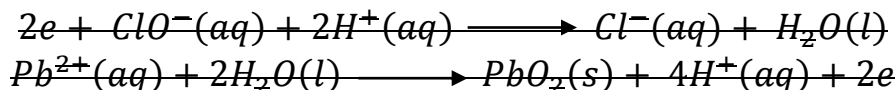
Carbon(IV) oxide, silicon(IV) oxide, germanium(IV) oxide and tin(IV) oxide can be formed by heating the elements in oxygen



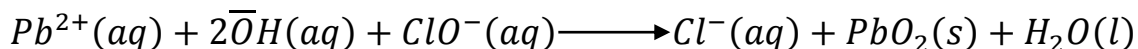
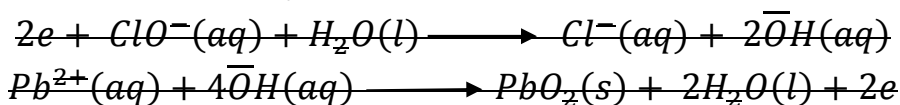
Lead(IV) oxide is formed by the reaction between dilead(II) lead(IV) oxide with **warm** dilute nitric acid.



It can also be prepared by heating a mixture of lead(II) nitrate and sodium chlorate(I) at about 300°C



Lead(IV) oxide can also be prepared by heating a mixture of lead(II) nitrate, calcium chlorate(I) and calcium hydroxide.



**(c) The table below shows the melting points of group IV dioxides.**

**Explain the trend in melting points of the oxides**

Oxide	$CO_2$	$SiO_2$	$GeO_2$	$SnO_2$	$PbO_2$
Melting point of oxide( $^{\circ}C$ )	-56.5	1700	1116	1827	752

*Carbon dioxide has the lowest melting point because it has a simple molecular structure with discrete molecules held by weak Van der Waals forces.*

*Silicon dioxide and germanium dioxide have giant covalent structures with a 3-dimensional network of strong covalent bonds. However, germanium dioxide has a lower melting point than silicon dioxide because germanium has a bigger atomic radius making the covalent bonds in germanium(IV) oxide longer and weaker than those in silicon(IV) oxide.*

*Tin(IV) oxide and lead(IV) oxide have giant ionic structures held by strong ionic bonds. However, lead(IV) oxide has a lower melting point than tin(IV) oxide because the lead(IV) ion has a bigger ionic radius than the tin(IV) ion hence weaker ionic bonds than those in tin(IV) oxide.*

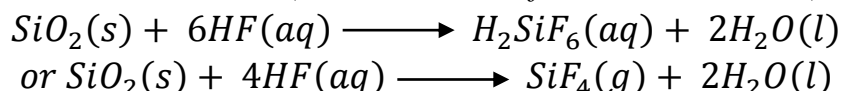
**(d) Discuss the reactivity of the above oxides with**

- (i) dilute and concentrated acids**
- (ii) dilute and concentrated alkalis**

**(i) reaction with dilute acids.**

**Carbon dioxide, germanium(IV) oxide, tin(IV) oxide and lead(IV) oxide do not react with dilute acids.**

Only silicon (IV) oxide reacts with dilute hydrofluoric acid to form hexafluorosilicic acid and water ( *or silicon tetrafluoride and water*)

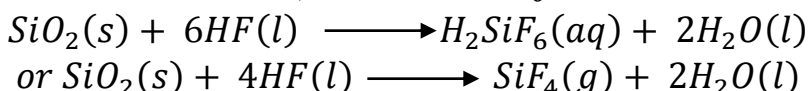


*N.B Silicon dioxide is an acidic oxide hence does not react with other dilute strong acids. However, it reacts with hydrofluoric acid because it is a weak acid the fluorine atom has a very small atomic radius and highly electronegative.*

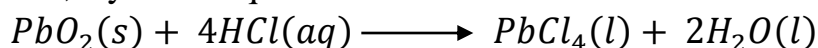
**reaction with concentrated acids**

**Carbon dioxide, germanium(IV) oxide and tin(IV) oxide do not react with concentrated acids.**

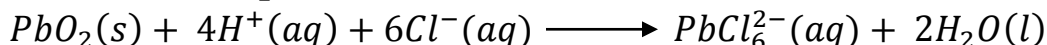
Silicon (IV) oxide reacts with **concentrated hydrofluoric acid** only to form **hexafluorosilicic acid** and **water** ( *or silicon tetrafluoride and water*)



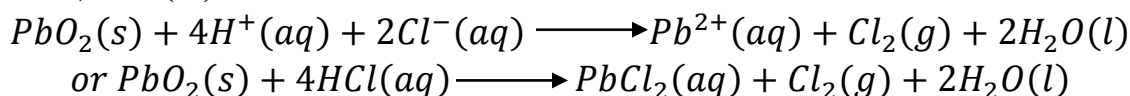
Lead(IV) oxide reacts with **cold concentrated hydrochloric acid** to form **lead(IV) chloride**, a yellow liquid and **water**.



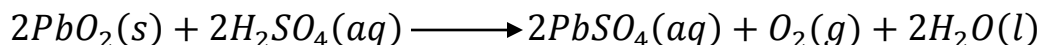
Lead(IV) oxide reacts with **excess cold concentrated hydrochloric acid** to form complex of **hexachloroplumbate(IV) ions** and **water**.



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

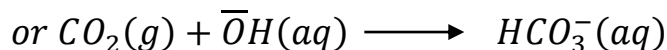
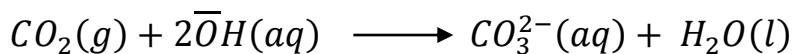


Lead(IV) oxide reacts with **hot concentrated sulphuric acid** to form **oxygen, lead(II) sulphate** and **water**.



**(ii) reaction with dilute alkalis**

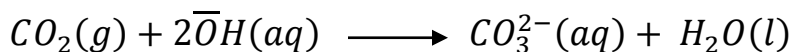
Carbon dioxide reacts with **cold dilute alkalis** to form **a carbonate** and **water** (or a hydrogencarbonate)



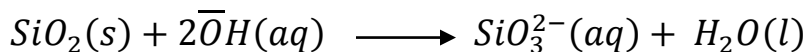
Silicon dioxide, germanium(IV) oxide, tin(IV) oxide and lead(IV) oxide **do not react with dilute alkalis**.

**reaction with concentrated alkalis**

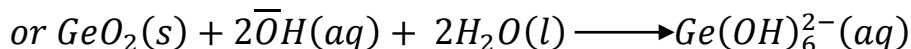
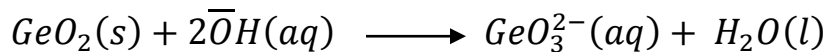
Carbon dioxide reacts with **hot concentrated alkalis** to form **a carbonate** and **water**



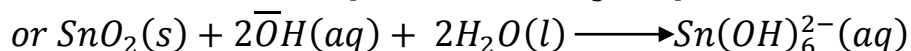
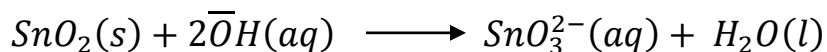
Silicon dioxide reacts with **hot concentrated alkalis** to form **a silicate** and **water**.



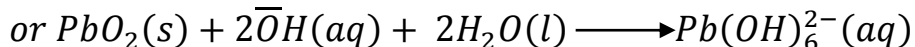
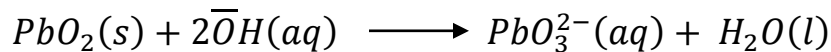
Germanium(IV) oxide reacts with **hot concentrated alkalis** to form **a germate(IV)**.



Tin(IV) oxide reacts with **hot concentrated alkalis** to form **a stannate(IV)**



Lead(IV) oxide reacts with **hot concentrated alkalis** to form **a plumbate(IV)**



**Redox properties of the dioxides**

Group IV dioxides are strong oxidising agents. Lead(IV) oxide is the most powerful oxidising agent among them.

**Qn. State what would be observed and explain your observation in each case when;**

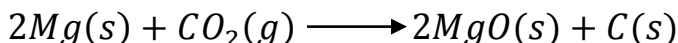
- (a) A piece of burning magnesium is lowered into a gas jar of dry carbon dioxide.**



**Observation;** magnesium continues to burn with a bright white flame forming a white ash and black specks.

**Explanation;**

Magnesium is oxidised by carbon dioxide to magnesium oxide, the carbon dioxide being reduced to carbon.

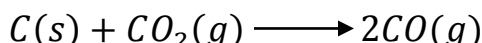


**(b) dry carbon dioxide is passed over red hot charcoal**

**Observation;** A colourless gas is formed.

**Explanation;**

Carbon is oxidised by carbon dioxide to carbon monoxide

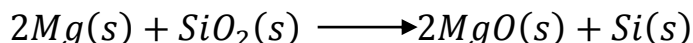


**(c) silicon(IV) oxide is heated with magnesium powder**

**Observation;** The grey and white solid mixture formed a white ash and grey solid.

**Explanation;**

Magnesium is oxidised by silicon dioxide to magnesium oxide, the silicon dioxide being reduced to silicon.

