

GROUP IV CHEMISTRY

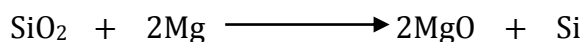
Occurance

- ☑ Carbon exists naturally as diamond and graphite in the crystalline form. Other non-crystalline (amorphous) forms of carbon known exist e.g. wood charcoal, animal charcoal, soot, sugar charcoal, lamp black, coke, coal e.t.c.
- ☑ Silicon exists naturally as silicon IV oxide, SiO_2 , in sand and as quartz, and also as a number of silicates in rocks and clays.
- ☑ Germanium minerals are rare but the element occurs as traces in ores of other metals and coal.
- ☑ Tin is extracted from the ore Tinstone, SnO_2 .
- ☑ Lead is extracted from the ore galena, PbS .

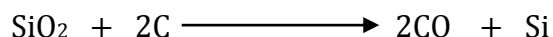
Extraction of the Elements: (Students' research)

SILICON

After oxygen, silicon is the most abundant element in the earth's crust. It occurs extensively as the oxide, silica, in various forms, for example, flint, quartz, sand, and as silicates in rocks and clays, but not as the free element, silicon. Silicon is prepared by reduction of silica, SiO_2 - Powdered "amorphous" silicon can be obtained by heating dry powdered silica with either powdered magnesium or a mixture of powdered aluminium and sulphur (this supplies additional heat). After the reaction has ceased, magnesium (or aluminium) oxide and any unchanged silica is removed by washing with hydrofluoric acid in a polythene vessel:



(If an excess of magnesium is used, magnesium silicide, Mg_2Si , is also produced.) The silicon obtained is a light brown hygroscopic powder. Crystalline or 'metallic' silicon is obtained industrially by the reduction of silica with carbon in an electric arc furnace:



The formation of silicon carbide, SiC (carborundum), is prevented by the addition of a little iron; as much of the silicon is added to steel to increase its resistance to attack by acids, the presence of a trace of iron does not matter. (Addition of silicon to bronze is found to increase both the strength and the hardness of the bronze.)

Silicon is also manufactured by the reaction between silicon tetrachloride and zinc at 1300K and by the reduction of trichlorosilane with hydrogen. Crystalline silicon has the tetrahedral diamond arrangement, but since the mean thermo-chemical bond strength between the silicon atoms is less than that found between carbon atoms ($\text{Si}-\text{Si}$, 226kJmol^{-1} , $\text{C}-\text{C}$, 356kJmol^{-1}), silicon does not possess the great hardness found in diamond. Amorphous silicon (silicon powder) is microcrystalline silicon.

GERMANIUM

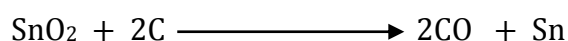
Germanium is a greyish-white, brittle solid, obtained by reducing the dioxide, GeO_2 , with hydrogen or carbon at red heat. Germanium is a rare element found in trace quantities in coke obtained from bituminous coal. When this coke is burnt, germanium dioxide, together with many other metal oxides, is deposited in the flue. The extraction of germanium

dioxide from this mixture is a complex process. Impure germanium and silicon are both purified by zone refining and both can be obtained in a very high purity, for example silicon pure to one part in 10¹⁰ can be obtained*. Germanium, like silicon, crystallises with a diamond structure, the mean thermochemical bond strength being Ge—Ge, 188 kJ mol⁻¹.

** Silicon and germanium are now used extensively in semi-conductors; for this purpose, extreme initial purity is needed, since the desired semi-conducting properties are conferred by the introduction of only a few parts per million of either a Group III element (for example indium), giving rise to a 'deficiency' of electrons in the silicon or germanium crystal, or a Group V element (for example arsenic) giving a 'surplus' of electrons.*

TIN

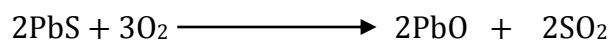
The common ore of tin is *tinestone* or *cassiterite*, SnO₂, found in Cornwall and in Germany and other countries. The price of tin has risen so sharply in recent years that previously disregarded deposits in Cornwall are now being re-examined. Tin is obtained from the tin dioxide, SnO₂, by reducing it with coal in a reverberatory furnace:



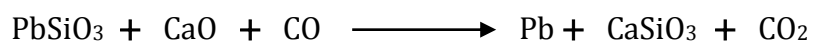
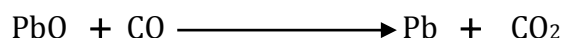
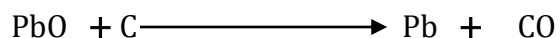
Before this treatment, the cassiterite content of the ore is increased by removing impurities such as clay, by washing and by roasting which drives off oxides of arsenic and sulphur. The crude tin obtained is often contaminated with iron and other metals. It is, therefore, remelted on an inclined hearth; the easily fusible tin melts away, leaving behind the less fusible impurities. The molten tin is finally stirred to bring it into intimate contact with air. Any remaining metal impurities are thereby oxidised to form a scum ('tin dross') on the surface and this can be skimmed off. Very pure tin can be obtained by zone refining. Tin exists in three different forms (allotropes). 'Grey tin' has a diamond structure, a density of 5.75 g cm⁻³ and is stable below 286 K. 'White tin' exists as tetragonal crystals, has a density of 7.31 g cm⁻³ and is stable between 286 and 434 K. Between 434 K and the melting point of tin, 505 K, tin has a rhombic structure, hence the name 'rhombic tin', and a density of 6.56 g cm⁻³.

