

GROUP IV ELEMENTS

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GROUP IV ELEMENTS

GROUP(IV) ELEMENTS

These elements include

- ✓ Carbon
- ✓ Silicon
- ✓ Germanium
- ✓ Tin
- ✓ Lead

Electronic configurations

Element	Symbol	Atomic number	Electronic configuration
Carbon	C	6	$1s^2 2s^2 2p^2$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Tin	Sn	50	$[\text{Kr}] 4d^{10} 5s^2 5p^2$
Lead	Pb	82	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^2$

Electronic configuration

All the elements in this group have an outer general electronic configuration of $ns^2 np^2$.

Occurrence

Carbon is both allotropic and isotopic, it exists as isotopes for example carbon has carbon-12 and carbon-14. Carbon exists naturally as diamond and graphite in crystalline form, its non-crystalline forms include wood charcoal, animal charcoal, lamp black, coke, coal which are collectively known as amorphous carbon.

Tin exists as tinstone SnO_2 , its allotropes are grey and white tin.

Silicon exists naturally as silicon(IV) oxide/silicon dioxide SiO_2 in sand as quartz and also as silicates in a number of rocks and clays.

Germanium is a rare mineral but the element occurs as traces in ores of other metals and in coal.

Lead exists as galena (lead(II) sulphide) PbS

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Properties of group(iv) elements

Element	C	Si	Ge	Sn	Pb
Atomic radius(nm)	0.077	0.117	0.122	0.142	0.154
Melting point($^{\circ}\text{C}$)	3730	1410	937	232	327
Boiling point($^{\circ}\text{C}$)	4830	2680	2830	2270	1730
1 st I.E(KJmol ⁻¹)	1086	786	760	708	715
2 nd I.E (KJmol ⁻¹)	2352	1577	1537	1411	1452
Electronegativity	2.5	1.8	1.8	1.8	1.0
Type of structure	Giant molecular	Giant molecular	Giant molecular	Giant metallic	Giant metallic
Density	3.5	2.33	5.35	7.23	11.3

Atomic radius

Generally atomic radius increases down the group, because the increase in screening effect due to addition of extra energy levels of electrons outweighs the increase in nuclear charge due to addition of protons to atomic nuclei of the elements. Thus the effective nuclear charge decreases leading to decrease in nuclear attraction for the outermost electrons hence increase in atomic radius.

However, the increase in atomic size from silicon to germanium is less than expected because germanium has a full inner 3-d sub-energy level of electrons which poorly shield the valency electrons from the nuclear charge. Consequently, the valence electrons experience a stronger nuclear attraction than expected resulting into slight increase in atomic radius from silicon to germanium.

In a similar way, the small increase in atomic radius between tin and lead is because of the filling of the inner 4f sub-energy level of electrons in lead which are poorest at shielding the valence electrons from the nuclear attraction.

Melting and boiling points

Generally, the melting points decrease down the group. This is because down the group, atomic radius increases and so the covalent bonds between atoms of the elements carbon, silicon and germanium increasingly become longer and weaker and the energy required to break them for melting to occur also decreases.

Increase in atomic radius through metallic elements tin and lead results into decrease in nuclear attraction for the delocalized electrons (i.e decrease in strength of metallic lattice) hence decrease in amount of energy required to break the metallic bonds.

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The melting point of tin is a low value compared to that of lead because tin forms a distorted cubic close-packed structure in which the metallic bond is weaker than in the regular cubic close-packed structure of lead.

Ionisation energies

Generally, the ionization energies decrease down the group. This is because the increase in shielding effect due to addition of extra energy levels of electrons outweighs the increasing nuclear charge due to addition of protons to atomic nucleus. This leads to decrease in effective nuclear charge, hence decrease in nuclear attraction for the outermost electrons; consequently, energy required to remove them decreases.

However, there is small decrease in ionization energies from silicon to germanium and also from tin to lead due to filling up of the d- and f-orbitals in which electrons poorly (weakly) shield the valence electrons from the nuclear charge.

Electrical conductivity

Diamond does not conduct electricity because there are no free/delocalized electrons in it, since all the four valence electrons per carbon atom are used to form covalent bonds. However, in graphite, only three out of the four valence electrons are used by each carbon atom to form three covalent bonds. The fourth electron is delocalized over all the carbon atoms in the layer. It is these delocalized electrons which conduct electricity in graphite.

Silicon and germanium are semi-conductors in which a few of the valency electrons in the atoms gain enough energy to become delocalized and so their conductivity increases with increase in temperature.

Tin and lead are metals which have delocalized electrons in their crystals which enable them to conduct electricity.

Metallic character

Carbon is non-metal, silicon and germanium are semi-metals while tin and lead are metals. Thus, the metallic character increases down the group. This is because atomic radius increases down the group. Therefore, the nuclear attraction for the outermost electrons decreases hence the tendency for atoms to lose electrons increases down the group and elements progressively become metals.

Density

Density of the elements increases down the group, this is because the relative atomic mass increases and its effect exceeds the increasing atomic radius.

Electronic configuration

All the elements in group(IV) have a general outer electronic configuration of ns^2np^2 .

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Oxidation states

All group (IV) elements have a general outer electronic configuration of ns^2np^2 . The elements have two oxidation states in their compounds – i.e. the +2 and +4 oxidation states. The +2 oxidation state corresponds to loss of two electrons in the p-orbital of the outermost energy level to form a divalent cation M^{2+} . The +4 state corresponds to the formation of four covalent bonds after promotion of s-orbital electron into a p-orbital in the outermost energy level, and the formation of four sp^3 hybridised orbitals.

However, the stability of the +2 oxidation state increases down the group while that of the +4 oxidation state decreases.

The increase in stability of the +2 oxidation state down the group is due to inert pair effect – i.e the inability of a pair of electrons in ns-orbitals of the outermost energy level to take part in bonding due to a high energy difference between the ns and the np orbitals.

The inert pair effect increase down group(IV) elements because from one element to the next, the number of electrons in the d- and f-orbitals with a poor shielding effect increases. The ineffectiveness of the inner d- and f-orbital electrons to shield the outer most s-orbital electrons from the increasing nuclear charge increases. The s-orbitals which are spherical in shape tend to penetrate and enter the atomic core, rendering the s-orbital electrons less available for bonding. Thus, in carbon, silicon, germanium and tin compounds, the +4 oxidation state is very stable compared to the +2 oxidation state, and compounds of carbon, silicon, germanium and tin in +2 oxidation state behave as reducing agents, being oxidized to compounds in the more stable +4 oxidation state.

However, the +2 oxidation state in lead compounds is more stable than the +4 state. Therefore, lead (IV) compounds behave as oxidizing agents which can be reduced to the more stable lead (II) compounds.

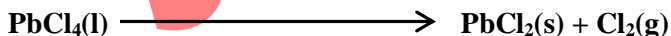
When inert pair effect is significant, the elements predominantly form ionic compounds but when it is less, the compounds formed are covalent.

Questions

1. State how the stability of the oxidation states of group IV elements vary down the group (Illustrate your answer with chlorides of carbon and lead)

The +2 oxidation state becomes more stable down the group whereas the +4 oxidation state becomes less stable.

Lead(IV) chloride decomposes at room temperature to lead(II) chloride and chlorine



However, carbon tetrachloride is very stable at room temperature.

2. Describe using oxides how the stability of the two oxidation states of group(IV) elements vary from carbon to lead.

Stability of the +2 state increases from carbon to lead, while stability of +4 oxidation state decreases from carbon to lead

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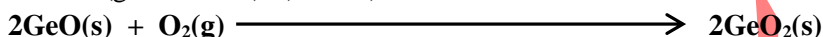
The monoxides of carbon, silicon, germanium and tin are unstable. Carbon monoxide (carbon(II) oxide) is readily oxidized to carbon dioxide (carbon(IV) oxide) by atmospheric oxygen



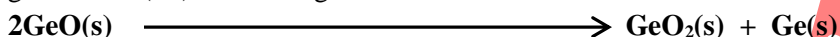
Silicon monoxide (silicon(II) oxide) disproportionates at room temperature to form silicon dioxide (silicon(IV)oxide) and silicon.