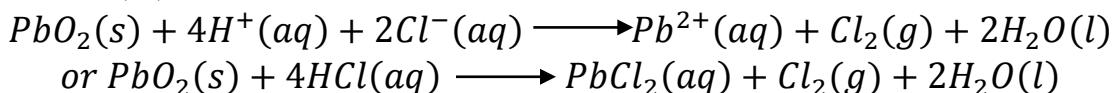


**(d) concentrated hydrochloric acid is added to lead(IV) oxide and the mixture heated.**

**Observation;** The dark brown solid dissolves forming a colourless solution and bubbles of a greenish yellow gas

**Explanation;**

Lead(IV) oxide oxidises concentrated hydrochloric acid to chlorine and itself reduced to lead(II) ions

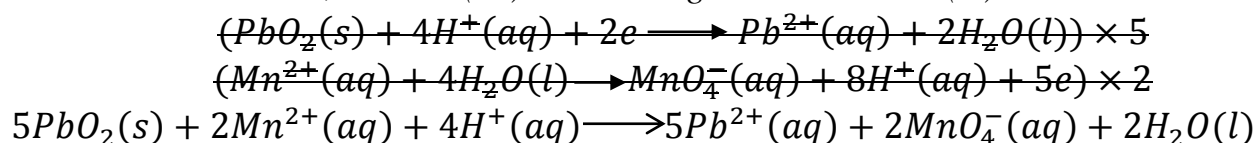


**(e) Lead (IV) oxide is added to a solution containing manganese (II) sulphate and concentrated nitric acid and the mixture boiled.**

**Observation;** Dark brown solid dissolves and the pale pink solution turns purple.

**Explanation;**

Manganese(II) ions are oxidised by lead(IV) oxide to manganate(VII) ions in acidic medium, the lead(IV) oxide being reduced to lead(II) ions.



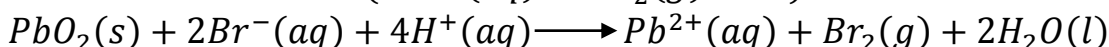
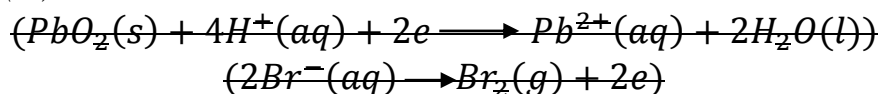


**(f) Lead (IV) oxide is added to sodium bromide solution followed by dilute nitric acid and the mixture heated.**

**Observation;** Dark brown solid dissolves to form a colourless solution and reddish brown vapours.

**Explanation;**

Bromide ions are oxidised by lead(IV) oxide to bromine, the lead(IV) oxide being reduced to lead(II) ions.

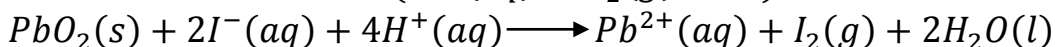
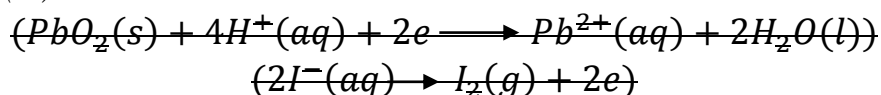


**(g) Lead (IV) oxide is added to potassium iodide solution followed by dilute nitric acid and the mixture heated.**

**Observation;** Dark brown solid dissolves to form a colourless solution and purple vapours.

**Explanation;**

Iodide ions are oxidised by lead(IV) oxide to iodine, the lead(IV) oxide being reduced to lead(II) ions.

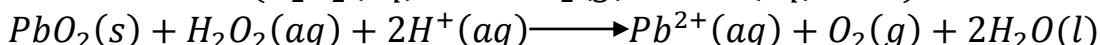
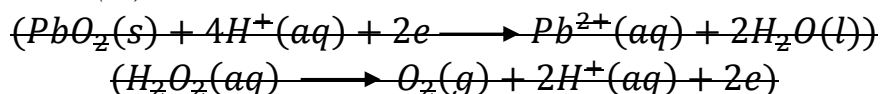


**(h) Dilute nitric acid is added to lead(IV) oxide followed by hydrogen peroxide**

**Observation;** Dark brown solid dissolves forming a colourless solution and bubbles of a colourless gas.

**Explanation;**

Hydrogen peroxide is oxidised by lead(IV) oxide to oxygen and the lead(IV) oxide being reduced to lead(II) ions.

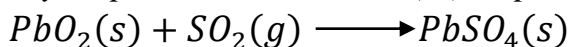


**(i) Sulphur dioxide is passed over heated lead(IV) oxide.**

**Observation;** Dark brown solid forms a white solid

**Explanation;**

Lead(IV) oxide is reduced by sulphur dioxide to lead(II) sulphate .



## THE MONOXIDES

Formula of the oxide	<i>CO</i>	<i>SiO</i>	<i>GeO</i>	<i>SnO</i>	<i>PbO</i>
Physical state	<i>Colourless gas</i>	Brown powder but unstable, readily disproportionates and known only to exist as a gas at 2300°C	A yellow solid but unstable, readily disproportionates	<i>Bluish-black solid</i>	<i>Yellow/orange powder</i>
Nature	<i>Neutral, but slightly acidic</i>	Neutral		<i>Amphoteric</i>	
Bonding and structure	<i>Simple molecular</i>	<i>Simple molecular</i>	<i>Covalent</i>	<i>Giant ionic</i>	<i>Giant ionic</i>

### (a) Structure and bonding

Carbon monoxide has a **simple molecular structure** with **discrete molecules** held by **weak Van der Waals' forces**.

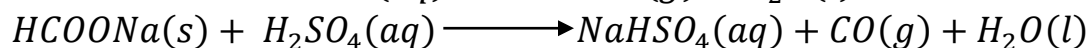
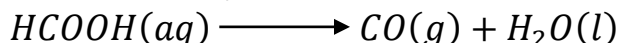
Silicon monoxide also has a **simple molecular structure** with **discrete molecules** held by **weak Van der Waals' forces**.

Germanium(II) oxide is held by **covalent bonds**

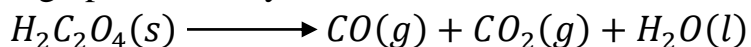
Tin(II) oxide and lead(II) oxide have **giant ionic structures** held by **strong ionic bonds**.

### (b) With relevant equations, describe how the monoxides of Group IV elements can be formed.

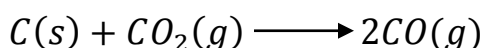
Carbon monoxide is formed by dehydration of methanoic acid with concentrated sulphuric acid. Sodium methanoate may be used instead of methanoic acid.



or carbon monoxide can also be formed by dehydration of oxalic acid with concentrated sulphuric acid and removing the carbon dioxide by passing the gaseous mixture through potassium hydroxide solution.

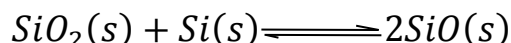


or carbon monoxide can be formed by passing a stream of carbon dioxide over red hot charcoal

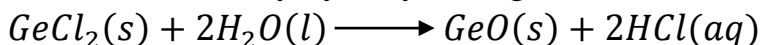


Silicon monoxide is formed when silicon(IV) oxide and silicon are heated in a vacuum at 1527°C. Silicon monoxide vapour is formed and forms a brown powder

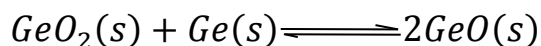
on cooling. However, the brown powder rapidly disproportionates into the dioxide and the metal.



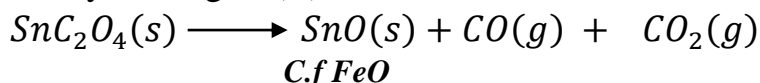
Germanium monoxide is formed by hydrolysis of germanium(II) chloride



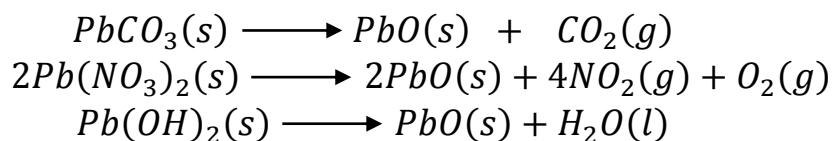
Germanium monoxide can also be formed reduction of germanium(IV) oxide with germanium.



Tin(II) oxide is formed by heating tin(II) oxalate in absence of air.



Lead(II) oxide is formed by heating lead(II) carbonate or lead(II) nitrate or lead(II) hydroxide.



**(c) Discuss the reactivity of the above oxides with**

**(i) dilute and concentrated acids**

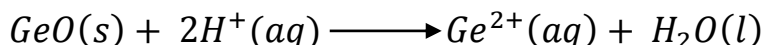
**(ii) dilute and concentrated alkalis**

**(i) reaction with dilute acids.**

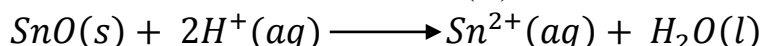
Carbon monoxide is neutral hence **does not react** with dilute acids.