LEAD

The principal ore of lead is *galena*, PbS. Although there are some galena deposits in Great Britain, much of this country's requirements must be imported. In the extraction of lead, the sulphide ore is first roasted together with quartz in a current of air:



Any lead(II) sulphate formed in this process is converted to lead(II) silicate by reaction with the quartz. The oxide produced is then mixed with limestone and coke and heated in a blast furnace. The following reactions occur:



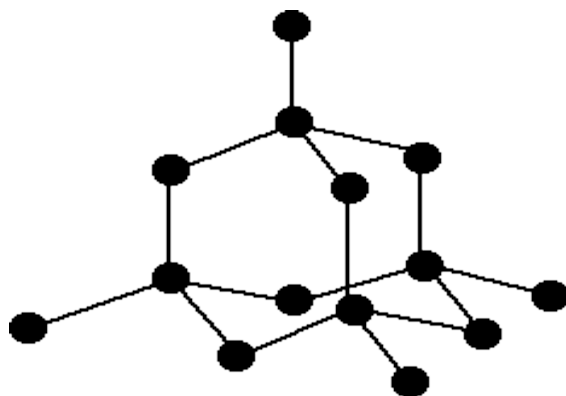
The last equation explains the function of the limestone. An older process, in which the ore was partially roasted, the air shut off and the temperature raised so that excess sulphide reacted with the oxide produced to give lead, is now obsolete.

Crude lead contains traces of a number of metals. The desilvering of lead is considered later under silver. Other metallic impurities are removed by smelting under controlled conditions when arsenic and antimony form a scum of lead(II) arsenate and antimonate on the surface while copper forms an infusible alloy which also takes up any sulphur, and also appears on the surface. The removal of bismuth, a valuable by-product, from lead is accomplished by making the crude lead the anode in an electrolytic bath consisting of a solution of lead in fluorosilicic acid. Gelatin is added so that a smooth coherent deposit of lead is obtained on the pure lead cathode when the current is passed. The impurities here (i.e. all other metals) form a sludge in the electrolytic bath and are not deposited on the cathode. Lead has only one form, a cubic metallic lattice. Thus we can see the change from non-metal to metal in the physical structure of these elements, occurring with increasing atomic weight of the elements carbon, silicon, germanium, tin and lead.

Structures of the elements

a) Diamond

In diamond, carbon forms a giant atomic structure in which every carbon atom forms four strong covalent bonds by sharing its four valence electrons with each of the four neighbours. The bonds are tetrahedrally arranged about each carbon atom. The network of strong covalent continues infinitely giving rise to a three-dimensional giant atomic covalent structure



NOTE

- a) Diamond is extremely hard because of the strength and uniformity of the bonding. There are no planes of weakness in its crystal structure.
- b) Diamond does not conduct electricity because all the four valence electrons of each C-atom are used in bonding.
- c) Silicon and Germanium are non-allotropic and both adopt giant-atomic /covalent structures similar to that of diamond.

b) Graphite

A graphite crystal has layers of hexagonal rings of C-atoms. Each layer is a giant atomic molecule in 2-D. Each C-atom is bonded covalently to three other atoms. (The atoms in the layer are joined by strong Covalent bonds). However, the layers are joined by weak forces (Van der Waal's). This makes it possible for one layer to slide over the other, and as such, graphite is slippery.

- c) Tin: Tin has three allotropic forms ie.
 - Grey tin
 - White tin and
 - Rhombic tin

White tin is the normal form at room temperature. Tin has a non-metallic diamond-like structure in grey tin. The other allotropes are metallic with close-packed structures.

Note: Lead has no allotropes. It is metallic with a cubic close-packed structure.

Metallic character

Metallic character generally increases down the group.

C is a non-metal; Si and Ge are metalloids, Sn and Pb show typical metallic properties.

The increase in metallic character shows itself in the structures of the elements, physical properties such as conductivity and malleability, increasing tendency to form M^{2+} ions and the acidic or basic properties of the oxides and hydroxides.

Valence and oxidation states

All group 4 elements have a general outer configuration $ns^2 np^2$. As such, the elements show two oxidation states +2 and +4.

The stability of the +2 ox-state increases down the group. This is due to the **inert-pair effect**.

🔗 Inert –pair effect is the inability of the ns^2 electrons to participate in bonding.

As the s-electrons are more penetrating, they experience greater nuclear attraction and become relatively more stable than the np-electrons. This makes them less available to be involved in bonding.

- ❖ Each element has four outer electrons $ns^2 np^2$. The shielding of the outer shell for C and Si is quite efficient. However, as we descend the group due to the presence of d and f electrons, which offer poor shielding, the outer s electrons are withdrawn into the atomic core and begin to behave as inner electrons.
- ❖ Hence, Pb and Sn often behave as if they only have two outer electrons and show valencies of +2 and +4.

Inert pair effect is also defined as the increase in stability of the lower ox state with increasing atomic no.

In C and Si compounds, the +4 oxidation state is very stable relative to the +2 state. The +2 state is very rare (ie. Unstable) and easily oxidized to the +4. Eg.

CO (in +2 state) is a very strong reducing agent, being oxidized to the more stable CO_2 (+4 oxidation state) e.g.

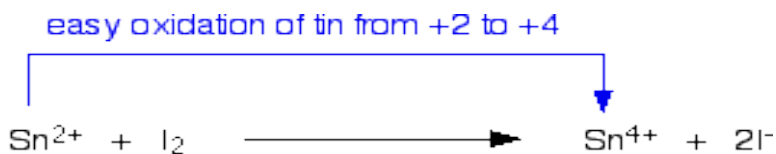


Silicon II oxide, SiO, is too unstable to exist at room temperature. At $2000^\circ C$, it disproportionates to Silicon IV oxide and Si.

GeO_2 is more stable than GeO . As such, GeO is readily converted to GeO_2 in a **disproportionation** reaction.