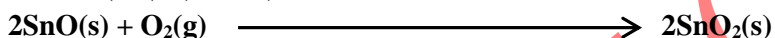
Germanium monoxide (germanium(II) oxide) is readily oxidized when heated in air to germanium dioxide (germanium(IV) oxide)



Germanium monoxide also disproportionates when heated in absence of air to form germanium(IV)oxide and germanium.



Tin monoxide (tin(II)oxide) oxidizes rapidly if exposed to air at room temperature forming tin dioxide (tin(IV) oxide)



The dioxides of carbon, silicon, germanium and tin are more stable than the monoxides.

Lead dioxide (lead(IV) oxide) is unstable, and decomposes on heating to form stable lead monoxide (lead(II) oxide) and oxygen gas.



Lead(IV)oxide is an oxidizing agent. For instance, it oxidizes hot concentrated hydrochloric acid to chlorine and is itself reduced to the more stable lead(II) chloride. This reaction is used to prepare chlorine in the laboratory.



The stability of the +2 oxidation state increases down group IV elements, explain.

Stability of the +2 oxidation state increases down the group due to inert pair effect- i.e the inability of a pair of electrons in s-orbital of the outermost energy level to take part in bonding. The inert pair effect increase down group(IV) elements because from one element to the next, the number of electrons in the d- and f-orbitals with a poor shielding effect increases. The ineffectiveness of the inner d- and f-orbital electrons to shield the outermost s-orbital electrons from the increasing nuclear charge increases. The s-orbital which is spherical in shape tend to penetrate and enter the atomic core, rendering the s-orbital electrons less available for bonding

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Anomalous behaviour of carbon

The chemical properties of carbon differ from those of other group(IV) elements because carbon;

- ✓ Has the smallest atomic radius
- ✓ Has the highest electronegativity
- ✓ Lacks accessible vacant d-orbitals hence limited to maximum covalence of 4

Carbon has the following anomalous properties

- ✓ Catenation; formation of stable bonds between carbon atoms resulting into formation of chains due to its small atomic radius.
- ✓ Multiple bond formation between carbon atoms and atoms of other elements also due to a small atomic radius.
- ✓ Maximum coordination number of carbon is 4 i.e carbon cannot expand its octet beyond 4 covalent bonds due to lack of vacant d-orbitals

Reasons why the chemistry of carbon differs from that of other group(IV) elements in the Periodic Table

Carbon has the smallest atomic radius in the group. This gives rise to

- ✓ Very high electronegativity/ very low electropositivity hence carbon is unable to form stable cations
 - ✓ Strong covalent bonds between carbon and other non-metal atoms
 - ✓ Multiple bond formation between its own atoms and atoms of some other non-metals.
- Carbon atom lack vacant 2d-orbitals. This explains why most compounds of carbon are resistant to hydrolysis; and why carbon does not form complexes.

Differences between the properties of carbon and the rest of the elements in group(IV) of the Periodic Table

- ✓ Carbon has a unique property of catenation. Catenation is the ability of an element to form covalent bonds between its own atoms resulting into formation of long chains or rings. Thus carbon atoms bond together in extremely long chains and rings.
The ability of carbon to catenate is due it's very small atomic radius. Thus the carbon-carbon covalent bonds are short and very strong. Down the group, atomic radius increases thus the element-element bond becomes longer and weaker, hence tendency to catenate decreases.
- ✓ Carbon unlike other members in the group can form multiple bonds with itself and with other non-metallic elements. Eg in alkenes, alkynes, carbonyl compounds, carboxylic acids and nitriles (see organic chemistry)
- ✓ Carbon shows a maximum covalency of four because it lacks empty 2d orbitals. Other elements have a maximum covalency of 6 (hence coordination number of 6) because their atoms have empty d-orbitals of the right energy, so they can expand their octets.
- ✓ Carbon does not form complex ions, because it has no lone pairs of electrons and lacks empty 2d-orbitals so it cannot accept/accommodate lone pairs of electrons from the ligands. The other members in the group form complex ions e.g. $[\text{SiF}_6]^{2-}$; $[\text{GeCl}_6]^{2-}$; $[\text{SnCl}_6]^{2-}$; $[\text{PbCl}_6]^{2-}$, etc, because

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their atoms have vacant d-orbitals of the right amount of energy required to accept lone pairs of electrons from the ligands.

- ✓ Carbon forms gaseous oxides while other members in the group form solid oxides.
- ✓ Carbon compounds are relatively inert (unreactive) whereas compounds of other members in the group are highly reactive.
- ✓ Carbon does not show inert pair effect

Structures of the elements

Carbon has giant covalent (or giant molecular) structure in its two crystalline allotropes i.e diamond and graphite

Structure of diamond

In diamond, each carbon atom is covalently bonded to four other atoms in a tetrahedral arrangement. The network of the strong covalent bonds continues in this way with an infinite number of carbon atoms giving rise to a three-dimensional giant molecular structure (or giant covalent structure).

Diamond does not conduct electricity because all the four valence electrons of each carbon atom in it are used to form covalent bonds leaving no delocalized electrons.

Diamond is extremely hard because of the strength and uniformity of the bonding. There are no planes of weakness in the crystal structure of diamond. For instance, there are no weak van der Waals forces

Uses of diamond

- ✓ Diamond is very hard and hence used as a drilling device, rock borers and glass cutters.
- ✓ Diamond is used to make jewelry because of its sparkling appearance.
- ✓ Diamond is bright and used to make laser beams.

Structure of graphite.

A graphite crystal consists of layers of hexagonal rings of carbon atoms. Each layer is a giant molecule in two dimensions only. Each carbon atom is at corner of a regular hexagon, bonded covalently to three other atoms in the same plane. The layers are held together by relatively weak van der Waals forces of attraction.

Graphite conducts electricity because each carbon atom in the layer uses three of its four valence electrons to form three covalent bonds with other carbon atoms, leaving one electron which is delocalized within the layer. It is these delocalised electrons that aid conduction of electricity.

Graphite is soft and slippery (greasy) because of the weak Van der Waals forces between the layers which enable the layers to slide (slip) over each other easily.

Uses of graphite

- ✓ Graphite is soft and can mark therefore used to make pencil.
- ✓ Graphite is mixed with clay to make pencil leads.
- ✓ Graphite is a good conductor of electricity and thus used as electrodes during electrolysis

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- ✓ It is soft and greasy, therefore used as lubricants especially in small bearings like those in dynamos.
- ✓ Graphite is used to make brushes for electric motors.
- ✓ Graphite (black lead) is used as a protective coating on iron to prevent rusting.

Silicon and germanium are non- allotropic and both adopt giant molecular structures similar to that of diamond.

The most common allotrope of tin is white tin. It has a giant metallic structure – with its atoms held by metallic bonds. The structure is a distorted cubic close-packed arrangement in which each atom is surrounded by 12 neighbouring atoms.

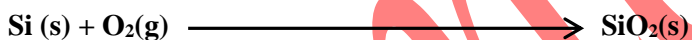
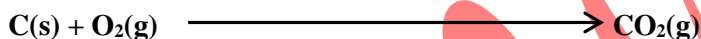
Lead is non-allotropic and adopts a giant metallic structure with a regular cubic-close packed structure.

Chemical properties of group(IV) elements

The chemical reactivity of the elements of group(IV) generally increases down the group from carbon to lead.

a) Reaction with air

When heated in air, the elements react with oxygen to form dioxides except lead which forms a monoxide.



Lead burns in oxygen at a temperature higher than its melting point of 600K, to form lead(II) oxide, at higher temperatures, lead(II) oxide reacts with more oxygen to form trilead tetraoxide.