Silicon monoxide is neutral hence **does not react** with dilute acids.

Germanium monoxide reacts with dilute acids to form germanium(II) salts and water.

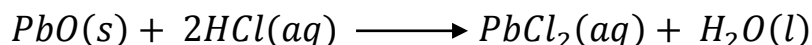


Tin(II) oxide reacts with dilute acid to form tin(II) salts and water.

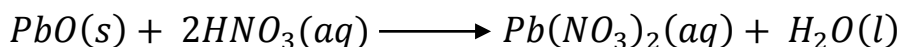


Lead(II) oxide reacts slowly with **cold dilute hydrochloric acid** and **dilute sulphuric acid** and the **reactions stop** due to formation of **insoluble lead(II) chloride** and **insoluble lead(II) sulphate** respectively.

Lead(II) oxide reacts with **hot dilute hydrochloric acid** to form **lead(II) chloride** and **water**.



However, lead(II) oxide reacts with dilute nitric acid to form lead(II) nitrate and water.

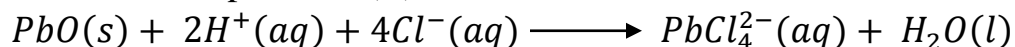


**reaction with concentrated acids**

Carbon monoxide **does not** react with concentrated acids.

Silicon monoxide **does not** react with concentrated acids

Lead(II) oxide reacts with **excess concentrated hydrochloric acid** to form complex of tetrachloroplumbate(II) ions; a colourless solution and water.

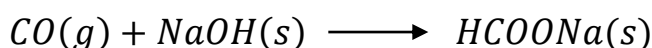


**(ii) reaction with dilute alkalis**

The monoxides **do not react with dilute alkalis.**

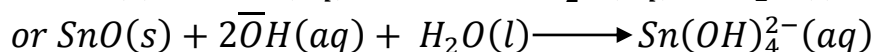
**reaction with concentrated alkalis**

Carbon monoxide reacts with **fused sodium hydroxide** to form **sodium methanoate**

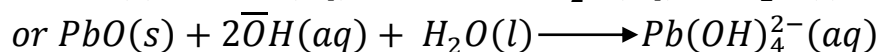
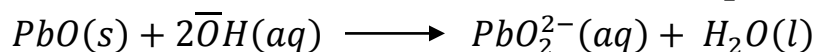


Silicon(II) oxide **does not react** with concentrated alkalis

Tin(II) oxide reacts with **hot concentrated alkalis** to form **stannate(II) ions**



Lead(II) oxide reacts with **hot concentrated alkalis** to form a **plumbate(II)**



**Redox properties of the monoxides**

Carbon monoxide is a reducing agent. It is oxidised in most of its reactions to carbon dioxide.

Tin(II) oxide and lead(II) oxide can be reduced by carbon, carbon monoxide or hydrogen.

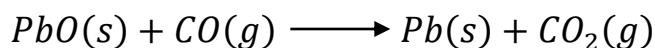
**Qn. State what would be observed and explain your observation in each case when;**

**(a) carbon monoxide is passed over heated lead(II) oxide.**

**Observation;** reddish brown hot solid formed a grey residue.

**Explanation;**

Carbon monoxide reduces lead(II) oxide to lead, itself oxidised to carbon dioxide



**(b) carbon monoxide is passed over heated copper(II) oxide.**

**(c) carbon monoxide is passed over heated iron(III) oxide.**

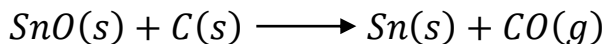
**(d) A mixture of carbon and lead(II) oxide is heated.**

**(e) A mixture of carbon and tin(II) oxide is heated.**

**Observation;** the black solid mixture formed a silvery white solid.

**Explanation;**

Carbon reduces tin(II) oxide to tin, itself oxidised to carbon monoxide

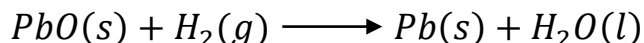


**(f) dry hydrogen is passed over heated lead(II) oxide.**

**Observation;** the reddish brown hot solid formed a grey solid and a colourless condensate.

**Explanation;**

Hydrogen reduces lead(II) oxide to lead, itself oxidised to water.



**(g) dry hydrogen is passed over heated tin(II) oxide.**

### THE TETRACHLORIDES

Formula of the chloride	$\text{CCl}_4$	$\text{SiCl}_4$	$\text{GeCl}_4$	$\text{SnCl}_4$	$\text{PbCl}_4$
Physical state	Colourless liquids				Yellow liquid
Bonding	All covalent				
Volatility	All non-volatile				
Shape	All tetrahedral				

#### (a) Structure and bonding

All the molecules are tetrahedral, covalent and liquids at room temperature. Although their bonds are polar, the molecules as a whole are non-polar due to their symmetry.

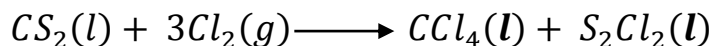
**Qn. Carbon tetrachloride is non-polar yet the carbon-chlorine bond is polar. Explain this observation.**

*Chlorine is more electronegative than carbon. The chlorine atom therefore tends to attract the bonding electrons towards itself hence acquires a partial negative charge ( $\delta^-$ ) and the carbon atom gains a partial positive charge ( $\delta^+$ ). This makes the carbon-chlorine bond polar.*

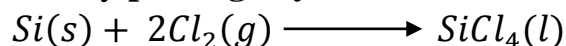
*However, the whole molecule is non-polar because it has a tetrahedral structure in which the chlorine atoms are symmetrically distributed about the carbon atom. This creates equal and opposite dipole moments in all directions that cancel out making the resultant dipole moment zero.*

**(b) With relevant equations, describe how the each of the above tetrachlorides is formed.**

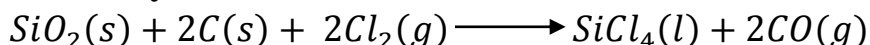
Carbon tetrachloride is formed by **the reaction between chlorine and carbon disulphide in presence of iron(III) chloride or aluminium(III) chloride catalyst at 30°C**



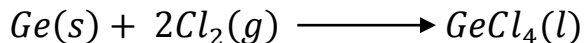
Silicon tetrachloride is formed by **passing dry chlorine over heated silicon.**



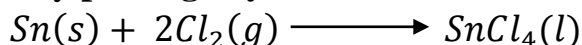
Silicon(IV) chloride can also be prepared by **heating a mixture of silicon(IV) oxide and carbon in a dry current of chlorine.**



Germanium tetrachloride is formed by **passing dry chlorine over heated germanium.**

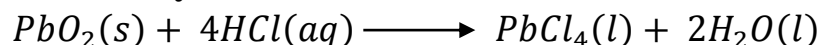


Tin tetrachloride is formed by **passing dry chlorine over heated tin.**



*Heated lead however reacts with dry chlorine to form a more stable lead(II) chloride but not lead(IV) chloride. Therefore this method cannot be used to form lead(IV) chloride.*

Lead(IV) chloride is therefore formed by the **reaction between lead(IV) oxide and cold concentrated hydrochloric acid.**



**(c) The table below shows the boiling points of the tetrachlorides of group IV elements.**

Tetrachloride	$CCl_4$	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
Boiling point( $^{\circ}C$ )	77	58	83	114	Decomposes

**Explain the trend in variation of the melting points of the chlorides.**

*Boiling point decreases from carbon tetrachloride to silicon tetrachloride and then increases to tin tetrachloride.*

*Lead tetrachloride decomposes even at room temperature.*

*The liquids are held by van der Waals' forces of attraction whose strength increases with increase in molecular size and increase in the total number of electrons in the molecules that can be polarised. Silicon tetrachloride has a lower boiling point than carbon tetrachloride because Silicon is much less*



*electronegative than carbon and the silicon tetrachloride molecules have greater repulsive forces than those of carbon tetrachloride.*

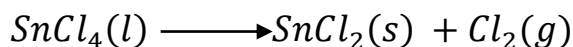
*Lead(IV) chloride is unstable. It decomposes even at room temperature to form more stable lead(II) chloride and chlorine because lead compounds are more stable in +2 oxidation state than the +4 oxidation state due to increase in inert pair effect.*

**(d) Discuss the trend in thermal stability of the tetrachlorides**

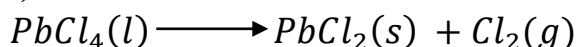
Thermal stability decreases from carbon tetrachloride to lead tetrachloride.

Carbon tetrachloride, silicon tetrachloride and Germanium tetrachloride are thermally stable hence do not decompose.

Tin tetrachloride **decomposes on strong heating** to form **tin(II) chloride and chlorine**.



Lead tetrachloride **decomposes slowly at room temperature and rapidly when heated to form lead(II) chloride and chlorine**.