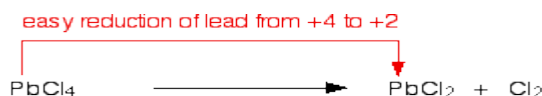


Therefore, Germanium II and Tin II compounds are strong reducing agents. For example, a solution containing tin (II) ions (for example, tin(II) chloride solution) will reduce a solution of iodine to iodide ions. In the process, the tin (II) ions are oxidised to tin (IV) ions.

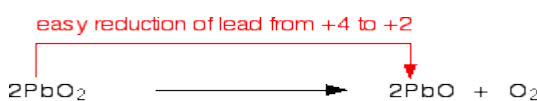


With Lead, however, the +2 oxidation state is more stable than the +4. Lead IV compounds therefore act as oxidizing agents.

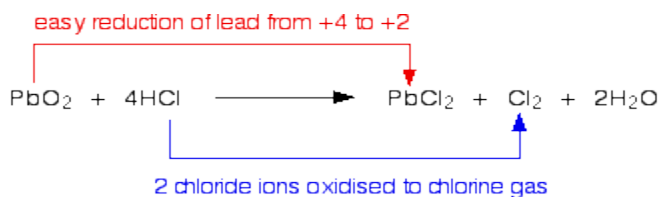
Lead (IV) chloride, for example, decomposes at room temperature to give lead(II) chloride and chlorine gas:



... and lead (IV) oxide decomposes on heating to give lead(II) oxide and oxygen.



Lead(IV) oxide also reacts with concentrated hydrochloric acid, oxidising some of the chloride ions in the acid to chlorine gas. Once again, the lead is reduced from the +4 to the more stable +2 state.



Differences between the chemistry of carbon and that of the other group members

Carbon behaves differently from the rest of the group members because of:

- ✓ Its small atomic size
- ✓ High electronegativity
- ✓ Non-availability of empty d-orbitals (and or d-orbital electrons)

Because of that carbon

- ☑ Is limited to a co-ordination number of 4 while others can have 6.
- ☑ Has 1 valence in most of its compounds, others have more than 1.
- ☑ Does not show inert-pair effect unlike others.
- ☑ Is more electronegative than the rest of the members.
- ☑ Forms compounds which are relatively inert, unlike others.
- ☑ Forms gaseous oxides unlike others.
- ☑ Can form stable multiple bonds with itself and other non-metals
- ☑ Can form long chains of its self or form rings (see organic chemistry)

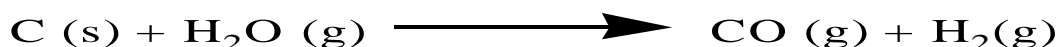
- ☑ Can form no complex ions, unlike the latter elements (SiF_6^{2-} , PbCl_4^- , SnCl_6^{2-} e.t.c exist)

CHEMICAL PROPERTIES OF THE ELEMENTS

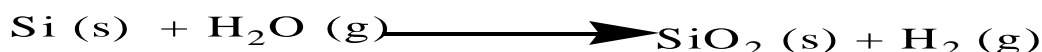
The elements are relatively unreactive, but reactivity increases down the group due to increase in electro positivity caused by increased atomic radius. Some of their reactions are:

With water:

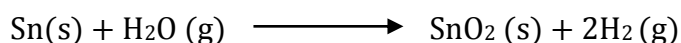
- Amorphous carbon (coke) reacts with steam when heated at blast furnace temperatures to produce water gas (a mixture of carbon monoxide and hydrogen)



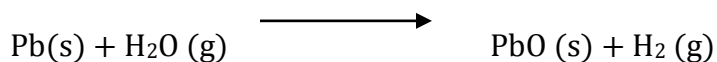
- Silicon (red hot) reacts with boiling water to form SiO_2 and hydrogen.



- Ge is not affected by water in any form at any temperatures.
- When heated, Sn is slowly attacked by steam to form SnO_2 and hydrogen.



- Lead reacts with both steam and soft cold water.
- ✓ With steam, it forms Lead II oxide and hydrogen.



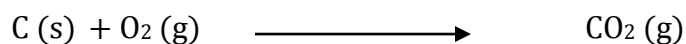
- ✓ With soft water, it slowly reacts to form lead II hydroxide and hydrogen.



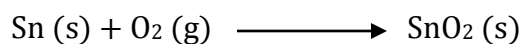
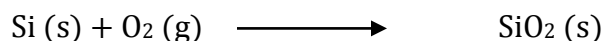
With air:

All elements react on heating to give the oxides.

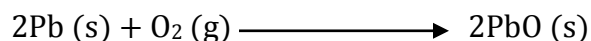
In limited oxygen, C forms CO, and forms CO_2 in plenty.



Silicon and Tin form SiO_2 and SnO_2 respectively.



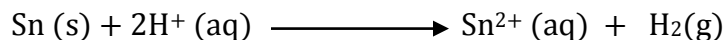
Lead forms PbO because at high temperatures is very unstable and reverts to PbO.



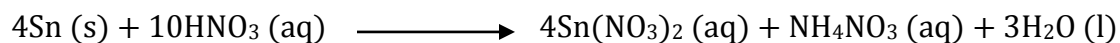
Reaction with dilute mineral acids

C, Si and Ge do not react with dilute mineral acids.

Sn slowly reacts with hot dilute HCl, the reaction being more rapid at higher acid concentrations, forming tin II chloride and hydrogen. It reacts with hot dilute sulphuric acid in the same sense.



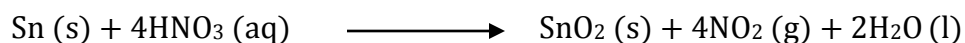
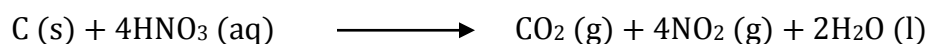
With dilute nitric acid, tin forms tin II nitrate, ammonium nitrate and water.