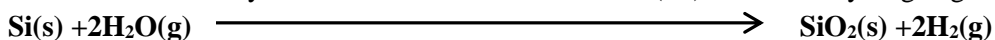


b) Reaction with water

Heated carbon reacts with steam to form carbon monoxide and hydrogen. A mixture of carbon monoxide and hydrogen is called a water gas



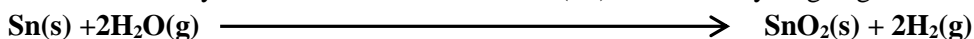
Heated silicon slowly reacts with steam to form silicon(IV) oxide and hydrogen gas.



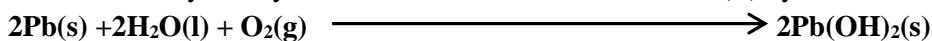
Germanium does not react with water or steam.

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Heated tin slowly reacts with steam to form tin(IV) oxide and hydrogen gas.



Lead reacts very slowly with soft aerated water to form lead (II) hydroxide.

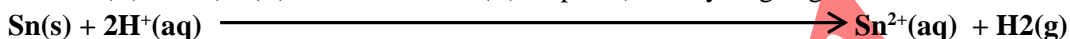


c) Reaction with mineral acids

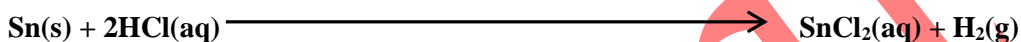
Reaction with dilute acid

Carbon, silicon and germanium do not react with dilute mineral acids.

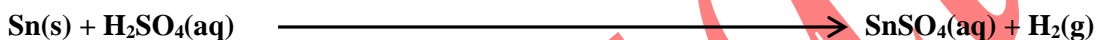
Tin reacts slowly with dilute hydrochloric acid and dilute sulphuric acid (non-oxidising acids) to form tin(II) salts (tin(II) chloride and tin(II) sulphate) and hydrogen gas..



Or



And



Tin is slowly oxidized by dilute nitric acid to tin(II) nitrate. The acid is reduced ammonium nitrate and water.



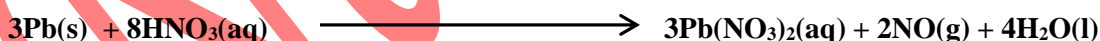
Lead is rendered passive by cold dilute hydrochloric acid due to formation of insoluble lead(II) chloride which prevents further attack on the metal by the acid.

However, lead reacts with dilute hydrochloric acid on heating to form lead(II) chloride and hydrogen gas.



Lead is rendered passive by dilute sulphuric acid due to formation of insoluble lead (II) sulphate.

It is readily oxidized by dilute nitric to lead(II) nitrate while the acid is reduced nitrogen monoxide and water.

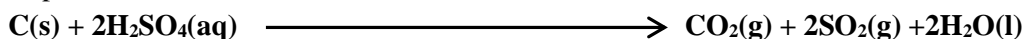


Lead reacts with ethanoic acid in presence of oxygen to form lead(II) ethanoate and water.

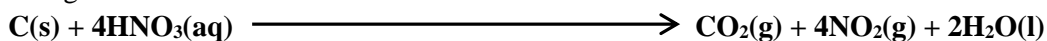


Reaction with concentrated acids

Carbon is oxidized by hot concentrated sulphuric acid to carbon dioxide. The acid itself reduced to sulphur dioxide and water.



Carbon is oxidized by hot concentrated nitric acid to carbon dioxide. The acid is then reduced to nitrogen dioxide and water.

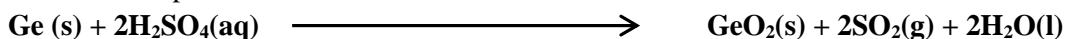


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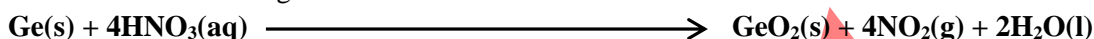
Silicon does not react with concentrated acids except hot concentrated hydrofluoric acid to form hexafluorosilicic acid and hydrogen gas.



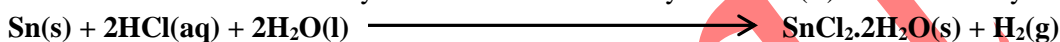
Germanium is oxidized by hot concentrated sulphuric acid to germanium(IV) oxide. The acid is reduced to sulphur dioxide and water.



Germanium is also oxidized by hot concentrated nitric acid to form germanium (IV) oxide. The acid is reduced to nitrogen dioxide and water.



Tin reacts with concentrated hydrochloric acid to form hydrated tin (II) chloride and hydrogen gas.



Tin is oxidized by hot concentrated sulphuric acid to tin(IV) sulphate. The acid is reduced sulphur dioxide and water



Tin is oxidized by hot concentrated nitric to tin(IV) oxide. The acid is reduced to nitrogen dioxide and water.



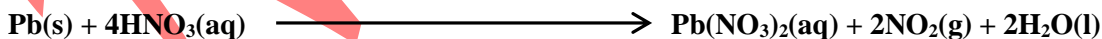
Lead reacts with hot concentrated hydrochloric acid to form lead (II) chloride and hydrogen gas.



Lead is oxidized by hot concentrated sulphuric acid to lead (II) sulphate. The acid is reduced to sulphur dioxide and water.



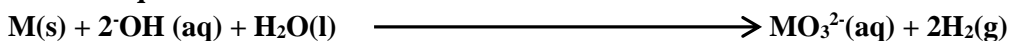
Lead is oxidized by hot concentrated nitric to lead (II) nitrate. The acid is reduced to nitrogen dioxide and water.



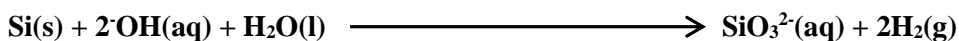
d) Reaction with alkalis

Carbon does not react with alkalis. Silicon, germanium, tin and lead react with hot concentrated sodium/potassium hydroxide solution to form a silicate, germinate, stannate and plumbate respectively with liberation of hydrogen gas.

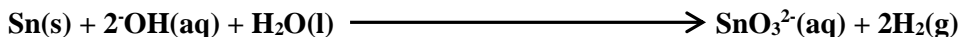
General equation



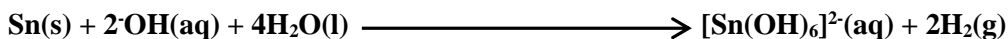
(M = Si, Ge, Sn)



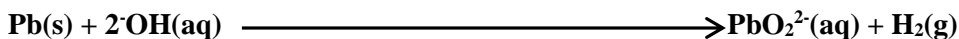
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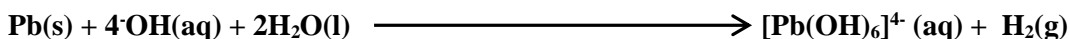
Or



And



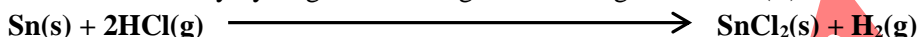
Or



e) Reaction with non-metals

Reaction with hydrogen chloride

Tin reacts with dry hydrogen chloride gas on heating to form tin(II) chloride and hydrogen gas



Lead reacts in a similar way;



Reaction with chlorine gas

Tin reacts with dry chlorine gas on heating to form tin(IV) chloride



Question

6g of solder were dissolved in excess hot dilute hydrochloric acid. The product was transferred to a 250 volumetric flask and diluted with water to the mark. 20cm³ of the resultant solution were pipetted in a conical flask followed by 2 drops of methyl orange indicator and titrated against a standard solution of sodium hydroxide until the end point. The volume of sodium hydroxide required was 32cm³.

