

## The chemistry of Group IV elements and their compounds.

### Introduction

- The group IV elements of the Periodic Table are carbon, silicon, germanium, tin and lead.

### Summary of some of the physical properties group IV elements

Element	Outer most E.C	Atomic radius(nm)	1 <sup>st</sup> I.E (kJ mol <sup>-1</sup> )	M.pt (°C)	B.pt (°C)	Type of structure	Electrical conductivity
C	2s <sup>2</sup> 2p <sup>2</sup>	0.077	1086	3730 <sup>d</sup>	4830 <sup>d</sup>	Giant covalent (or giant molecular)	Poor/non conductor <sup>d</sup> Fairly good <sup>gr</sup>
Si	3s <sup>2</sup> 3p <sup>2</sup>	0.117	787	1410	2680		Semi-conductors
Ge	4s <sup>2</sup> 4p <sup>2</sup>	0.122	760	937	2830		
Sn	5s <sup>2</sup> 5p <sup>2</sup>	0.142	707	232	2270	Giant metallic (Giant molecular <sup>grey tin</sup> )	Good
Pb	6s <sup>2</sup> 6p <sup>2</sup>	0.154	715	327	1730		

(gr-graphite; d-diamond)

### General remarks about the elements

- All the elements have four electrons in their outermost energy levels. Thus, their general outermost electronic configuration is **ns<sup>2</sup>np<sup>2</sup>** and all exhibit a valency of 4.
- Carbon and tin exhibit **allotropy**.  
Crystalline forms of carbon are graphite, diamond and buckminsterfullerene.  
Amorphous forms of carbon (also called impure forms of carbon) are charcoal, coke, soot and lampblack.  
Tin exists as grey tin, white tin and rhombic/brittle tin.
- Metallic character increases from carbon to lead.  
Carbon and silicon are non-metals, germanium is a metalloid (has both metallic and non-metallic characters); tin and lead are metals. The increase in metallic character down the group is due to increase in atomic radius. Effective nuclear charge of the nucleus decreases and the nuclear attraction for the outermost electrons decreases. Thus, the tendency for the atoms to lose outermost electrons increases from carbon to lead.
- Electropositivity of the elements also increases from carbon to lead for similar reasons.
- Electrical conductivity increases from carbon to lead.  
As atomic radius increases down the group, the outermost electrons become far away from the nucleus and weakly attracted by the nucleus.

Thus, the outermost electrons become increasingly delocalised and the electrical conductivity therefore, increases.

Carbon in form of graphite is a conductor while in form of diamond, is a non-conductor. Silicon and germanium are semiconductors in transistors. While tin and lead are metals and good electrical conductors.

- There is a general increase in atomic radius down the group. (Refer to previous notes for explanation).

However, the difference in atomic radii between silicon and germanium is less than expected. This is because germanium atom has a fully filled 3d sub-energy level which poorly shields the outermost/valency electrons from nuclear attraction. This results into stronger nuclear attraction of the outermost electrons, therefore, the atom contracts and becomes smaller.

Similarly, the small difference in atomic radii between tin and lead is because of the filling of 4f sub-energy level which poorly shields the outermost electrons from the nuclear attraction.

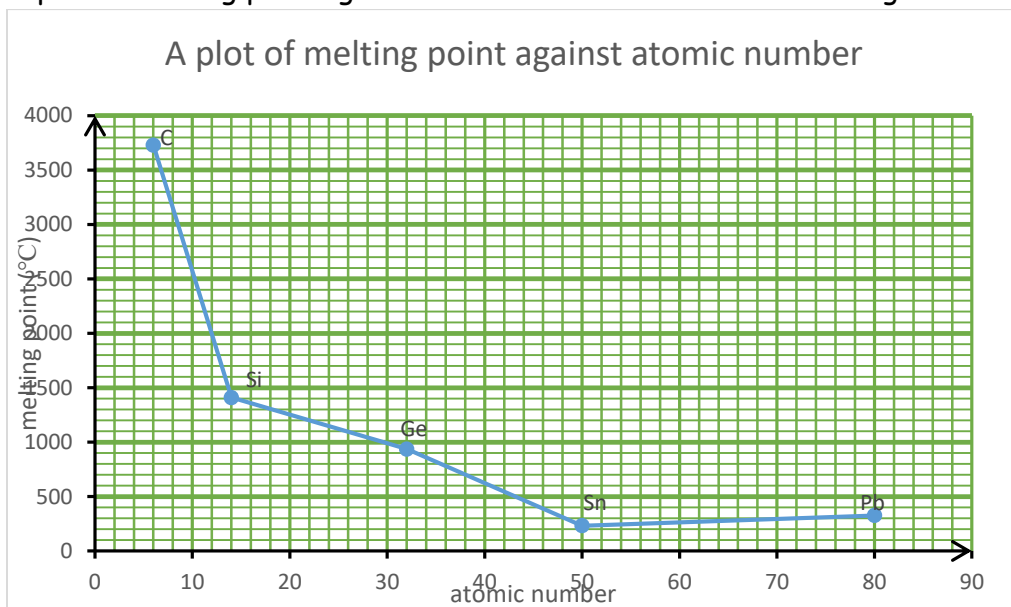
- There is a general decrease in the ionisation energy down the group. However, the trend is irregular because of the filling of d and f sub-energy levels which poorly shield the outermost electrons from nuclear attraction.