Lead is rendered passive by dilute hydrochloric acid and sulphuric acids because of the formation of insoluble PbCl_2 and PbSO_4

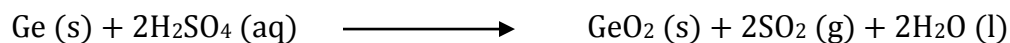
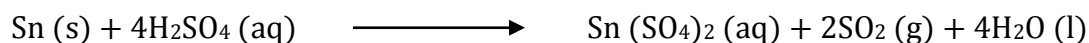
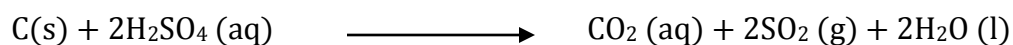
Reaction with conc. Acids

When heated with hot concentrated nitric acid, the elements (except Si) form dioxides apart from Lead, for it forms the nitrate. Silicon dissolves incompletely in conc nitric acid giving SiO_2 , NO, H_2O .

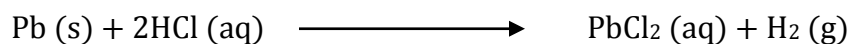
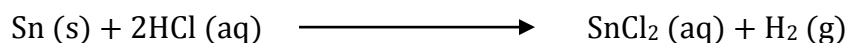


Cold, conc.

The elements react with hot concentrated sulphuric acid according to the equations below

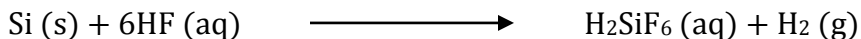


With Concentrated hydrochloric acid tin reacts vigorously to form tin II chloride and lead reacts on boiling to form lead II chloride.



(PbCl_2 is soluble in hot solutions)

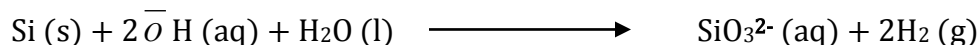
- ☑ Silicon is not attacked by acids except concentrated hydrofluoric acid which reacts with it to form hexafluorosilic acid and hydrogen gas.



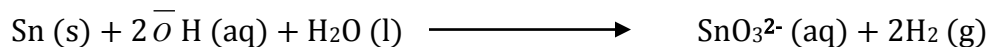
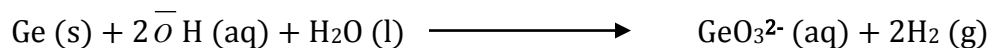
Reaction with alkalis

- ☑ Carbon does not react with alkalis.

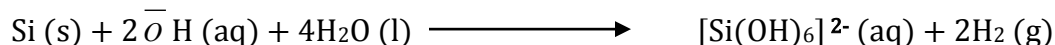
Silicon reacts readily with hot concentrated aqueous alkalis to form silicates and hydrogen.



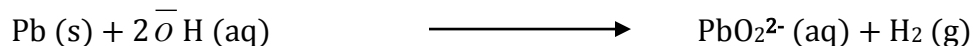
Germanium and tin react with hot alkalis to form a germanate IV and stannate IV salts respectively, in addition to hydrogen gas, respectively.



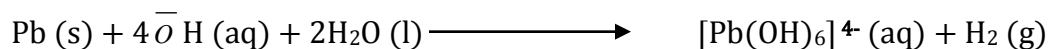
or



Lead is attacked very slowly by hot concentrated alkalis to form hydrogen and the corresponding plumbate II solution.



Or



Intext questions:

Qn.1: 2.8g of solder were boiled with dilute Nitric acid; the resultant solution was diluted and made up to 250cm³. 20cm³ of this solution was titrated with 0.04M acidified potassium dichromate, 20cm³ of the dichromate solution was required for complete reaction. Calculate the percentage of tin in solder (76.5%)

b) Explain why potassium manganate(VII) can't be used instead of potassium dichromate.

Qn.2: 0.2g of magnesium was heated with excess silicon; the product was reacted with excess dilute Hydrochloric acid to evolve 93.3cm³ of a gaseous hydride. Determine the mass of silicon that reacted with magnesium

COMPOUNDS OF GROUP IV ELEMENTS

THE OXIDES

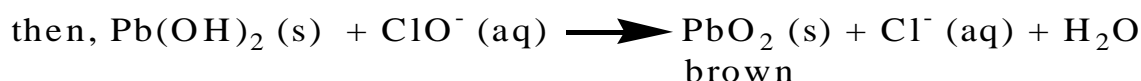
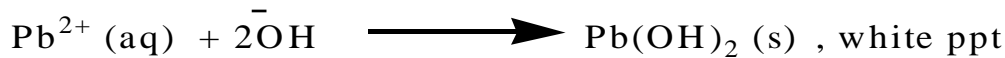
The elements form two types of oxides. The dioxides, in the +4 oxid-state, and the monoxides, in the +2 oxid-state.

a) The dioxides, MO₂

CO₂, SiO₂, GeO₂ and SnO₂ can be made by heating the elements in air (see rxns with air).

Lead (IV) oxide can be prepared by the action of an alkaline chlorate(I) solution on a solution of a lead(II) salt say, Pb(NO₃)₂. The reaction can be considered in two stages:

- Formation of a white precipitate.
- The white precipitate of lead hydroxide (or hydrated lead (II) oxide) is then oxidized by the chlorate (I) to the brown dioxide:



Overall eqn:

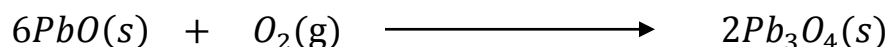
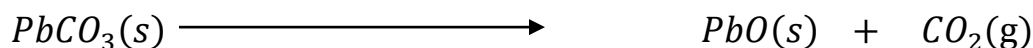


Lead (IV) oxide also can be prepared by heating trilead tetra oxide (Pb₃O₄) with excess dilute nitric acid. A dark brown precipitate (PbO₂) is formed.