Given that the initial volume of hydrochloric acid was 80cm³ of concentration 1.02M. Calculate the percentage composition by mass of solder if sodium hydroxide contains 0.16g l⁻¹

Solution



Also



$$\begin{aligned} \text{Rfm of NaOH} &= 23 + 16 + 1 \\ &= 40 \end{aligned}$$

40g of sodium hydroxide contains 1 mole

$$\begin{aligned} 0.16\text{g of sodium hydroxide will contain } & \frac{1}{40} \times 0.16 \\ &= 0.004\text{M} \end{aligned}$$

1000cm³ of sodium hydroxide solution contains 0.004 moles

$$32\text{cm}^3 \text{ of sodium hydroxide solution will contain } \frac{0.004}{1000} \times 32$$

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$$= 0.000128 \text{ moles}$$

Mole ratio of $\text{HCl}:\text{NaOH} = 1:1$

Hence moles of hydrochloric acid = 0.000128 moles

20cm³ of solution contains 0.000128 moles of hydrochloric acid

250cm³ of solution contains will contain $\frac{0.000128}{20} \times 250$
 $= 0.0016 \text{ moles}$

Original moles of $\text{HCl} = \frac{1.02}{1000} \times 80$
 $= 0.0816 \text{ moles}$

Moles of HCl reacting with tin = $0.0816 - 0.0016$
 $= 0.08 \text{ moles}$

Moles of tin reacting = $\frac{1}{2} \times 0.08$
 $= 0.04 \text{ moles}$

1 mole of tin weighs 119g

0.04 moles of tin will weigh 119×0.04
 $= 4.76\text{g}$

Percentage of tin = $\frac{\text{mass of tin}}{\text{mass of solder}} \times 100\%$
 $= \frac{4.76}{6} \times 100\%$
 $= 79.33\%$

Percentage of lead = $100 - 79.33$
 $= 20.67\%$

EXERCISE

3.8g of solder was dissolved in excess dilute hydrochloric acid. The solution was diluted in 250cm³. 25cm³ of this solution required 23.5cm³ of 0.01M potassium dichromate(VI) solution for complete reaction

- Write half equation for the reduction of potassium dichromate
- Determine the percentage by mass of tin in solder

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Compounds of group(IV) elements

Group(IV) elements form compounds in two oxidation states i.e +2 and +4.

Compounds in +2 oxidation state are formed when 2 electrons in the p-subshell have participated in bonding. compounds in +4 oxidation state are formed when 4 electrons have bonded i.e those in the s and p-subshell, however the stability of the +2 oxidation state increases down the group due to iner pair effect. The common compounds are discussed below.

The oxides

Group (IV) elements form monoxides in which the elements have an oxidation state of +2 and dioxides in which they have oxidation state of +4. The ability to form stable dioxides decreases down the group whereas the ability to form stable monoxides increases.

The Monoxides (MO)

Appearance

Carbon monoxide (carbon(II) oxide), CO is a colourless and poisonous gas

Silicon monoxide (silicon(II) oxide), SiO is a brown powder

Germanium monoxide (germanium(II) oxide), GeO is a yellow solid when hydrated and black powder when anhydrous

Tin monoxide (tin(II) oxide) SnO is dark grey or brown powder

Lead(II) oxide, PbO is a yellow solid when cold and brown (or reddish-brown) solid when hot.

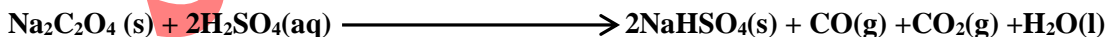
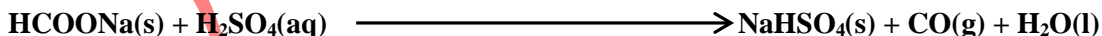
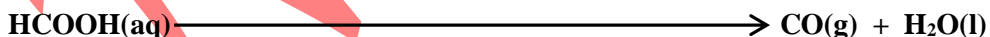
Preparation of the monoxides

Carbon monoxide is prepared by passing carbon dioxide over red hot carbon (coke). The carbon reduces the carbon dioxide to carbon monoxide.

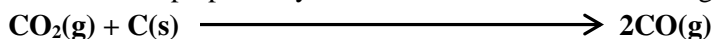


It can also be made by heating concentrated sulphuric acid with methanoic acid, sodium methanoate or sodium oxalate (also called sodium ethanedioate)

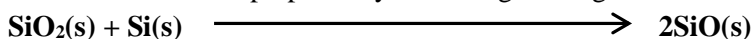
Concentrated H_2SO_4



It can also be prepared by reduction of carbon dioxide using coke



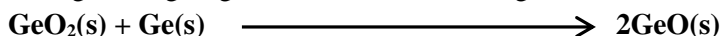
Silicon monoxide is prepared by the strong heating silicon dioxide with silicon.



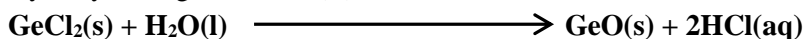
GROUP IV ELEMENTS

Germanium monoxide can be prepared by:

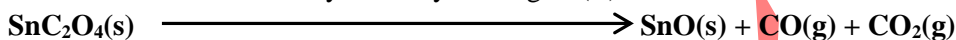
Strong heating of germanium dioxide with germanium



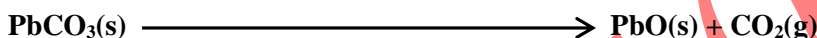
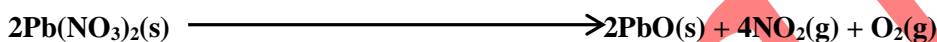
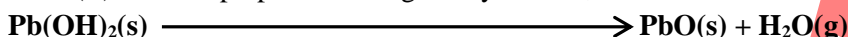
Hydrolysis of germanium (II) chloride



Tin monoxide is most easily made by heating tin(II) oxalate in absence of air.



Lead (II) oxide is prepared heating the hydroxide, nitrate or carbonate of the metal.



Structure of the monoxides

Oxide	CO	SiO	GeO	SnO	PbO
Bonding	Covalent	Covalent	Ionic	Ionic	Ionic
Structure	Simple molecular	Simple molecular	Giant ionic	Giant ionic	Giant ionic

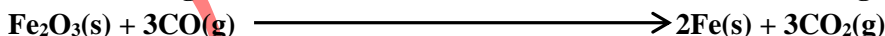
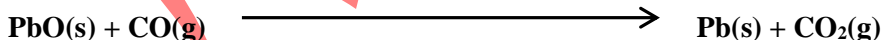
Stability of the monoxides.

The stability of the monoxides of group(IV) elements increases from carbon monoxide to lead monoxide because of increase in the stability of the +2 oxidation state down the group.

Carbon monoxide is very unstable. It is readily oxidized by oxygen in air to carbon dioxide.

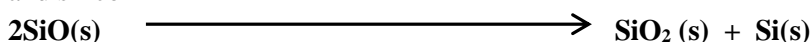


It is a reducing agent. It can reduce hot (heated) oxides of copper, zinc, lead and iron and is itself oxidized to carbon dioxide as illustrated below.



Since carbon monoxide is a strong reducing agent, it is used in the extraction of less reactive metals like iron and zinc from their respective ores.

Silicon monoxide is also unstable and disproportionates at room temperature to silicon(IV) oxide and silicon

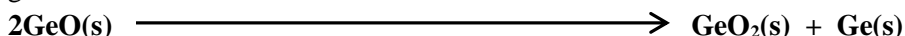


Germanium monoxide is readily oxidized when heated in air to germanium(IV) oxide

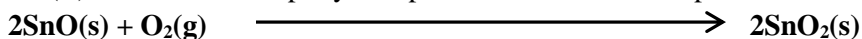


GROUP IV ELEMENTS

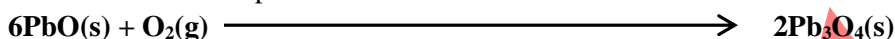
It also disproportionate when heated in absence of air to form germanium(IV) oxide and germanium.