The general decrease down the group is due to increase in the atomic radius down the group. The outermost electrons become far away from the nucleus and weakly attracted by the nucleus in the same direction and hence easily removed/lost.

- Graphite is soft in contrast to diamond which is hard. In graphite, the carbon atoms are arranged in flat layers of linked hexagons. In the rings, each carbon atom is bonded to three other carbon atoms by strong covalent bonds. Between the hexagonal layers are the **weak** van der Waals' forces. These forces are easily broken hence, graphite is soft.
- In diamond, each carbon atom uses its four valency electrons to form covalent bonds with other four carbon atoms. This results into a 3-dimensional structure (giant molecular structure) with extensive network of strong carbon-carbon bonds. Thus, diamond is a very hard substance with a high melting point.

Diamond is a non-conductor of electricity due to lack of delocalised electrons whereas graphite is a fairly good conductor of electricity due to the presence of delocalised electrons within the layers.

- A plot of melting point against atomic number takes the following form:



The melting point decreases from carbon to tin and then increases from tin to lead. Carbon has a very high melting point because it has a macromolecular structure composed of carbon atoms due to its ability to catenate. The structure has extensive network of short and strong carbon-carbon bonds to be broken before it melts. Silicon and germanium also have giant covalent structures which contain many hundreds of thousands of atoms joined by strong covalent bonds. This accounts for their relatively high melting points.

On descending the group, the atomic radius increases hence the element-element bond becomes longer and weaker. Thus, melting point decreases.

Tin and lead have giant metallic structures. Their melting points are much lower than those of the other group members. This is because they use only two electrons per atom for metallic bond formation while the other group members use all the four valency electrons (except, carbon in the form of graphite which uses three electrons) to form giant molecular structures; which need a lot of energy to break before the element melts.

Melting point of lead is higher than that of tin. This because lead is more metallic than tin. The melting points of tin and lead are much lower than for most metals because the metallic bonds are so weak.

## Uses of Group IV elements

- Carbon has a wide range of uses depending on its form. In form of wood charcoal is used as domestic fuel and to absorb poisonous gases because of its porous nature. Animal charcoal is used in sugar production to remove the brown colour and to remove

colour from solutions. Coke is used as a fuel in furnaces and ovens. Coke is also used as a reducing in the extraction of iron, zinc, tin and lead from their ores. Lampblack is used in printer's ink, black shoe polish, carbon papers, car tyres and Indian ink.

Graphite is used as a lubricant in moving parts of machines (for example dynamos and electric motors), in nuclear reactors (in which uranium atoms are split up to generate energy) to absorb excess neutrons produced and to make electrodes since it conducts electricity. Diamond is used to make glass cutters, drilling devices and as an abrasive for smoothing hard materials. It is also used as precious gemstone in jewellery and ornamental objects.

- Silicon and germanium in pure form are used as semiconductors in transistors. Ferrosilicon (an alloy of silicon) is a deoxidiser in steel manufacture.
- Tin is used in tin plating and marking alloys (like bronze and solder).
- Lead is extensively used as sheets in roofing and sometimes for dam-coursing, as a lining in vessels required to withstand corrosion due to acids and water and, in gas pipes. It is also used to make accumulator plates and shielding material against dangerous radiations (such as X-rays, gamma rays), covering underground telephone/electrical cables; making lead shot, paints and alloys (e.g. type metal, pewter, common solder and soft solder).

## Oxidation states of group IV elements

- The elements exhibit two oxidation states in their compounds/ions that is, +2 and +4 (or valencies of 2 and 4 in their compounds/ions).  
The oxidation of +4 involves the use of all the four electrons in the outermost energy level (i.e. both electrons in outermost s and p sub energy levels are involved).  
The oxidation of +2 involves only the pair of electrons in the outermost p sub energy level.
- The stability of +2 oxidation state increases from carbon to lead while that of +4 decreases from carbon to lead. This is due to **inert pair effect**.