Procedure:

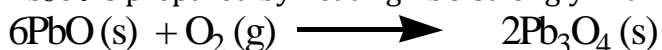
Lead(II) carbonate, nitrate oxalate or acetate is heated strongly until no further change. Decomposition occurs leaving lead(II) oxide as a brown residue when hot yellow on cooling. The lead(II) oxide is then heated in a stream of oxygen at 400°C in a crucible to form trilead tetraoxide. To this is then added hot dilute nitric acid and the mixture filtered.

The residue is lead(IV) oxide which is then dried between filter papers:



The Lead (IV) oxide is then filtered off, washed well with hot distilled water and dried.

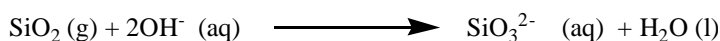
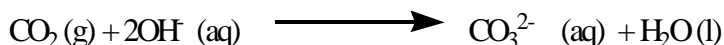
- ☒ Pb₃O₄ is prepared by heating PbO strongly in air to 450°C



Oxide properties

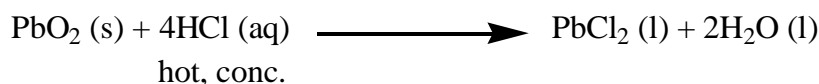
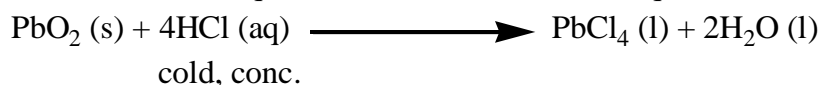
- ☒ CO₂ dissolves in water to form weak carbonic acid

- ☑ SiO₂ is insoluble and does not react with water
- ☑ **Both CO₂ and SiO₂ are acidic in nature.** They react with aqueous caustic alkalis to form the corresponding carbonates and silicates respectively, in addition to water.



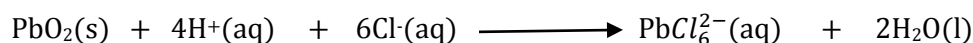
- ☑ **The dioxides of Ge, Sn and Pb are amphoteric in nature.**

- ☑ They react with concentrated acids forming the corresponding salts and water.

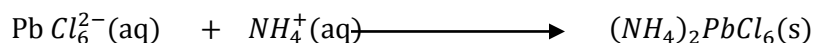


Note:

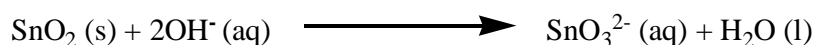
If reacted with excess ice cold conc. Hydrochloric acid, PbO₂ forms hexachloroplumbate(IV) ions:



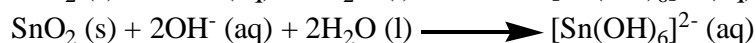
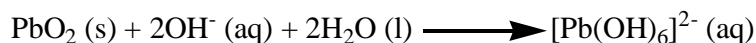
The complex ion reacts with concentrated Ammonium chloride to form a yellow precipitate of Ammonium hexachloroplumbate(IV)



- ☑ They also react with fused or aqueous caustic alkalis to form the corresponding complex salts.

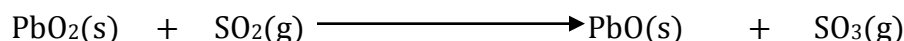


or

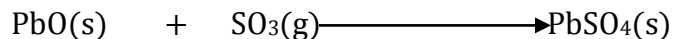


- ☑ Lead(IV) oxide reacts with sulphur dioxide to deposit a white solid of lead(II) sulphate, the reaction can be considered in two stages:

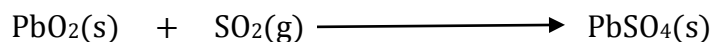
First: oxidation of sulphur dioxide to trioxide, and reduction of lead(IV) to lead(II) oxide



Second: combination of PbO and SO₃



Overall reaction:



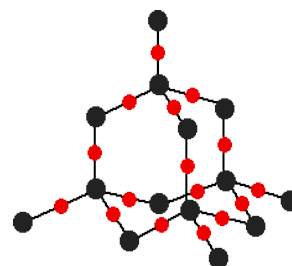
- Thus, acidic character of the oxides decreases down the group. MO_2 becomes more basic.

Question: Compare the acidity of SnO_2 and PbO_2

Answer: SnO_2 is more acidic because of its greater tendency to react with alkalis to form salts without change in oxidation state.

Structure of the dioxides

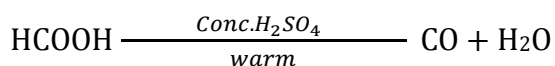
- CO_2 adopts a simple molecular structure in which its molecules are held together by weak van der Waals forces that are easily broken at room temperature. Therefore, CO_2 exists as a gas at room temperature.
- SiO_2 adopts a giant molecular (or giant covalent) structure similar to that of diamond. As such SiO_2 is a solid at room temperature with a high melting point.
- The dioxides of Ge, Sn and Pb assume structures that are intermediate between giant molecular and ionic.



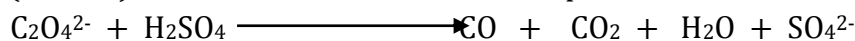
b) The monoxides, MO

☒ CO can be prepared by

- Reduction of CO_2 by coke
$$\text{CO}_2(\text{g}) + \text{C}(\text{s}) \longrightarrow 2\text{CO}$$
- Dehydration of methanoic acid by concentrated sulphuric acid.