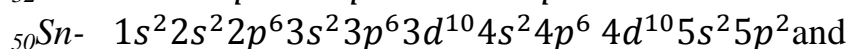
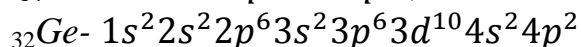
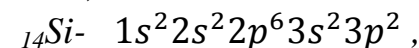
This decrease in thermal stability is because **cationic size increases from carbon(IV) ion to lead(IV) ion, element-chlorine bond length increases and bond strength decreases**. Hence a **decreasing amount of energy** is required to **break the increasingly weakening bonds**.

**Hydrolysis of the tetrachlorides**

Apart from tetrachloromethane, other tetrachlorides are easily hydrolysed (*react with water*) to form dioxides (white solids) apart from lead(IV) oxide which forms a brown solid. This is the same reason why the tetrachlorides fume in moist air.

This is due to presence of empty d- orbitals that accommodate lone pairs of electrons from the oxygen atom in water.

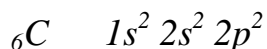
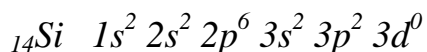
Note; From the electronic configurations;



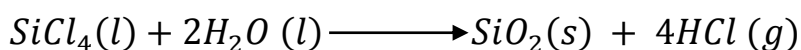
$_{82}\text{Pb}-1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^2$ : Silicon, germanium, tin and lead have empty 3d orbitals, 4d orbitals, 5d orbitals, and 6d orbitals responsible for hydrolysis respectively.



**Explain why silicon (IV) chloride fumes in moist air and also forms a white solid but carbon(IV) chloride does not.**



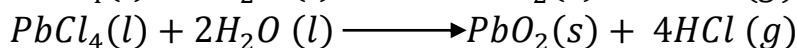
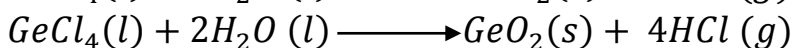
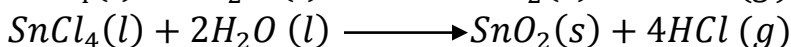
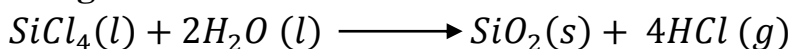
*The silicon atom in silicon tetrachloride has an empty 3d-orbital to accommodate lone pairs of electrons from the oxygen atom in water hence silicon tetrachloride easily undergoes hydrolysis to form silicon(IV) oxide and hydrogen chloride. However, the carbon atom in carbon tetrachloride lacks an empty d-orbital hence does not undergo hydrolysis.*



**(a) Discuss the reactions of tetrachlorides of group IV elements with water.**

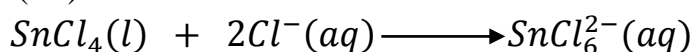
Carbon tetrachloride **does not react** with water.

Other tetrachloride **reacts with water** to form **corresponding dioxides** and **hydrogen chloride gas**.

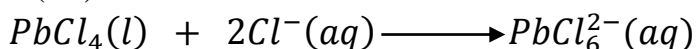


**(b) reaction with acids**

Tin(IV) chloride reacts with cold concentrated hydrochloric acid to form hexachlorostannate(IV) ions.



Lead(IV) chloride reacts with cold concentrated hydrochloric acid to form hexachloroplumbate(IV) ions



**Qn. When cold concentrated hydrochloric acid was added to lead(IV) oxide, a yellow liquid was formed. On addition of excess hydrochloric acid, a yellow solution was formed. Explain this observation.**

## THE DICHLORIDES

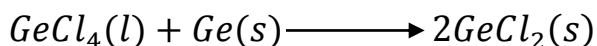
The dichlorides of carbon and silicon do not exist due to decrease in stability of the +2 oxidation state on ascending the group.

Only germanium(II) chloride, tin(II) chloride and lead(II) chloride exist

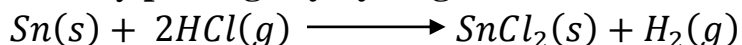
Formula of the chloride	$GeCl_2$	$SnCl_2$	$PbCl_2$
Physical state	<i>All solids</i>		
Bonding	<i>Mainly covalent</i>	<i>Mainly covalent</i>	<i>Mainly Ionic</i>
Shape	<i>V-shaped in vapour phase</i>		

**(a) With relevant equations, describe how the each of the above dichlorides is formed.**

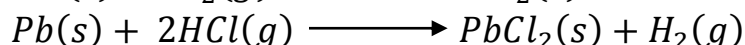
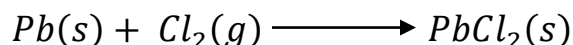
Germanium(II) chloride is formed by **passing germanium(IV) chloride vapour over heated germanium.**



Tin (II)chloride is formed by **passing dry hydrogen chloride over heated tin.**



Lead(II) chloride is formed by **passing dry chlorine or dry hydrogen chloride over heated lead.**

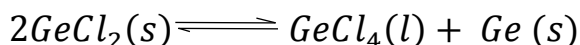


**(b) The melting point of lead(II) chloride is 500°C whereas that of tin(II) chloride is 247°C. Explain this observation.**

The **tin(II) ion has a smaller ionic radius than the lead(II) ion**. Therefore the **tin(II) ion has a higher charge density and polarising power** than the lead(II) ion. This makes **tin(II) chloride mainly covalent** whereas **lead(II) chloride is mainly ionic**. Covalent bonds need a lower amount of energy to break than ionic bonds.

**(c) Discuss the thermal stability of the dichlorides**

Germanium(II) chloride **decomposes on heating to form germanium(IV) chloride and germanium**



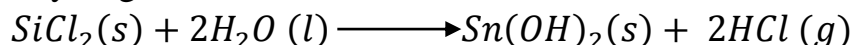
Tin(II) chloride and lead(II) chloride **are stable to heat** hence do not decompose.

**(d) Discuss the difference in solubility of tin(II) chloride and lead(II) chloride in;**

**(i) water**

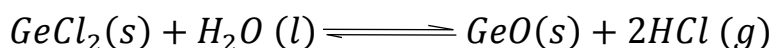
**(ii) concentrated hydrochloric acid**

(i) Tin(II) chloride is **very soluble in cold water** due to hydrolysis to form tin(II) hydroxide and hydrogen chloride.

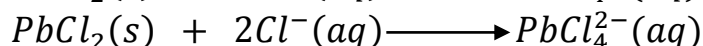
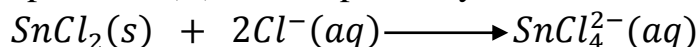


Lead(II) chloride is **sparingly soluble in cold water** because it does not undergo hydrolysis. However, lead(II) chloride is more soluble in hot water.

*Germanium(II) chloride is also hydrolysed by water to form germanium(II) oxide and hydrogen chloride*



(ii) Both tin(II) chloride and lead(II) chloride are soluble in concentrated hydrochloric acid due to formation of soluble complexes of tetrachlorostannate(II) ions and tetrachloroplumbate(II) ions respectively.



## THE HYDRIDES

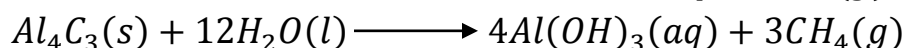
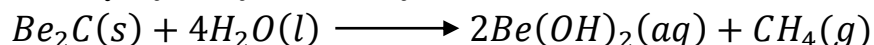
Formula of the hydride	$\text{CH}_4$	$\text{SiH}_4$	$\text{GeH}_4$	$\text{SnH}_4$	$\text{PbH}_4$
Name	Methane	Silane	Germane	Stannane	Plumbane
Physical state	All colourless gases				
Bonding	All covalent				
Structure	All simple molecular				
Shape	All tetrahedral				

### (a) Structure and bonding

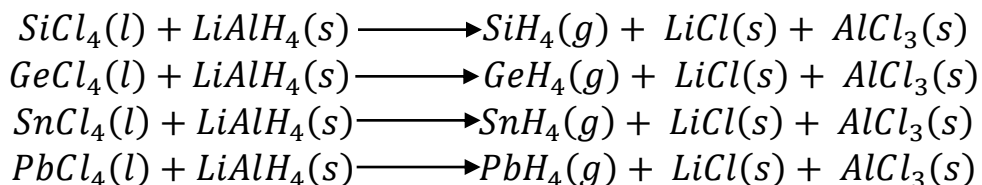
The metals form covalent hydrides with a simple molecular structure, tetrahedral in shape. They are all colourless gases.

### (b) With relevant equations, describe how the hydrides of group IV elements can be formed.

Methane is formed by **hydrolysis of beryllium carbide or aluminium carbide**



Silane, Germane, Stannane and Plumbane are formed by reduction of their corresponding tetrachlorides by Lithium aluminium tetrahydride in presence of dry ether at 0 °C



(c) The table below shows the boiling points of the hydrides of group IV elements.

Hydride	$\text{CH}_4$	$\text{SiH}_4$	$\text{GeH}_4$	$\text{SnH}_4$	$\text{PbH}_4$
Boiling point( $^{\circ}\text{C}$ )	-161.5	-111.9	-88	-52	-13

Explain the trend in variation of the melting points of the hydrides.