Tin(II)oxide oxidizes rapidly if exposed to air at room temperature forming tin(IV) oxide

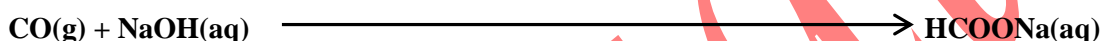


Lead(II) oxide is stable at room temperature. When it is heated very strongly in air, it oxidizes further to form a red powder of trilead tetraoxide



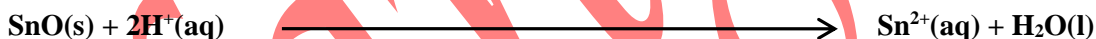
Chemical properties of the monoxides

Carbon monoxide is slightly acidic, reacting with hot concentrated sodium hydroxide solution to form sodium methanoate.

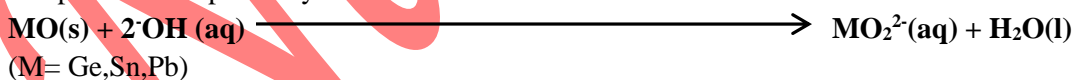


Silicon monoxide is a neutral oxide.

GeO, SnO and PbO are all amphoteric (becoming more basic on moving down the group, although they don't lose their acidic character completely). They react with acids to form salts and water.



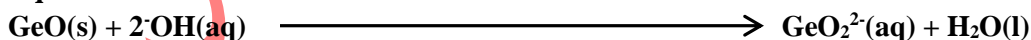
They react with alkalis such as sodium/potassium hydroxide solution to form a germanate, stannate and plumbate respectively.



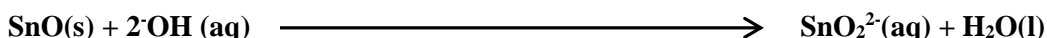
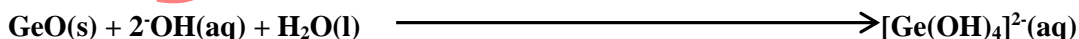
Or



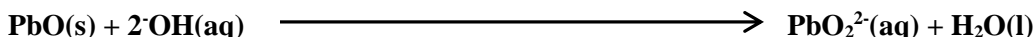
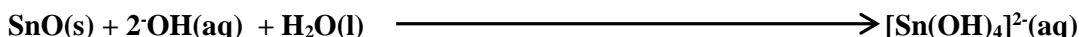
Equations



Or



Or



GROUP IV ELEMENTS

Or



The Dioxides (MO_2)

Appearance

Carbon dioxide (carbon(IV) oxide) CO_2 is a colourless gas

Silicon dioxide (silicon(IV) oxide) SiO_2 is a white crystalline solid

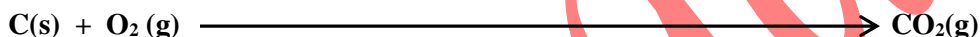
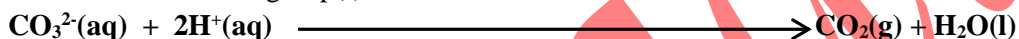
Germanium dioxide (germanium(IV) oxide) GeO_2 is a white crystalline solid

Tin dioxide (tin(IV)oxide) SnO_2 is a white solid

Lead dioxide (lead(IV)oxide) PbO_2 is a dark brown solid

Preparation of the dioxides of group(IV) elements

Carbon dioxide is made by action of a dilute mineral acid on a carbonate (dilute sulphuric acid and calcium carbonate may not be used in this case because the reaction forms an insoluble calcium sulphate which prevents further reaction) or by heating carbon strongly in excess air, or by heating carbonates other than group(I) metal carbonates



Silicon dioxide is made by heating silicon strongly in air

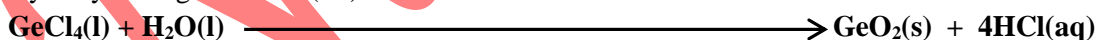


Germanium dioxide is made by any of the following methods

Heating the element strongly in air



Hydrolysis of germanium(IV) chloride

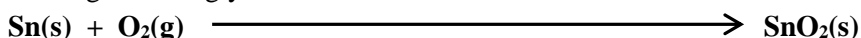


Heating germanium with concentrated nitric acid.

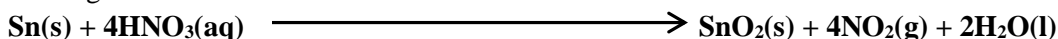


Tin dioxide can be made by any one of the following methods

Heating tin strongly in air



Heating tin with concentrated nitric acid

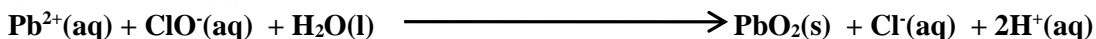


GROUP IV ELEMENTS

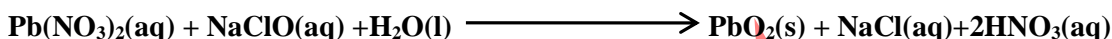
Lead dioxide can be made by (i) heating trileadtetraoxide with dilute nitric acid.



Warming a soluble lead(II) salt solution (such as lead(II) nitrate solution) with sodium hypochlorite (sodium chlorate(I)) solution.



Or



Question

State and explain what would be observed when lead(II) ethanoate solution is warmed with sodium hypochlorite solution.

A brown precipitate

The hypochlorite ions in sodium hypochlorite solution oxidised lead(II) ions in lead(II) ethanoate solution to insoluble lead(IV) oxide as a brown precipitate. The hypochlorite ions are reduced to chloride ions.

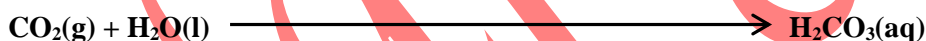


Structures of the dioxides of group(IV) elements

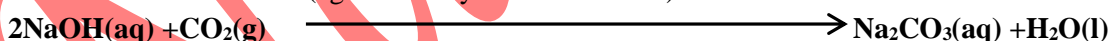
Oxide	CO ₂	SiO ₂	GeO ₂	SnO ₂	PbO ₂
Bonding	Covalent	Covalent	Covalent	Ionic	Ionic
Structure	Simple molecular	Giant covalent	Giant molecular	Giant ionic	Giant ionic

Properties of the dioxides of group(IV) elements

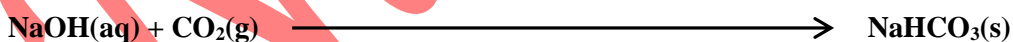
Carbon dioxide is acidic. It reacts with water to form weak acidic solution of carbonic acid.



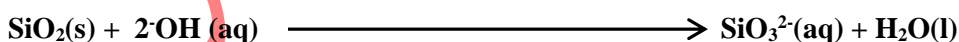
It also reacts with alkalis (eg sodium hydroxide solution) to form a salt and water



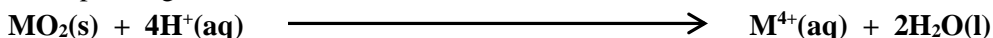
Or



Silicon dioxide is also acidic; it therefore reacts with hot concentrated sodium hydroxide solution to form sodium silicate and water.

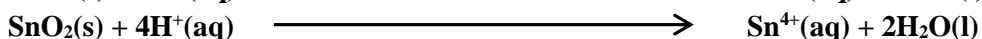
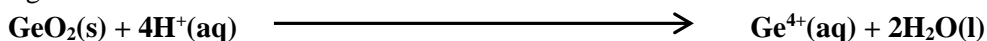


The dioxides of germanium, tin and lead are amphoteric in nature. They react with acids to form corresponding salts and water.

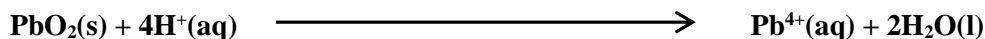


(M = Ge, Sn, Pb)

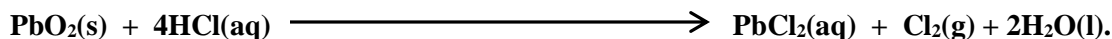
Eg



GROUP IV ELEMENTS



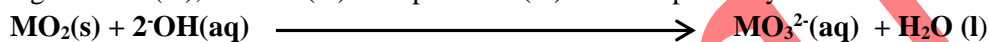
Lead(IV) oxide oxidises hot concentrated hydrochloric acid to chlorine and itself reduced to lead(II) chloride and water.