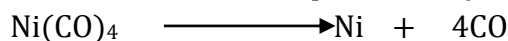


The gas is passed through caustic soda solution to remove any sulphur dioxide or carbon dioxide produced in side reactions. Carbon monoxide is also obtained when an ethanedioate (oxalate) is heated with concentrated sulphuric acid:



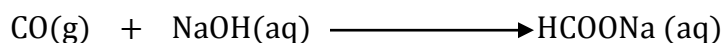
The carbon dioxide is removed by passage of the gas through a mixture of sodium and calcium hydroxides.

Very pure carbon monoxide is produced by heating nickel tetracarbonyl



Because the +2 ox-state of C is unstable, CO **RAPIDLY** reacts with oxygen to form the more stable CO_2 in the +4 ox-state. Hence CO is a reducing agent.

****CO reacts with Sodium hydroxide above 450°C and 700kpa to form sodium methanoate**

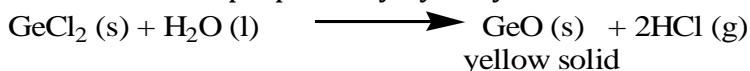


- ☑ SiO is an unstable oxide which only exists at very high temperatures. It is obtained by heating SiO₂ very strongly with Si. A brown powder SiO is formed.



On cooling, SiO disproportionates to form SiO₂ and Si.

- ☑ CO, SiO and GeO have simple molecular structures and are predominantly neutral.
- ☑ GeO is prepared by reducing Germanium (IV) oxide with Ge (as for SiO) but the GeO is also unstable and tends to disproportionate.
- ☑ GeO can also be prepared by hydrolysis of Germanium (II) chloride.

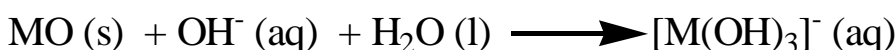


- ☑ SnO is made by heating Tin II oxalate. PbO is prepared by action of heat on the hydroxide or nitrate.



***Tin(II) oxalate is used since both the oxalate (C₂O₄²⁻) and CO gas are reducing agents which prevent oxidation of SnO to more stable SnO₂ ***

- ☑ GeO, SnO and PbO are predominantly ionic and are amphoteric in nature.



Where M stands for Ge, Sn or Pb.

THE HALIDES

These are of two types: (a) MX₄ (b) MX₂

a) THE TETRAHALIDES, MX₄

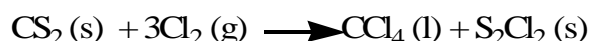
All elements form tetra halides. These are all covalent volatile liquids. However, PbI₄ and PbBr₄ do not exist.

Preparation

The Tetrachlorides of Si, Ge, Sn can be made by direct synthesis i.e. by passing dry chlorine over the heated element.

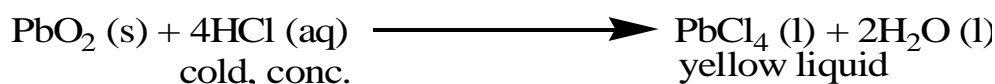


- CCl₄ is prepared by action of chlorine on Carbon disulphide:

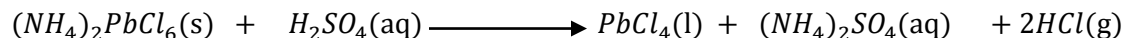


QN. Why don't we prepare Carbon tetrachloride by direct synthesis?

- PbCl_4 is prepared by action of conc. HCl on Lead IV oxide.



- It can also be prepared from Ammonium hexachloroplumbate (IV) on reaction with conc. Sulphuric acid.



All tetrahalides form tetrahedral, simple molecular structures with bond angles of 109.5° . therefore the tetrahalides have low melting points and boiling points and are all volatile liquids at room temperature.

Thermo stability

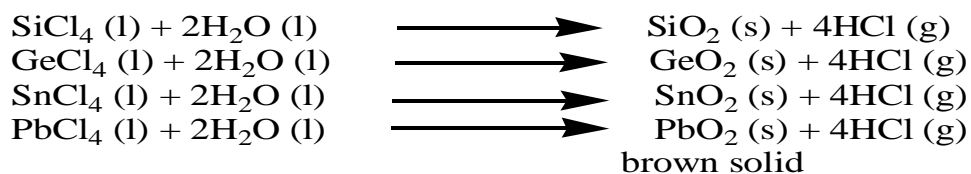
As the atomic size of the elements increases down the group, the M-Cl bond becomes longer and therefore weaker, down the group, the MCl_4 become less stable. Eg. PbCl_4 decomposes at room temp. to form PbCl_2 and chlorine gas, SnCl_4 decomposes on heating to SnCl_2 and chlorine. There is also a ↓se in stability of +4-ox state down the group.

Hydrolysis of the tetra chlorides

- ❖ ALL the tetra chlorides **except** CCl_4 fume in most air, because they are easily hydrolyzed by water to form MO_2 and HCl gas.
- ❖ All but carbon are able to use vacant d orbitals to allow the water ligands to donate their lone pairs required for hydrolysis to take place.

The ease of hydrolysis is in the order

$\text{SiCl}_4 > \text{GeCl}_4 > \text{SnCl}_4 > \text{PbCl}_4$, as metallic character decreases down the group.



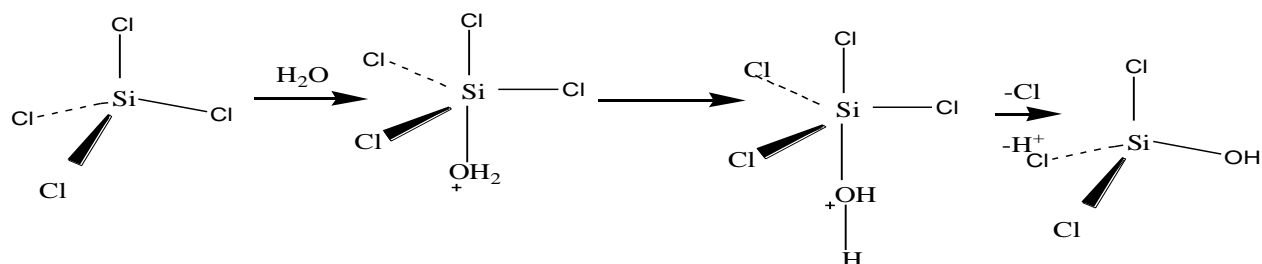
Why is CCl_4 not hydrolysed, yet SiCl_4 is?