*Boiling point increases from methane to plumbane.*

*This is because molecules of the hydrides are covalent and held by weak van der Waals' forces of attraction whose strength increases with increase in molecular weight and molecular size.*

(d) The table below shows the decomposition temperatures of the hydrides of group IV hydrides. Explain the trend in thermo stability of the hydrides.

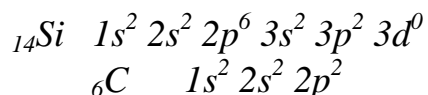
Hydride	$\text{CH}_4$	$\text{SiH}_4$	$\text{GeH}_4$	$\text{SnH}_4$	$\text{PbH}_4$
Decomposition temperature( $^{\circ}\text{C}$ )	800	450	285	150	0

*Since decomposition temperature decreases from methane to Plumbane, thermo stability decreases in the same order. This is because ionic radius increases from carbon(IV) ion to lead(IV) ion, effective overlap of orbitals decreases, bond length increases, bond strength decreases from one hydride to the next. Therefore the amount of energy required to break the bonds decreases.*

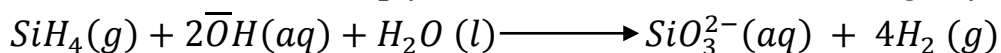
## Hydrolysis of the hydrides

Only silane is immediately hydrolysed by water containing a trace of alkali, but methane and other hydrides are unexpectedly not hydrolysed.

**Qn. Explain why methane does not react with water but silane does.**



*The silicon atom in silicon(IV) hydride has an empty 3d-orbital to accommodate lone pairs of electrons from the oxygen atom in water hence easily undergoes hydrolysis to form silicate ions and hydrogen gas. However, the carbon atom in carbon tetrachloride lacks an empty d-orbital hence does not undergo hydrolysis.*

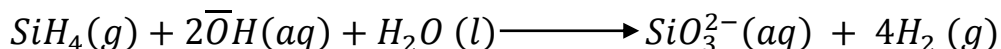


*N.B. An alkaline catalyst is required because the Si—H bond is less polar since hydrogen and silicon have almost equal electronegativity.*

**(a) Discuss the reactions of hydrides of group IV elements with water.**

Methane, germane, stannane and plumbane **do not react** with water

Only silane reacts with water in presence of an alkali to form silicate ions and hydrogen gas



**(b) Discuss the reactivity of the above hydrides with**

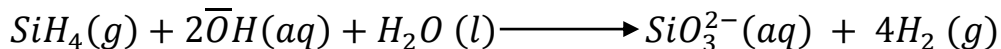
**(i) acids**

**(ii) alkalis**

(i) The hydrides **do not react** with acids

(ii) Methane **does not react** with alkalis

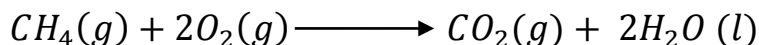
Silane reacts with **aqueous alkalis** to form **silicate ions** and **hydrogen gas**



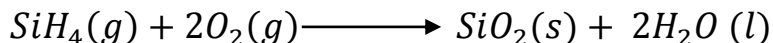
Germane, stannane and plumbane **do not react** with alkalis

**(c) Describe the combustion of group IV hydrides.**

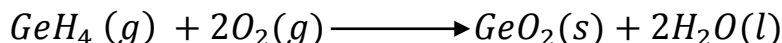
Methane burns in air at **temperatures above 500 °C** to form **carbon dioxide** and **water**.



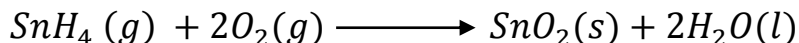
Silane burns **spontaneously in air** to form **silicon dioxide** and **water**.



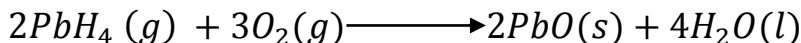
Germane burns in air at **an intermediate temperature** to form **Germanium(IV) oxide and water**



Stannane burns in air to form **tin(IV) oxide and water**



Plumbane burns in air to form **lead(II) oxide and water**



### RED LEAD

**Formular:**  $\text{Pb}_3\text{O}_4$

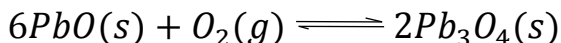
**IUPAC name:** *Dilead(II) lead(IV) oxide*

**Other names:** *trilead tetraoxide, lead(II,II, IV) oxide*

The red solid is a mixed oxide of lead(II) oxide and lead(IV) oxide in a ratio of 2:1 respectively

#### Preparation

It is prepared by heating lead(II) oxide in air at about  $470^\circ\text{C}$  for several hours.



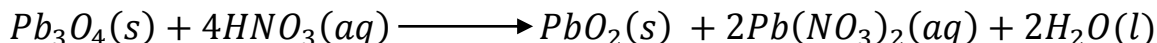
#### Reaction of the mixed oxide with acids

##### (i) Nitric acid

The dilead(II) lead(IV) oxide reacts with warm dilute nitric acid to form lead(IV) oxide, lead(II) nitrate and water. *This reaction is used to prepare lead(IV) oxide.*

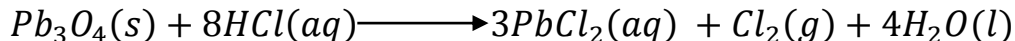
##### Observation:

*The red solid dissolves to form a brown solid and a colourless solution.*



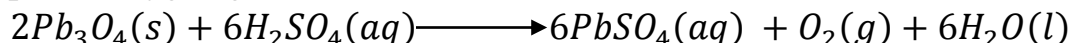
##### (ii) Hydrochloric acid

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



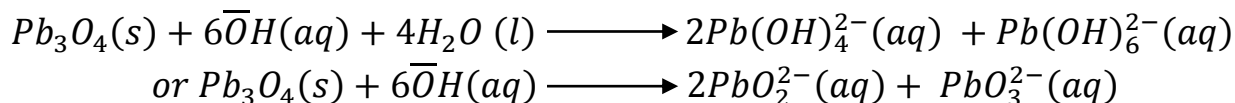
##### (iii) Sulphuric acid

Dilead(II) lead(IV) oxide reacts with *hot concentrated* sulphuric acid to form lead(II) sulphate, oxygen gas and water.



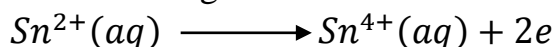
### Reaction with sodium hydroxide.

Dilead(II) lead(IV) oxide reacts with **hot concentrated sodium hydroxide** to form both **plumbate(II)** and **plumbate(IV)** ions.



### Reducing reactions of tin(II) ions

Solutions of tin(II) ions are good reducing agents. During the redox reactions, they are oxidised to tin(IV) ions according to the half-cell reaction below;



However, solutions of tin(II) ions can be reduced by zinc which has a greater negative standard electrode potential than tin

Tin(II) ions reduce each of the following;

- Iron(III) ions to iron(II) ions
- Acidified potassium permanganate solution to manganese(II) ions
- Acidified potassium dichromate solution to chromium(III) ions
- Iodine solution to iodide ions

**Qn. State what would be observed and write equations when tin(II) chloride solution was added to**

- acidified potassium dichromate solution**
- acidified potassium manganate(VII) solution**
- iron(III) chloride solution**

### QUALITATIVE ANALYSIS FOR $Pb^{2+}$ AND $Sn^{2+}$ IONS

The deductions given are general and **DO NOT** depend on any previous tests that could have been done. The tests for tin(II) ions are only required for theory purposes.

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$Pb^{2+}$	Add sodium hydroxide drop wise until in excess	White precipitate soluble in excess to form a colourless solution	$Zn^{2+}, Al^{3+}, Pb^{2+}$ probably present	Lead(II) ions react with hydroxyl ions to form insoluble lead(II) hydroxide. $Pb^{2+}(aq) + 2\overline{OH}(aq) \longrightarrow Pb(OH)_2(s)$ lead(II) hydroxide is amphoteric hence reacts with excess hydroxide ions to form a soluble complex of plumbate ions. $Pb(OH)_2(s) + 2\overline{OH}(aq) \longrightarrow Pb(OH)_4^{2-}$
	Add ammonia solution drop wise until in excess	White precipitate insoluble in excess	$Al^{3+}, Pb^{2+}, Mg^{2+}, Ba^{2+}$ Probably present	Lead(II) ions react with hydroxyl ions to form insoluble lead(II) hydroxide. $Pb^{2+}(aq) + 2\overline{OH}(aq) \longrightarrow Pb(OH)_2(s)$