Lead(IV) oxide reacts with cold(ice cold) concentrated hydrochloric acid (at 0°C) to form lead(IV) chloride (a yellow liquid) and water.



The dioxides of Ge, Sn and Pb also react with hot concentrated sodium hydroxide solution to form a germanate(IV), stannate(IV) and plumbate(IV) salts respectively.

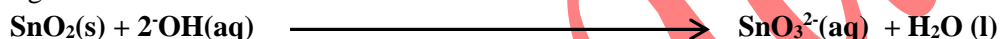


Or



(M = Ge, Sn, Pb)

Eg



Or



and



Or



Or



Thermal stability of the dioxides.

The stability of the dioxides of group(IV) elements decreases from carbon dioxide to lead dioxide because of decrease in the stability of the +4 oxidation state down the group.

The dioxides of carbon, silicon, germanium and tin are stable even at high temperatures. Lead (IV) oxide however, decomposes on warming to form the more stable lead (II) oxide with liberation of oxygen.



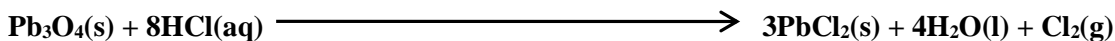
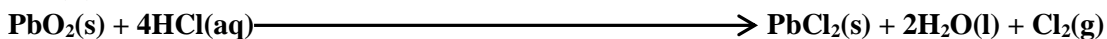
Tri-lead tetra-oxide (also called di-lead(II) lead(IV) oxide or red lead oxide) Pb_3O_4 is a red powder prepared by heating lead(II) oxide in air at about 400°C. It is a mixed oxide.



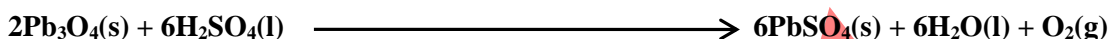
It is a mixed oxide which resembles lead(IV) oxide in some of its chemical properties as explained below

GROUP IV ELEMENTS

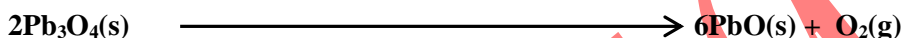
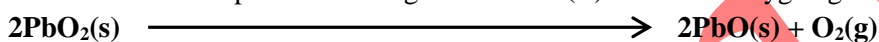
Both oxides oxidise hot concentrated hydrochloric acid to chlorine, themselves being reduced to lead(II) chloride and water.



Both oxides react with hot concentrated sulphuric acid to form lead(II) sulphate, oxygen gas and water



Both oxides decompose on heating to form lead(II) oxide and oxygen gas.



Lead (IV) oxide as an oxidizing agent

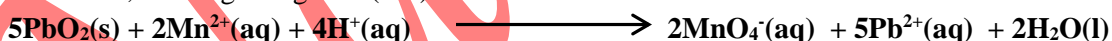
Lead(IV) oxide oxidizes the hot concentrated hydrochloric acid to chlorine and it's reduced to lead(II) chloride and water.



Observation:

The brown solid dissolves with effervescence of a greenish –yellow gas forming a colorless solution..

lead(IV) oxide oxidises hot manganese(II) salts in aqueous solution in presence of concentrated nitric acid, forming manganate(VII) ions.



Observation:

A purple solution forms.

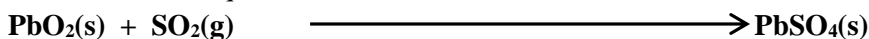
Hot lead(IV) oxide oxidizes sulphur dioxide to sulphur trioxide and itself is reduced to lead(II) oxide.



The lead(II) oxide and sulphur trioxide then react to form lead(II) sulphate.



Thus the overall equation of reaction is



Observation

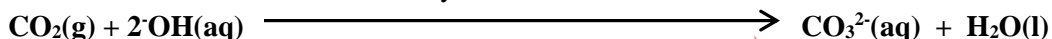
Brown solid turns to a white solid.

GROUP IV ELEMENTS

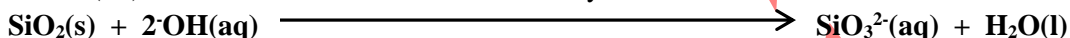
Using carbon dioxide, silicon(IV) oxide and lead(IV) oxide to illustrate your answer, explain the trend in the acidic nature of oxides of the group(IV) elements.

The acidic nature of the oxides decreases from carbon dioxide to lead(IV) oxide. Carbon dioxide and silicon(IV)oxide are acidic while lead(IV) oxide is amphoteric.

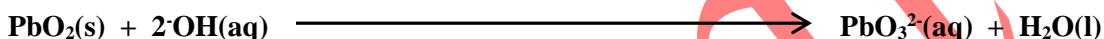
Carbon dioxide reacts with sodium hydroxide solution to form sodium carbonate and water.



Silicon(IV)reacts with hot concentrated sodium hydroxide solution to form a silicate and water.



Lead(IV) oxide reacts with hot concentrated sodium hydroxide solution to form a plumbate and water.



Or



It also reacts with cold concentrated hydrochloric acid to form lead(IV) chloride and water.



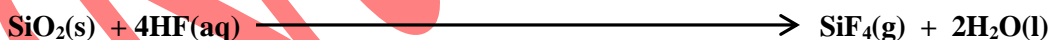
Write equation(s) for the reaction between silicon(IV) oxide and Magnesium



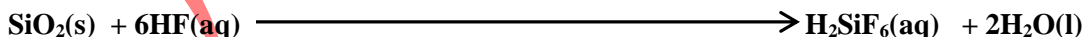
Or



Hydrofluoric acid



Or



Explain why carbon dioxide is a gas at room temperature while silicon dioxide is a solid with a very high melting point.

Carbon is very electronegative atom and has a very small atomic radius. Therefore, it is capable of forming strong double bonds with oxygen leading to formation of discrete molecules of carbon dioxide at room temperature with weak Van der Waals' of attraction between the molecules hence gaseous at room temperature.

GROUP IV ELEMENTS

Silicon has a lower electronegativity and a larger atomic radius hence cannot form multiple (double) bonds with oxygen but forms single silicon-oxygen bonds with each silicon atom bonded to four oxygen atoms in a three dimensional giant covalent structure which is strong, hence silicon dioxide is a solid with a high melting point.

When red lead oxide Pb_3O_4 was reacted with nitric acid, a solid was formed.

Write an equation for the reaction that took place

The mixture from (a) was filtered and the residue warmed with concentrated hydrochloric acid.

State what was observed.

Explain your answer.

The filtrate from (a) was divided into two parts

- (i) To the first part was added aqueous potassium iodide. State what was observed and write the equation for the reaction.*
- (ii) The second part was evaporated to dryness and heated strongly. Explain what was observed and write the equation for the reaction that took place*

The chlorides

The elements form two types of chlorides i.e the tetrachlorides MCl_4 in which the elements are in the +4 oxidation state and the dichlorides, MCl_2 in which the elements are in the +2.

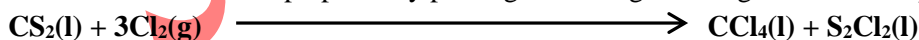
a) The tetrachlorides (MCl_4)

Appearance

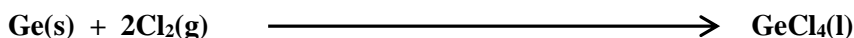
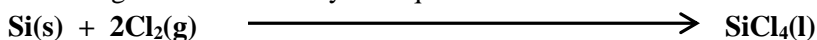
The tetrachlorides of carbon, silicon, tin and germanium are colourless covalent liquids but lead tetrachloride (lead(IV) chloride) is a yellow liquid.

Preparation

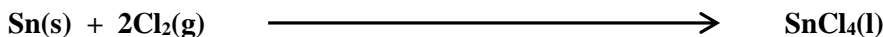
Carbon tetrachloride is prepared by passing chlorine gas through carbon disulphide.