CCl_4 is immiscible with water and does not react with it. The C-Cl bond is so strong (average bond enthalpy = $+338 \text{ KJmol}^{-1}$). However, the hydrolysis reaction



is favoured thermodynamically and will occur, given sufficient time (many years). This reaction proceeds at an extraordinarily slow rate.

The Si-Cl bond in SiCl_4 is far more polar than the C-Cl bond in CCl_4 , it is longer and weaker. As a result, SiCl_4 gives off fumes in moist air and easily hydrolyses. The products are hydrogen chloride and a white precipitate of SiO_2 .



Because Si has empty 3d orbitals close in energy to the occupied 3p orbitals, the incoming water molecule can form a bond with the Si before the existing bonds are broken. Such a mechanism is not possible for C because the 3d orbitals are too far away in energy from its 2p orbitals.

Therefore,

Explanation 1:

There are no d-orbitals in the second shell of the C atom. As a result, when a water molecule attacks a CCl_4 molecule, the carbon atom does not have an empty orbital to accept/coordinate the incoming electron pair.

The problem with this explanation is that it suggests that the hydrolysis of haloalkanes by a similar mechanism should also be impossible.

Explanation 2:

The difference in behavior of CCl_4 and SiCl_4 with water is a result of the much smaller size of a carbon atom compared to a silicon atom. As a result, it is impossible for water molecules to attack a carbon atom when it is surrounded by four relatively large chlorine atoms in CCl_4 and is strongly bonded to them.

b) THE DIHALIDES

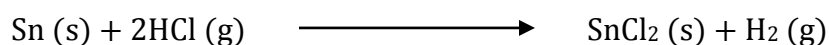
Are solids, only formed by Ge, Sn and Pb.

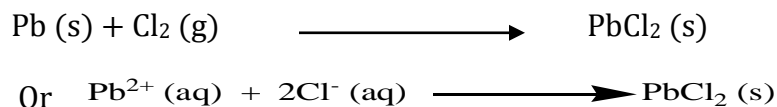
Their stability and ionic character increase down the group. PbCl_2 is the most stable dichloride.

Di halides of Sn and Ge are strong reducing agents.

PbCl_2 is prepared by heating Pb in a stream of chlorine gas, and by precipitation of the white solid from Lead II nitrate by adding a solution of chloride ions.

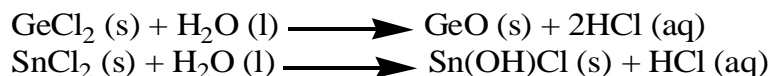
Anhydrous SnCl_2 is best prepared by heating a tin in a stream of hydrogen chloride or action of acid on metal.





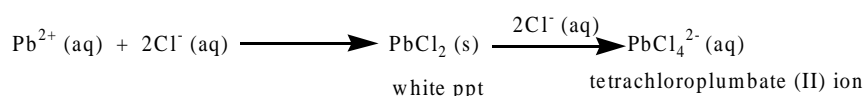
Hydrolysis

GeCl₂ is readily hydrolyzed to give GeO and HCl. SnCl₂ hydrolyses readily but doesn't dissolve satisfactorily in water, it precipitates a basic chloride.



Though ionic, PbCl₂ has a very low solubility product in water. As a result, it is sparingly soluble in cold water. It dissolves in hot water, for its solubility increases with temperature.

It dissolves in concentrated hydrochloric acid because of formation of a soluble complex.



THE HYDRIDES

All elements in group IV form covalent hydrides of the type MH₄.

The tetra hydrides are covalent, have simple molecular structures and are tetrahedral in shape.

The tetrahydrides become less stable down the group. This is because the M-H bonds become longer and weaker with increasing size of the element. There is also a decrease in stability of the +4 oxidation state down the group. Hence, stability is in the order CH₄ > SiH₄ > GeH₄ > SnH₄ > PbH₄.

Carbon, however, has a wide range of chain and ring compounds this is attributed to the small atomic size of carbon, so it can form stable long chain hydrides. The hydrides of carbon are called hydrocarbons and these include: the alkanes, alkenes, arenes, and alkynes. (See organic. chem.).

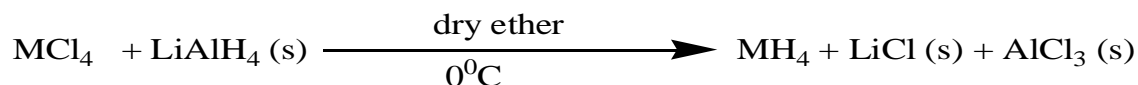
Silicon forms a series of hydrides called **Silanes**, similar to alkanes with general formula Si_nH_{2n + 2}, but the chain length is limited to eight Si atoms only because Si-Si bonds are longer and weaker due to the big atomic radius of Si. Because of this, silanes are far more reactive than alkanes and are strong reducing agents. They easily ignite in air and explode in chlorine.

Silicon doesn't form ring compounds and has no analogues of alkenes, or alkynes because sp² and sp hybridization in silicon are not energetically favoured.

Similar germanium compounds called **Germanes** with general formula $\text{Ge}_n\text{H}_{2n+2}$ exist, limited to 5 Ge atoms. They are unstable straight-chain colourless gases and volatile liquids.