<b>Pb<sup>2+</sup></b>	Add sodium carbonate solution drop wise until in excess	White precipitate Insoluble in excess	$Mg^{2+}, Ca^{2+}, Ba^{2+}$ $Zn^{2+}, Pb^{2+}$ Probably present	lead(II) ions react with carbonate ions to form insoluble Lead(II) carbonate. $Pb^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow PbCO_3(s)$
	Add dilute sulphuric acid	White precipitate	$Pb^{2+}, Ba^{2+}$ or $Ca^{2+}$ Probably present	lead(II) ions react with sulphate ions to form insoluble lead(II) sulphate. $Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$
	Add dilute sulphuric acid and heat	White precipitate insoluble on heating	$Pb^{2+}$ Present	lead(II) ions react with sulphate ions to form insoluble lead(II) sulphate. $Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$ Lead(II)sulphate is insoluble on heating
	Add dilute hydrochloric acid	White precipitate	$Pb^{2+}$ Present	lead(II) ions react with chloride ions to form insoluble lead(II) chloride. $Pb^{2+}(aq) + 2Cl^{-}(aq) \longrightarrow PbCl_2(s)$
	Add dilute hydrochloric acid and heat/warm/ Boil	White precipitate soluble on heating and reprecipitates on cooling	$Pb^{2+}$ Present	lead(II) ions react with chloride ions to form insoluble lead(II) chloride. $Pb^{2+}(aq) + 2Cl^{-}(aq) \longrightarrow PbCl_2(s)$ Lead(II) chloride is soluble in hot water but insoluble in cold water
	Add potassium iodide solution	Yellow precipitate	$Pb^{2+}$ Present	lead(II) ions react with iodide ions to form insoluble lead(II) iodide. $Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_2(s)$
	Add potassium iodide solution followed by dilute sodium hydroxide solution	Yellow precipitate soluble in sodium hydroxide solution	$Pb^{2+}$ Present	lead(II) ions react with iodide ions to form insoluble lead(II) iodide. $Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_2(s)$
	Add potassium chromate(VI) solution followed by sodium hydroxide solution.	Yellow precipitate soluble in sodium hydroxide solution to form a yellow solution.	<b>Pb<sup>2+</sup> confirmed present</b>	lead(II) ions react with chromate ions to form insoluble Lead(II) chromate. $Pb^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$  Note; Lead(II) chromate is soluble in dilute nitric acid to form a yellow solution.Its however insoluble in ethanoic acid.

<b>Sn<sup>2+</sup></b>	Add sodium hydroxide solution drop wise until in excess	White precipitate soluble in excess to form a colourless solution	Zn <sup>2+</sup> , Al <sup>3+</sup> , Pb <sup>2+</sup> , Sn <sup>2+</sup> probably present	Tin(II) ions react with hydroxyl ions to form insoluble tin(II) hydroxide. $\text{Sn}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \longrightarrow \text{Sn}(\text{OH})_2(\text{s})$ Tin(II) hydroxide is amphoteric hence reacts with excess hydroxide ions to form a soluble complex of Stannate ions. $\text{Sn}(\text{OH})_2(\text{s}) + 2\text{OH}^{-}(\text{aq}) \longrightarrow \text{Sn}(\text{OH})_4^{2-}$
	Add ammonia solution drop wise until in excess	White precipitate insoluble in excess	Al <sup>3+</sup> , Pb <sup>2+</sup> , Mg <sup>2+</sup> , Ba <sup>2+</sup> , Sn <sup>2+</sup> probably present	Tin(II) ions react with hydroxyl ions to form insoluble tin(II) hydroxide. $\text{Sn}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \longrightarrow \text{Sn}(\text{OH})_2(\text{s})$
	Add acidified potassium permanganate solution	The purple solution turns colourless	Sn <sup>2+</sup> present	Tin(II) ions reduce manganate(VII) ions in acidic medium to manganese(II) ions, as they are oxidised to tin(IV) ions.
				$(\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5\text{e}^{-} \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})) \times 2$ $(\text{Sn}^{2+}(\text{aq}) \longrightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{e}^{-}) \times 5$ $2\text{MnO}_4^{-}(\text{aq}) + 16\text{H}^{+}(\text{aq}) + 5\text{Sn}^{2+}(\text{aq}) \longrightarrow 2\text{Mn}^{2+}(\text{aq}) + 5\text{Sn}^{4+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$
	Add acidified potassium permanganate solution until no further decolourisation. Then sodium sulphide solution	Dirty yellow precipitate	Sn <sup>2+</sup> present	Tin(II) ions reduce manganate(VII) ions in acidic medium to manganese(II) ions, as they are oxidised to tin(IV) ions. The tin(IV) ions formed reacts with sulphide ions to form insoluble tin(IV) sulphide.
				$2\text{MnO}_4^{-}(\text{aq}) + 16\text{H}^{+}(\text{aq}) + 5\text{Sn}^{2+}(\text{aq}) \longrightarrow 2\text{Mn}^{2+}(\text{aq}) + 5\text{Sn}^{4+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$ $\text{Sn}^{4+}(\text{aq}) + 2\text{S}^{2-}(\text{aq}) \longrightarrow \text{SnS}_2(\text{s})$
	Add iron(III) chloride solution	Brown solution turns green	Sn <sup>2+</sup> present	Tin(II) ions reduce iron(III) ions to iron(II) ions, as the tin(II) ions are oxidised to tin(IV) ions
				$2\text{Sn}^{2+}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq}) \longrightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$
	Add acidified potassium dichromate solution	Orange solution turns green	Sn <sup>2+</sup> present	Tin(II) ions reduce dichromate(VI) ions in acidic medium to chromium(III) ions, as they are oxidised to tin(IV) ions.
				$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{Sn}^{2+}(\text{aq}) + 14\text{H}^{+}(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Sn}^{4+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$
	Add mercury(II) chloride solution	A white precipitate which slowly turns grey	Sn <sup>2+</sup> present	Tin(II) ions reduce mercury(II) chloride to mercury(I) chloride as they are oxidised to tin(IV) ions
				$\text{Sn}^{2+}(\text{aq}) + 2\text{HgCl}_2(\text{aq}) \longrightarrow \text{Hg}_2\text{Cl}_2(\text{s}) + \text{Sn}^{4+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$

<b>Sn<sup>2+</sup></b>	<i>Add ammonium molybdate solution followed by dilute sulphuric acid</i>	<i>A blue colouration</i>	<i>Sn<sup>2+</sup> present</i>	<i>Not required</i>
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## UNIQUENESS OF CARBON

**In some of its properties, carbon behaves uniquely from the other elements.**

### **1. State the reasons for this unique behaviour.**

- Carbon has the smallest atomic radius among the elements
- Carbon has the greatest electronegativity compared to other elements
- Carbon has a maximum covalency of 4
- Carbon can form very stable multiple covalent bonds with itself and many other elements
- Carbon does not show inert pair effect

### **2. State the properties in which carbon behaves uniquely from other elements**

- Carbon (diamond) has an abnormally high melting point than other elements
- Carbon has the ability to form long chains of carbon atoms. Other elements do not catenate
- Carbon reacts with air to form gaseous oxides. Other elements form solid oxides.
- Carbon does react with chlorine. Other elements react with chlorine to form tetrachlorides. Lead forms lead(II) chloride
- Carbon reacts with sulphur to form a liquid, carbon disulphide. Other elements form solid sulphides.

*Note; The chemistry of carbon compounds is not included here since question is specific to carbon*

## THE GREEN HOUSE EFFECT

The level of Carbon dioxide in the atmosphere has shown an increase since industrial revolution. This is due to the extensive combustion of fossil fuels and the production of the gas from car exhausts, and the destruction of large areas of rainforest to burn the trees as a source of fuel. The carbon dioxide is slowly building up in the atmosphere, which results into an overall increase in the temperature of the atmosphere (greenhouse effect).

## USES OF GROUP IV ELEMENTS

1. A number of carbon allotropes have different uses;
  - Diamond, the hardest naturally occurring substance known, is used for making jewellery and, industrially, for cutting and drilling equipment.
  - Graphite is used in making lead pencils and as electrodes in electrolysis
  - Wood charcoal is used in drawing and as a fuel
  - Animal charcoal is used to remove brown colour from sugar
  - Lamp black is used in making shoe polish and printer's ink
  - Coke in extraction of iron as a reducing agent and manufacture of producer gas and water gas
2. Silicon and germanium are used as semiconductors in transistors.
3. Tin is used in making alloys like bronze, solder and type metal(Sn, Pb and Sb)
4. Lead is used in making alloys like solder.

## MISCELLANEOUS TOPICAL QUESTIONS

### *Short answer type questions*

1. Carbon, silicon, germanium, tin and lead are group IV elements in increasing atomic number.
  - (a) (i) Write the general outermost configuration of the elements. (01 mark)
  - (ii) Tin and lead show *inert pair effect*. Briefly explain what is meant by the term *inert pair effect* and give an example to illustrate your answer. (3 ½ marks)
- (b) State the reason why carbon has a very high melting point compared to other elements. (1 ½ marks)
- (c) (i) Write the formulae of the hydrides formed by the elements. (2 ½ marks)
- (ii) Identify the thermally most stable hydride in c (i) above. (½ mark)

2. The elements tin and lead belong to group IV of the Periodic Table. Describe the reactions of the elements with:
- (a) Water (03 marks)
  - (b) Concentrated sulphuric acid. (03 marks)
  - (c) Alkalis (03 marks)
3. (a) State the conditions and write equations for the reaction between carbon and;
- (i) water (2 ½ marks)
  - (ii) sulphuric acid. (2 ½ marks)
- (b) Compare the reactions of carbon and silicon with:
- (i) concentrated nitric(V) acid. (2 ½ marks)
  - (ii) concentrated sodium hydroxide. (2 ½ marks)
4. (a) Draw the structures and name the shapes of the following species. (09 marks)

Species	Structure	Shape
$CO_2$		
$SiO_2$		
$CCl_4$		
$CH_4$		
$CS_2$		
$SnO_3^{2-}$		

- (b) Briefly explain why  $CO_2$  adopts the shape you have named in (a) above. (02 marks)
- (c) Compare the bond angle of  $CS_2$  and  $SnO_3^{2-}$ . Give a reason for your answer. (03 marks)

5. (a) Carbon, silicon, germanium and tin belong to group IV of the Periodic Table and their respective bond energies are given below.