### Definition

Inert pair effect refers to the inability of the outermost s sub energy level electrons to take part in chemical bonding among the group IV elements; and hence only the outermost p sub energy level electrons are used.

- The inert pair effect is due to increase in atomic radius from carbon to lead. In large atoms such as those of tin and lead, the inner d and f electrons poorly shield the outer-shell electrons as well as the inner core s and p electrons from nuclear attraction.  
The outermost s sub shell electrons being more penetrating, are much more strongly attracted by the nucleus compared with the outermost p sub shell electrons since they are less penetrating.

The outermost s sub shell electrons effectively become sucked into the inner core of electrons and thus, become 'inert' (unable to participate in chemical bonding/less available for bonding).

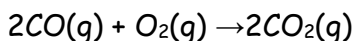
### Trends in relative stability of oxidation states; +2 and +4

- The relative stability in +2 and +4 oxidation states in elements can be illustrated by use of their oxides/chlorides as follows:

(a) In carbon and silicon, the +4 oxidation state is more stable relative to +2 oxidation state. +2 oxidation state is rare and easily reverts (or is easily oxidised) to +4.

For example;

(i) Carbon monoxide is readily oxidised to the more stable carbon dioxide while the decomposition carbon dioxide to carbon monoxide and oxygen does not occur.



(ii) Silicon monoxide is not known except at extremely very high temperatures while stable silicon(IV) oxide (silica) is widely distributed for example, in soils, glass, quartz and rocks.

Silicon monoxide disproportionates at room temperature/on cooling.



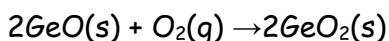
(iii) Similarly, carbon dichloride and silicon(II) chloride do not exist. However, carbon tetrachloride and silicon(IV) chloride exist and are stable.

(b) Germanium compounds exist in both oxidation states, the +4 oxidation state being more stable.

For example;

(i) Germanium(IV) oxide is more stable than germanium(II) oxide.

Germanium(II) oxide is readily oxidised to a more stable germanium(IV) oxide.



(ii) Germanium(II) oxide also disproportionates at high temperatures and in absence of air to a more stable germanium(IV) oxide and elemental germanium.

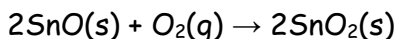


(iii) Both germanium(II) chloride and germanium(IV) chloride exist and are stable.

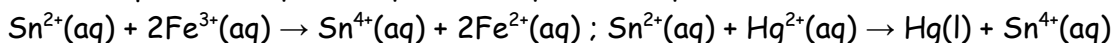
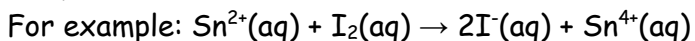
(c) +4 oxidation state in tin compounds is slightly more stable than +2 oxidation state.

For example:

(i) Tin(II) oxide smoulders in air forming a more stable tin(IV) oxide.

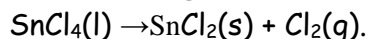


(ii) Tin(II) compounds are very powerful reducing agents forming tin(IV) compounds.



- (iii) Both tin(II) chloride and tin(IV) chloride exist and are stable. However, tin(IV) chloride is less stable than tin(II) chloride.

Tin(IV) chloride readily decomposes on heating to more stable tin(II) chloride and chlorine gas is evolved.

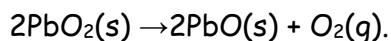


Also tin(IV) chloride rapidly hydrolyses in water but tin(II) chloride sparingly dissolves in water.

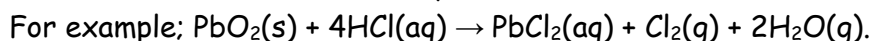
- (d) In contrast, +2 oxidation state in lead compounds is more stable than +4 oxidation state.

For example;

- (i) Lead(IV) oxide readily decomposes to give stable lead(II) oxide with evolution of oxygen on slight warming yet, lead(II) oxide and tin(IV) oxide are very stable under similar conditions.



- (ii) Lead(IV) oxide is a strong oxidising agent forming stable lead(II) compounds while lead(II) oxide is relatively stable.



- (iii) Both lead(II) chloride and lead(IV) chloride exist and are stable.

However, lead(IV) chloride is less stable than lead(II) chloride.

Lead(IV) chloride readily decomposes on gently warming to a more stable lead(II) chloride and chlorine gas is evolved.



Also, lead(IV) chloride rapidly hydrolyses in water but lead(II) chloride sparingly dissolves in water.