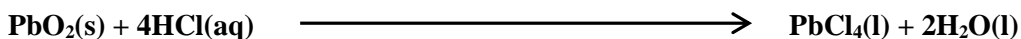
The tetrachlorides of silicon, tin and germanium can be prepared by heating the elements in dry chlorine gas as illustrated by the equations below.



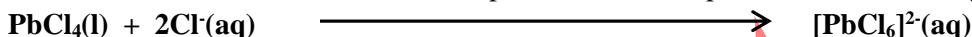
GROUP IV ELEMENTS



Lead(IV) chloride is prepared by reacting lead(IV) oxide with cold concentrated hydrochloric acid at 0°C.



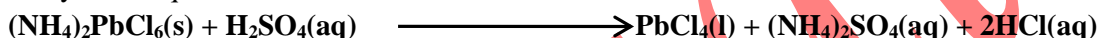
However, if the acid is in excess, some of the lead(IV) chloride reacts with the chloride ions present in the excess acid to form the hexachloroplumbate(IV) complex ion which is also yellow.



Addition of a concentrated solution of ammonium chloride to the solution containing the above complex ions gives an immediate pale yellow precipitate of ammonium hexachloroplumbate(IV)



When this solid is treated with concentrated sulphuric acid at about 0°C, lead(IV) chloride is formed as a yellow liquid.



9.12g of an inorganic compound *X* contains 0.5g of nitrogen, 0.16g hydrogen, 4.14g of lead and 4.2g of chlorine. Given that 9.12g of *X* contains 0.02 moles at s.t.p

a) Determine the molecular formula of *X*

b) *X* is an ionic compound containing a complex anion of lead and a simple cation. Name

(i) compound *X*

(ii) complex anion of lead in *X*

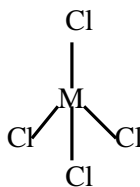
c) The complex anion in b(ii) above can be prepared from lead(IV) oxide and hydrochloric acid.

i) State the conditions for the reaction leading to the formation of the anion.

ii) Write the formula and give the IUPAC name of any other complex ion formed by lead in the same oxidation state as the anion in b(ii) above.

Bonding and structure of the tetrachlorides

The bonding in the tetrachlorides is covalent. They all have a simple molecular structure with weak van der Waals' forces of attraction binding molecules together. Therefore, all of them are volatile liquids at room temperature. The individual molecules have a tetrahedral shape.



GROUP IV ELEMENTS

In the tetrachlorides MCl_4 , the chlorine atom is more electronegative than the central group (IV) atom M. Therefore, the chlorine atom attracts the bonding electrons more towards itself and acquires a partial negative charge while the group(IV) atom acquires a partial positive charge. This unequal distribution of bonding electrons establishes a dipole moment in the direction of the more electronegative chlorine atom, hence making the M-Cl bonds in the tetrachlorides MCl_4 polar.

However, the tetrachloride molecule is non-polar because of the symmetrical tetrahedral arrangement of the M-Cl bonds. Therefore, the effects of bond polarity in the opposite directions cancel out each other, so that the net dipole moment in the whole molecule, MCl_4 is zero, thus making the molecule to be nonpolar.

Thermal stability of the tetrachlorides

Thermal stability decreases down the group

Explanation:

The atomic radius of group(IV) elements increases down the group (from carbon to lead), so the covalent bond between the group(IV) atom and chlorine becomes longer and weaker down the group. Thus amount of energy required to break the covalent bonds in the tetrachlorides decreases hence the decrease in thermal stability. This means that CCl_4 , $SiCl_4$ and $GeCl_4$ are stable even at high temperatures, where as $SnCl_4$ and $PbCl_4$ decompose readily on heating.

Lead tetrachloride $PbCl_4$ and tin tetrachloride $SnCl_4$ decomposes even at room temperature to form a dichloride and chlorine gas

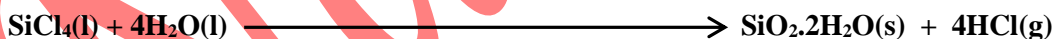


Hydrolysis of the tetrachlorides

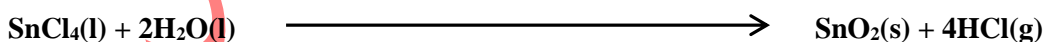
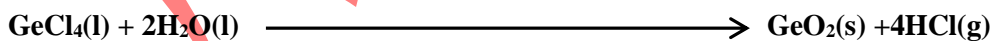
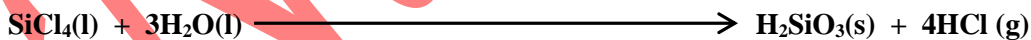
All the tetrachlorides except for carbon tetrachloride (because carbon lacks a vacant d-orbital that accommodate the lone pairs of electrons from the water molecules) are hydrolysed by water to form the dioxides and hydrogen chloride.



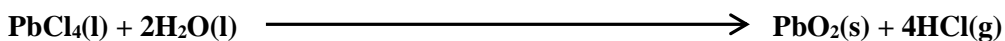
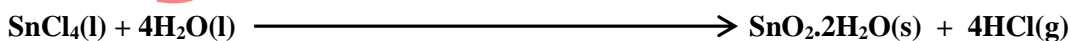
Or



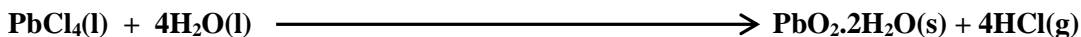
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Or



Or



GROUP IV ELEMENTS

The tetrachlorides of silicon, germanium, tin and lead are hydrolysed because these elements have empty (vacant) d-orbitals of the right energy which can accommodate lone pairs of electrons from water molecules.

Carbon tetrachloride is not hydrolysed because the carbon ($1s^2 2s^2 2p^2$) atom in the molecule lacks vacant d-orbitals to accommodate the lone pairs of electrons from water molecules.

Question

State what would be observed and write equations for the reactions that would take place, if any, when the following compounds are treated with water.

a) Carbon tetrachloride

Two separate layers form

b) Silicon tetrachloride

White fumes and a white precipitate

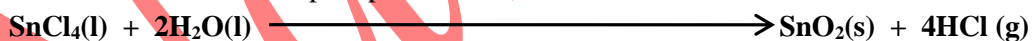


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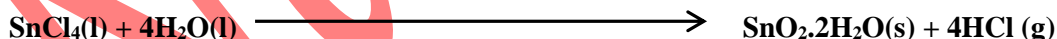


c) Tin(IV) chloride

White fumes and a white precipitate

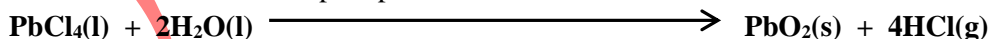


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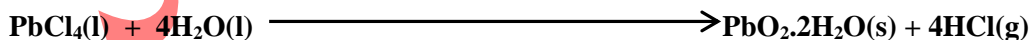


d) Lead(IV) chloride

White fumes and a brown precipitate



Or

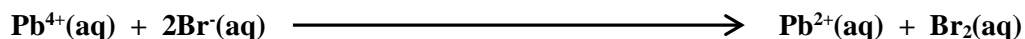


Note:

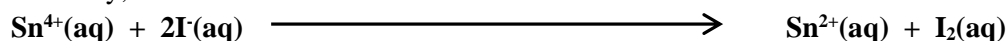
The tetrabromide and tetraiodides of lead and tin do not exist. They cannot be prepared because of the strong oxidising action of lead(IV) and tin(IV) ions and the strong reducing action of bromide and iodide ions. Therefore, when a solution containing lead(IV) ions is mixed with one containing bromide ions, the lead(IV) ions would oxidize the bromide ions to bromine.

GROUP IV ELEMENTS

The bromide ions would reduce the lead(IV) ions to lead(II) ions, so it's impossible to form lead(IV) bromide but instead lead(II) bromide is formed



Similarly;



Questions

Explain why lead(IV) chloride exists but lead(IV) bromide does not.