Bond	C—C	Si—Si	Ge—Ge	Sn—Sn
Bond energy(kJmol <sup>-1</sup> )	346	175	168	156

- (i) State the trend in bond energy. Give a reason for your answer. (1 ½ marks)
- (ii) How does bond energy affect the tendency of the above elements to catenate? (01 mark)
- (b) Describe the reactions of the elements in (a) above with concentrated hydrochloric acid. (02 marks)
- (c) Write equation for the formation of silane. (1 ½ marks)
6. (a) Lead(IV) oxide reacts with hydrochloric acid by redox reaction.
- (i) State the conditions for the reaction. (01 mark)
- (ii) Write the reduction and oxidation half reactions for the redox reaction that occurs above. (02 marks)
- (b) Lead(IV) oxide was added to a solution of manganese(II) sulphate in the presence of concentrated nitric acid.
- (i) State what was observed. (½ mark)
- (ii) Write the equation for the reaction that took place. (1 ½ marks)
7. (a) State how the following anhydrous chlorides can be prepared.
- (i) tin(II) chloride (01 mark)
- (ii) tin(IV) chloride (01 mark)
- (b) State the reasons why tin(IV) chloride exists but tin(IV) bromide does not. (02 marks)
- (c) Write equations for the reaction of each of the chlorides in (a) (i) with water. (02 marks)
- (d) (i) State what would be observed when sodium hydroxide solution was added drop wise until in excess to a solution of tin(IV) ions. (1 ½ marks)
- (ii) Write equations for the reaction(s) in d(i) above. (02 marks)
- (e) (i) State what would be observed and write equation for the reaction that would take place when tin(II) chloride is added to an acidified solution of sodium dichromate(VI) (2 ½ marks)
- (ii) Give a reason for your answer in (e)(i) (01 mark)
8. Carbon, silicon, germanium, tin and lead are in group IV of the Periodic Table.
- (a) State
- (i) the common oxidation states exhibited by the elements in their ions or compounds. (01 mark)

- (ii) how the stability of the oxidation states of the elements in (a) (i) vary down the group. (01 mark)
- (b) Give a reason for your answer in (a)(ii) (01 mark)
- (c) Compare the thermal stabilities of carbon tetrachloride and lead tetrachloride. (*Include equations of reactions if any*) (2 ½ marks)
- (d) Describe the reaction if any between each of the carbon tetrachloride and lead tetrachloride with water. (3 ½ marks)
9. (a) Compare the thermal stabilities of silicon(IV) chloride and tin(IV) chloride. (*Include the equations of reactions if any*) (2 ½ marks)
- (b)(i) Write equation for the reaction between tin and chlorine. (1 ½ marks)
- (ii) State the conditions for the reaction. (01 mark)
- (c) State what would be observed and write equation for the reaction that would take place if the product in (b) (i) was exposed to moist air. (2 ½ marks)
- (d) State why silicon(IV) chloride readily undergoes hydrolysis whereas carbon tetrachloride does not. (02 marks)
- 10.(a)(i) Write the electronic configuration of tin( Atomic number is 50)
- (ii) State the common oxidation states exhibited by tin in its compounds. (01 mark)
- (b)(i) State how anhydrous tin(II) chloride can be prepared. (01 mark)
- (ii) Draw the structure and name the shape of tin(II) chloride. (01 mark)
- (c) Write equation for the reaction between tin(II) chloride and water. (1 ½ marks)
- 11.(a)(i) Draw the structure and name the shape of tin(IV) chloride. (01 mark)
- (ii) State how anhydrous tin(IV) chloride can be prepared. (01 mark)
- (iii) Write equation for the reaction leading to formation of tin(IV) chloride. (1 ½ marks)
- (b) State what would be observed and write equation for the reaction that would take place if tin(IV) chloride is treated with water. (02 marks)
12. The atomic number of element Q is 32.
- (a) Write the electronic configuration of Q. (01 mark)
- (b) Write the formula of the;
- (i) hydride of Q. (½ mark)
- (ii) chloride of Q. (½ mark)
- (c) Water was added to the chloride of Q. State whether the resultant solution was neutral, acidic or alkaline. Explain your answer giving an equation for the reaction. (03 marks)



13. The elements tin and lead belong to group IV of the Periodic Table.
- Write equation for the formation of the tetrachlorides of the elements. (02 marks)
  - Tin(IV) chloride fumes in moist air. Explain this observation. (03 marks)
14. (a) Lead is an element in group IV of the Periodic Table.
- Write the general electronic configuration of group IV elements. (0½ mark)
- State what would be observed and write an equation when lead(IV) oxide was heated on a deflagrating spoon and quickly plunged in gas jar of sulphur dioxide. (2 ½ marks)
  - When red lead (trilead tetroxide) was heated with nitric acid, a solid was formed. Write the equation for the reaction. (1 ½ marks)
  - The mixture in (c) was filtered and the residue warmed with concentrated hydrochloric acid.
    - What was observed? Explain your answer. (2 ½ marks)
    - Write the equation for the reaction. (1 ½ marks)
  - The filtrate from (d) was divided into three parts.
    - to the first part was added aqueous potassium iodide. State what was observed and write equation for the reaction. (02 marks)
    - aqueous sodium chromate solution was added to the second portion. State what was observed and write equation for the reaction. (02 marks)
    - the third part was evaporated to dryness and then heated strongly. Explain what was observed and write equations for the reaction that took place. (3 ½ marks)
15. (a) Write:
- the formulae of the possible oxides of lead. (1 ½ marks)
  - equation to show how each of the oxides in (a)(i) can be prepared. (1 ½ marks)
- Describe how the oxides in (a) react with dilute nitric acid. (04 marks)
  - When one of the oxides in (a) was added to a mixture of a manganese(II) salt and concentrated nitric acid, a purple solution was formed.
    - Identify the oxide (½ mark)
    - Write the equation for the reaction that took place. (1 ½ mark)
16. Trilead tetraoxide (red lead oxide),  $Pb_3O_4$  can be prepared when lead(II) oxide is heated in excess oxygen.
- Write equation for formation of  $Pb_3O_4$ . (1 ½ marks)
  - Write equation for the reaction of  $Pb_3O_4$  with;
    - hot concentrated sodium hydroxide solution. (1 ½ marks)

- (ii) hot concentrated hydrochloric acid. (1 ½ marks)
- (c) Lead(II) oxide is almost insoluble in dilute hydrochloric acid, but readily dissolves in concentrated hydrochloric acid. Explain this observation. (4 ½ marks)
17. Lead and iron form mixed oxides of the formulae  $Pb_3O_4$  and  $Fe_3O_4$  respectively.
- (a) Write the:
- (i) IUPAC name of the mixed oxide of lead that represents the ratio in which the oxides mix. (01 mark)
- (ii) equation to show that is  $Pb_3O_4$  a mixed oxide. (1 ½ marks)
- (b)  $Pb_3O_4$  oxidises hot concentrated hydrochloric acid to a pale green gas and itself reduced to a colourless solution which forms a white precipitate on cooling.
- (i) Identify the pale green gas and the white precipitate. (01 mark)
- (ii) Write the equation for the reaction between  $Pb_3O_4$  and hot concentrated hydrochloric acid. (01 mark)
- (c) State any two other chemical properties to show the similarity between iron and lead. (01 mark)
18. Write equation for the reaction between sodium hydroxide and; (09 marks)
- (i) lead(II) oxide
- (ii) lead(IV) oxide
- (iii) Tin(IV) oxide
- (iv) Tin(II) oxide
- (v) Carbon(II) oxide
- (vi) tin
- 19.(a) A compound Q contains 63.7% lead, 14.8% carbon, 1.8% hydrogen and the rest being oxygen. When vapourised, 0.225g of Q occupies  $15.5\text{ cm}^3$  at standard temperature and pressure.
- (i) Calculate the empirical formula of Q. (02 marks)
- (ii) Deduce the molecular formula of Q. (03 marks)
- (b) Compound Q decomposed on heating to form a yellow residue on cooling and a colourless vapour that turned limewater milky and formed a yellow precipitate with 2,4-dinitrophenyl hydrazine in presence of sulphuric acid.
- (i) Write the name and formula of Q. (01 mark)
- (ii) Write equation leading to formation of the yellow precipitate. (1 ½ marks)