Sn and Pb do not catenate.

- Tetra hydrides of Si, Ge, Sn and Pb are prepared by reduction of the respective tetra chlorides with LiAlH_4 at 0°C in the presence of ether.



Where M = Si, Sn, Ge and Pb.

Hydrolysis

CH_4 , just like CCl_4 , does not undergo hydrolysis due to lack of empty d-orbitals of right energy.

SiH_4 , SnH_4 and PbH_4 hydrolyze in presence of alkalis to form corresponding salts and H_2 .

Read about:

Practical analysis of Pb^{2+} and Sn^{2+} , Sn^{4+} salts in soln; and quantitative determinations.

Test for Pb^{2+} : To the test solution, add potassium chromate (VI) solution followed by dilute sodium hydroxide solution:

Observation: A yellow precipitate soluble in the alkali to form a yellow solution:

The above test is also used to distinguish between Pb^{2+} ions from Ba^{2+} ions, since barium chromate is insoluble in the alkali.

IN – TEXT QUESTIONS

- 1) Diamond and graphite both are allotropic forms of carbon; however, only graphite is used as a lubricant. Why?
- 2) What are the properties responsible for the anomalous behavior of carbon?
- 3) Why is tin and lead incapable of showing the property of catenation?
- 4) Why is trisilylamine a very weak Lewis base and trimethylamine a good Lewis base?
- 5) Give reactions to show that CO_2 is an acidic oxide and SnO_2 is an amphoteric oxide.
- 6) Explain the following briefly:
 - i. SiO_2 is as hard as diamond.
 - ii. CCl_4 is not hydrolyzed while SiCl_4 or SnCl_4 get hydrolyzed easily.
 - iii. PbBr_4 and PbI_4 do not exist.
 - iv. SiO_2 is a solid whereas CO_2 is a gas.
7. Carbon, silicon, tin and lead are elements in Group IV of the PT.
 - a) i) Write the formulae of the oxides of the elements in the +4 ox-state.
 - ii) State the trend in the acid nature of the oxides.

- b) Discuss the reaction of the oxides in (a) above with
 - i) Sodium hydroxide
 - ii) Mineral acids.
- c) Write an equation for the reaction to show how Lead IV oxide can be prepared from
 - i) Lead II nitrate solution
 - ii) Tri lead tetra oxide.
- d) Sulphur dioxide gas was passed over heated Lead IV oxide
 - i) State what was observed.
 - ii) Explain your observation.
8. Carbon, silicon, tin and lead are elements in Group IV of the periodic table.
 - a) i) State two important oxidation states exhibited by C, Si, Sn, and Pb.
 - ii) Describe how the stability of the two oxidation states varies down from carbon to lead. Use the oxides to illustrate your answer.
 - b) Describe what would be observed and write equations for the reactions when the tetra chlorides of C, Si, Sn and Pb are reacted with water.
 - c) i) Write an equation to show how lead II chloride can be prepared.
 - ii) State the type of bond which exists in the chlorides of lead.
 - iii) State two physical properties which show that lead II chloride exhibits the type of bond you have stated in c)(ii) above.
 - d) State what would be observed and write equation for the reaction when
 - i) Lead II acetate is added to potassium iodide solution.
 - ii) Iron III chloride solution is added to lead acetate solution and the mixture boiled.
9. Explain the following:
 - i) Lead(IV) chloride exist but lead (IV) iodide does not exist
 - ii) When potassium dichromate(VI) and Potassium chromate (VI) are separately added to an aqueous solution containing lead(II) ions, a yellow precipitate is observed in both cases.
10. Compare and contrast the chemistry of silicon, germanium, tin and lead by referring to the properties and bond types of their oxides and chlorides.
 - b) Give brief experimental details to indicate how you could prepare in the laboratory a sample of either tin(IV) chloride or tin(IV) iodide.
 - c) How far does the chemistry of the oxides and chlorides of carbon support the statement that 'the head element of a group in the Periodic Table is not typical of that group'? (
11. What physical and chemical tests could you apply to the oxides and chlorides of Group IV elements to show the changes in their properties as the atomic number of the element increases? At the bottom of Group IV tin and lead exhibit two oxidation states. Why are these elements not classified as 'transition' metals?
12. State two physical and two chemical properties which clearly illustrate the differences between a typical metal and a typical non-metal.
 - (b) For any given group in the Periodic Table, the metallic character of the element increases with the increase in atomic weight of the element.'

Discuss this statement as it applies to the Group IV elements, C, Si, Ge, Sn, Pb, indicating any properties of carbon which appear anomalous. Illustrate your answer by considering:

- (i) The physical properties of the elements,
 - (ii) The reaction of the oxides with sodium hydroxide,
 - (iii) The reaction of the chlorides with water,
 - (iv) The stability of the hydrides to heat,
 - (v) The changes in the stability of oxidation state (IV) with increase in atomic weight of the element
13. The chemical properties of the elements in a given group of the Periodic Table change with increasing atomic number.
- (a) Explain the main factors responsible for this, illustrating your answer by reference to the Group IVB elements, carbon to lead.
 - (b) Apply the factors outlined under (a) to predict the main chemical properties and bonding relationships of the last three members of Group V of the Periodic Table containing the elements nitrogen, phosphorus, arsenic, antimony and bismuth.
14. Give an account of the chemical properties of the element tin and describe four of its principal compounds. The element germanium (Mendeleef's ekasilicon) lies in Group IV of the Periodic Table below carbon and silicon and above tin and lead. What properties would you predict for this element, for its oxide GeO_2 and for its chloride GeCl_4 ?
15. By reference to the elements carbon, silicon, tin and lead, show how the properties of an element and those of its compounds can be related to:
- (a) The group in the Periodic Table in which the element occurs,
 - (b) Its position in that group.