The bromide ion has a larger ionic radius than the chloride ion, hence the bromide ion is a stronger reducing agent than the chloride ion.

Therefore, the bromide ion reduces lead(IV) ions to lead(II) ions thus lead(IV) bromide cannot exist.

The chloride ion cannot reduce lead(IV) ions hence lead(IV) chloride exists

The dichlorides (MCl_2)

Stable dichlorides are only formed by germanium, tin and lead.

Appearance

Germanium(II) chloride, GeCl_2 is a pale yellow solid

Tin(II) chloride, SnCl_2 is a white solid

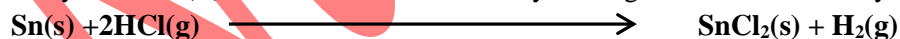
Lead(II) chloride, PbCl_2 is a white solid

Preparation of the dichlorides

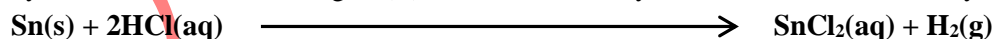
Germanium(II) chloride is made by passing the vapour of germanium(IV) chloride over hot germanium.



Anhydrous tin (II) chloride is best obtained by heating tin in a current of dry hydrogen chloride.



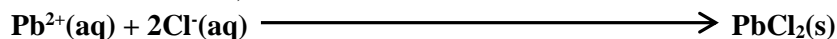
Hydrated tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ can be obtained by heating tin with concentrated hydrochloric acid or reacting tin(II) oxide and dilute hydrochloric acid followed crystallization.



Or



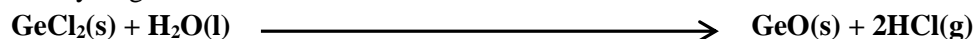
Lead (II) chloride is prepared by precipitation during which dilute hydrochloric acid or sodium chloride solution is added to an aqueous solution of a lead(II) salt (e.g lead(II) nitrate or lead(II) ethanoate solutions)



GROUP IV ELEMENTS

Hydrolysis of the dichlorides

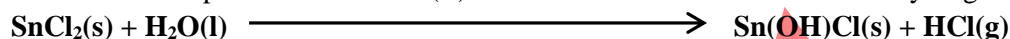
Germanium(II) chloride is covalent and is hydrolysed by water forming germanium(II) oxide and hydrogen chloride.



Observation:

Yellow solid turns to a white solid and white fumes are formed.

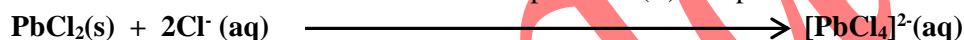
Anhydrous tin(II) chloride is predominantly covalent. It reacts with water (is hydrolysed) to form a white suspension of basic tin(II) chloride with liberation of fumes of hydrogen chloride.



If water is hot and present in a large excess, tin(II) chloride is hydrolysed to form tin(II) hydroxide and hydrogen chloride.



Although lead(II) chloride is ionic, it is insoluble in cold water but soluble in hot water. It is more soluble in concentrated hydrochloric acid than in water because it reacts with chloride ions in the acid to form a soluble tetrachloroplumbate(II) complex ion.

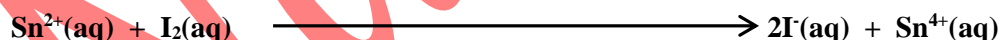


Note:

Tin(II) chloride is also soluble in concentrated hydrochloric acid due to formation of a soluble tetrachlorostannate(II) complex ion.



Tin(II) chloride is a strong reducing agent, reducing mercury(II) ions to mercury; iron(III) ions to iron(II) ions; iodine to iodide ions; acidified dichromate(VI) ions to chromium(III) ions and acidified manganate(VII) ions to manganese(II) ions. The tin(II) ions are oxidized to tin(IV) ions.



The hydrides MH_4

All the elements form tetravalent hydrides – i.e methane CH_4 , silane SiH_4 , germane GeH_4 , stannane SnH_4 and plumbane PbH_4 .

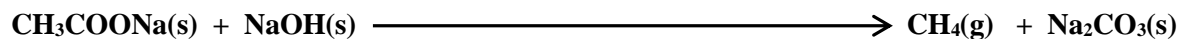
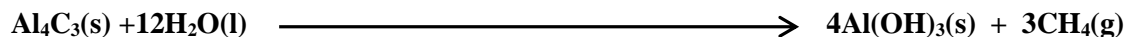
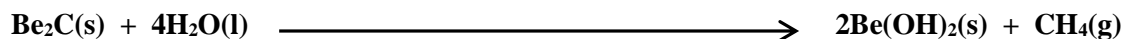
They are covalent, colourless gases at room temperature, with simple molecular structures.

Their boiling points increase from methane to plumbane because of increase in molecular mass from methane to plumbane so the van der Waals forces of attraction between the molecules also increase in strength in the same direction.

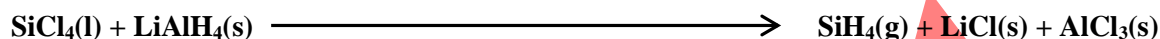
Preparation

GROUP IV ELEMENTS

Methane is prepared by hydrolysis of beryllium carbide or aluminium carbide or heating sodium ethanoate with soda lime (solid mixture of sodium hydroxide and calcium oxide)



The hydrides of the silicon, germanium, tin and lead can be made by reduction of their tetrachlorides with lithium aluminium hydride at 0°C in the presence of ether, e.g.



Silane, SiH₄, can also be prepared by reacting magnesium silicide with dilute hydrochloric acid



Thermal stability of the tetrahydrides

When heated, they all decompose to form the element and hydrogen gas and the ease to decompose increases down the group due to decrease in decomposition temperatures shown in the table below

Hydride	Decomposition temperature (°C)
CH ₄	800
SiH ₄	450
GeH ₄	285
SnH ₄	150
PbH ₄	0

Therefore, thermal stability of the hydrides decreases down the group. This is because atomic radius increases down the group, so the covalent bonds formed between atoms of group(IV) elements and hydrogen becomes longer and weaker, resulting into decrease in the decomposition temperature hence decrease in thermal stability.

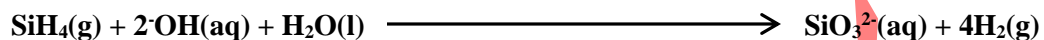
As their thermal stability decreases, the ease to decompose into the element and hydrogen gas increases and hence they become stronger reducing agents. Thus PbH₄ is the strongest reducing agent where as CH₄ is the weakest reducing agent.

GROUP IV ELEMENTS

Hydrolysis of hydrides

Methane does not react with water (ie is not hydrolysed) because the carbon atom lacks empty 2d-orbitals so it cannot accept the lone pairs of electrons from the water molecules.

Silane, SiH_4 is hydrolysed slowly by water and more rapidly in the presence of an alkali to form a silicate and hydrogen gas. This is because the silicon atom has empty (vacant) 3d-orbitals which can accommodate lone pairs of electrons from the oxygen atoms of water molecules.



Germane, stannane and plumbane are surprisingly resistant to hydrolysis.

The decomposition temperatures of hydrides of group IV elements of the Periodic Table are given the below

Formula of the hydride	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
Decomposition temperature ($^\circ\text{C}$)	800	450	285	150	0

- (i) State the relationship between the decomposition temperatures and thermal stability of the hydrides *Both the decomposition temperature and thermal stability of the hydrides decrease from methane to plumbane*
- (ii) Explain your answer in (a) (i)
This is because atomic radius of the elements increases from carbon to lead. Thus the group(IV) atom - hydrogen bond (M-H) strength decreases resulting into decrease in amount of energy required to break the covalent bond
- (iii) Write the equation for the reaction of silicon tetrahydride with sodium hydroxide solution.
$$\text{SiH}_4(\text{g}) + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{SiO}_3^{2-}(\text{aq}) + 4\text{H}_2(\text{g})$$