20. D is a dark-brown solid which on heating loses mass to form a yellow compound E, D reacts with cold concentrated hydrochloric acid to form a colourless liquid F of formula mass 349. On warming, F decomposes to form a white solid G. G dissolves in both concentrated sodium hydroxide and concentrated hydrochloric acid.
- (a) Identify D, E, F and G. (04 marks)
- (b) Write equations for all the five reactions that take place. (05 marks)
21. Explain each of the following observations.
- (a) Carbon tetrachloride is stable to water but other group(IV) tetrachlorides are readily hydrolysed. (03 marks)
- (b) Carbon atoms are able to form long chains to a greater extent than other group IV elements. (03 marks)
- (c) Although both silicon dioxide and carbon dioxide are covalent, carbon dioxide is a gas whereas silicon dioxide is solid of high melting point. (04 marks)
- (d) Iron(III) chloride and tin(II) chloride cannot exist together in solution. (2 ½ marks)
- (e) The carbon- oxygen bond is polar but carbon dioxide is non-polar. (03 marks)
- (f) The bonds in carbon tetrachloride are polar yet the carbon tetrachloride molecule is not polar. (03 marks)
- (g) Silicon(IV) chloride is hydrolysed by water whereas carbon tetrachloride is not. (1 ½ marks)
- (h) Lead(IV) chloride exists but lead(IV) bromide does not. (02 marks)
- (i) Both graphite and copper conduct electricity. (02 marks)
- (j) Silicon(IV) oxide is a solid of very high melting point. However, lead(IV) oxide easily decomposes when heated. (2 ½ marks)
- (k) Lead(II) chloride is insoluble in ethanol whereas lead(IV) chloride readily dissolves in ethanol. (03 marks)
- (l) When an aqueous solution of sodium chlorate(I) was and lead(II) nitrate was warmed, a brown precipitate was formed. (2 ½ marks)

***Long answer type questions***

22. The elements carbon, silicon, tin and lead are in group IV of the Periodic Table. Carbon differs in some properties from other members of the group.

(a) (i) Give two reasons why carbon differs from other members of the group. (02 marks)

(ii) State two properties that distinguish carbon from other members of the group. (02 marks)

(b) Describe the reactions of the dioxides of these elements with sodium hydroxide. (06 marks)

(c) Describe the reactions of the chlorides of group IV elements with water. (04 marks)

(d) Write an equation for the reaction to show how you would prepare:

(i) lead(II) oxide. (01 mark)

(ii) lead(IV) oxide. (01 mark)

(e) Describe the reactions of lead(IV) oxide with hydrochloric acid. (04 marks)

23. Carbon, Silicon, germanium and tin are some of the elements in group IV of the Periodic Table.

(a) Describe the trend among the elements in;

(i) metallic character (02 marks)

(ii) electropositivity (3 ½ marks)

(b) Describe the reactions of the elements with:

(i) air (04 marks)

(ii) nitric acid (05 marks)

(iii) Chlorine (03 marks)

(c) Excess tin(II) chloride solution was added to iodine solution.

(i) State what was observed. (01 mark)

(ii) Write equation for the reaction that took place. (1 ½ marks)

24. Both tin and lead are group IV elements.

(a) State the oxidation states exhibited by tin and lead in most of their compounds. (02 marks)

(b) Write equations to show how the chlorides and the oxides of tin and lead in the +4 oxidation state can be formed. (06 marks)

(c) Compare the thermo stability of the following compounds of tin and lead

(i) the tetrachlorides

(ii) the dioxides (06 marks)

(d) State two similarities in the chemistry of the following compounds of tin and lead. (*Illustrate your answers with equations*)

- (i) oxides
  - (ii) chlorides (06 marks)
- 25.(a) Compare the thermo stability of the monoxides and dioxides of group IV elements. (04 marks)
- (b) Describe the reactions of the oxides of:
- (i) carbon and tin with sodium hydroxide. (5 ½ marks)
  - (ii) lead with hydrochloric acid. (04 marks)
- (f) Explain the following observations.
- (i) carbon(IV) oxide is a gas whereas silicon(IV) oxide is a solid. (04 marks)
  - (ii) silicon(IV) oxide reacts with hydrofluoric acid but does not react with hydrofluoric acid. (2 ½ marks)
- 26.The elements Carbon, silicon, tin and lead belong to group IV of the Periodic Table.
- (a) State the oxidation states of the elements. (01 mark)
  - (b) Explain the trend in the stability of the oxidation states. (03 marks)
  - (c) (i) State the type of bonding that is in the chlorides of lead.(01 mark)
  - (ii) State two physical properties of each chloride that shows the type of bonding you have mentioned above. (04 marks)
  - (d) Describe the reactions of the chlorides of the elements above with water. Write equations for the reactions that take place. (04 marks)
  - (e) Describe the reaction of the oxides of these elements with sodium hydroxide. Write equations for the reactions that take place. (07 marks)
- 27.(a) Carbon, silicon, tin and lead belong to group IV of the Periodic Table.
- (i) State the two oxidation states exhibited by these elements. (01 mark)
  - (ii) Explain how the stability of the two oxidation states varies from carbon to lead. (03 marks)
  - (b) Describe the reactions between:
    - (i) the elements in (a) above with sulphuric acid. (06 marks)
    - (ii) silicon(IV) chloride with water (02 marks)
    - (iv) Lead(IV) oxide and hydrochloric acid. (04 marks)
  - (c) State two chemical properties in which carbon differs from the rest of the group IV elements. (02 marks)
  - (d) Give reasons why carbon differs from the rest of the group IV elements. (02 marks)

28. The elements carbon, silicon, germanium, tin and lead belong to group IV of the Periodic Table.

(a) Describe the reactions of the elements with;

(i) water (05 marks)

(ii) sodium hydroxide solution (04 marks)

(iii) Sulphuric acid (04 marks)

(b) Below are the boiling points of the tetrachlorides of group IV elements.

Tetrachloride	$CCl_4$	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
Boiling point( $^{\circ}C$ )	76.4	57.0	86.0	118	Decomposes

State and explain the trend in the boiling points of the tetrachlorides.

(04 marks)

(c) State what would be observed and write equation for the reaction that would take place if excess concentrated hydrochloric acid was mixed with lead(IV) oxide and heated. (03 marks)

29. Explain each of the following observations.

(a) Solid lead(II) chloride can be prepared in the laboratory by heating lead(II) oxide with dilute hydrochloric acid and cooling. When lead(II) oxide is treated with concentrated hydrochloric acid under the same conditions, no solid is formed. (04 marks)

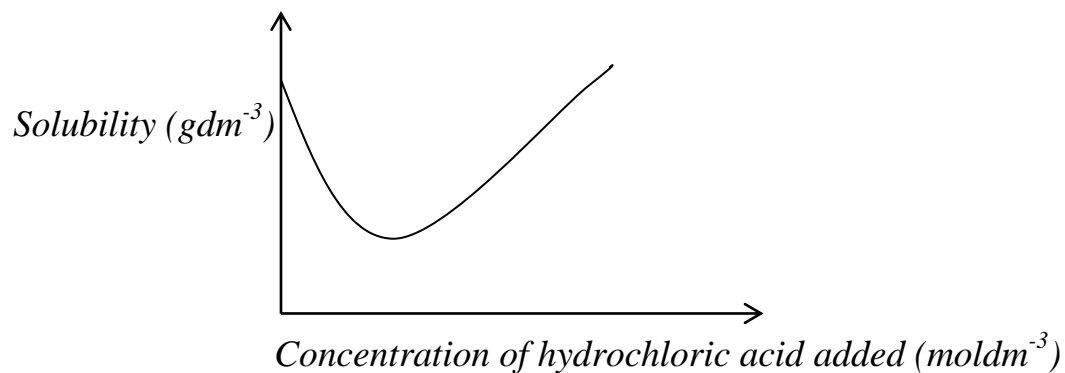
(b) When concentrated hydrochloric acid is added to lead(II) ethanoate solution, a white precipitate is formed which dissolves in excess acid. (05 marks)

(c) When lead(IV) chloride is added to water, white fumes and a brown precipitate are observed. (03 marks)

(d) When lead(IV) oxide was added to a solution containing manganese(II) sulphate and concentrated nitric acid and the mixture boiled, the colour of the solution changed from pale pink to purple. (04 marks)

(e) Diamond melts at  $4827^{\circ}C$  and silicon melts at  $2355^{\circ}C$  although both have similar structures. (04 marks)

(f) When concentrated hydrochloric acid is added to lead(II) nitrate solution drop wise until in excess, the curve below is obtained. Explain the shape of the graph. (04 marks)



- (g) The bond dissociation energy of the hydrides of group IVB are in the order  $\text{CH}_4 > \text{SiH}_4 > \text{GeH}_4 > \text{SnH}_4 > \text{PbH}_4$ . However, the boiling points are in the reverse order. (05 marks)
- (h) The boiling points of the hydrides of group IV elements are in the order  $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4 < \text{PbH}_4$  whereas the boiling points of the hydrides of group VII elements are in the order  $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$  (05 marks)