### Question

1. Carbon, silicon, tin and lead are elements of group IV of the Periodic Table.

(a) State:

- (i) the common oxidation states shown by the elements group IV of the Periodic Table in their compounds/ions.
- (ii) how the stability of the oxidation states of the elements in their compounds or ions vary down the group. (Illustrate your answer with the chlorides of carbon and lead)

(b) Give a reason for your answer in (a)(ii).

2. Explain the following observations.

- (a) Carbon which is in the same group as lead in the Periodic Table shows one valency of 4 in its compounds but lead shows two valencies of 2 and 4.
- (b) Lead(IV) oxide decomposed when heated to give lead(II) oxide and oxygen but carbon dioxide does not.

## Uniqueness of carbon

- Carbon, the first member in the group shows unique properties from the rest of the other group members. This is because of its small atomic radius which leads to high electronegativity and high ionisation energy. Carbon atom also lacks easily accessible d-orbitals.

- Carbon differs from the other group members in the following ways:

Carbon;

- (i) has a maximum valency of 4. This is due to lack of d orbitals of suitable energy to enable it expand its octet. This also explains why carbon compounds are relatively inert.

The other atoms can expand their octets to maximum valency of 6 by using their empty d orbitals of suitable energy.

- (ii) catenates unlike the other elements.

**Catenation** is the ability of an element to form bonds between atoms of the same element.

Catenation enables carbon atom to form stable compounds containing long chains and rings of carbon atoms, with single, double and triple bonds. It is this property that enables carbon to form millions of compounds and have a whole branch of chemistry devoted to it.

The ability of carbon to catenate is as a result of the fact that it has a valency which is greater than 2 and the strength of  $C - C$  bond is almost similar to that of  $C - O$  and  $C - Cl$  bonds. This makes the compounds more stable in air (which could cause ready oxidation) and water (which could cause ready hydrolysis).

In comparison, the  $Si - O$  bond is much stronger than the  $Si - Si$  bond.

Bond	Average bond energy ( $\text{kJ mol}^{-1}$ )	Bond	Average bond energy ( $\text{kJ mol}^{-1}$ )
$C - O$	360	$Si - O$	464
$C - Cl$	338	$Si - Cl$	380
$C - C$	348	$Si - Si$	226

**Note:**

For an element **E** to catenate, it must have a valency  $\geq 2$  and must form  $E - E$  bonds which are similar or greater in strength to those of E to other elements, particularly  $E - O$  bonds. This makes the compounds stable when exposed to air and water.

- (iii) forms stable multiple bonds with itself and with other elements. The other elements in group IV form no such compounds.
- (iv) forms gaseous oxides unlike the other elements which form solid oxides.

**Explanation:**

The carbon atom has the smallest atomic radius. The carbon and oxygen atoms closely approach. This results into effective overlap of their p-orbitals and hence, formation of stable multiple bonds between oxygen and carbon atoms.

As a result, only discrete molecules of carbon dioxide are formed with only weak van der Waals forces of attraction between them. Hence, carbon dioxide can only exist in gaseous state at room temperature.

The other atoms of the other elements have larger atomic radii. The atoms of the other elements and oxygen atoms cannot closely approach each; the effective overlap of their p-orbitals is not possible and, therefore no multiple bonds are formed between the atoms. The atoms only form strong single bonds with oxygen atoms.

Silicon atom, for example, forms only single, strong covalent bonds with four oxygen atoms. This gives silicon(IV) oxide a three dimensional giant molecular structure which makes it a solid at room temperature.

- (v) forms compounds which are relatively inert unlike the others.
- (vi) does not show inert pair effect unlike the others.

## Chemical properties of the elements

### A. Reaction with air (oxygen)

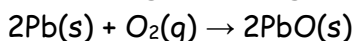
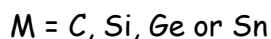
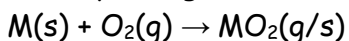
- At room temperature;

Carbon, germanium and tin are unaffected by air.

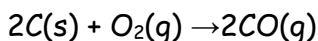
Silicon oxidises only superficially in air.

Lead tarnishes rapidly in air by acquiring a thin grey layer of oxide which later forms a basic carbonate. This protects it from further attack.

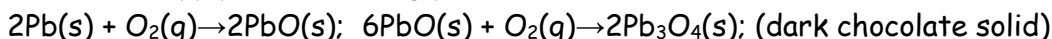
- On strong heating, all the group members will react with air (oxygen) to form the corresponding dioxides **except** lead which forms a monoxide called lead(II)oxide.



- Carbon forms carbon monoxide when heated in limited supply of air (oxygen).



- In excess supply of air, strongly heated lead forms trilead tetraoxide,  $Pb_3O_4$ .

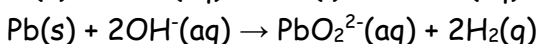
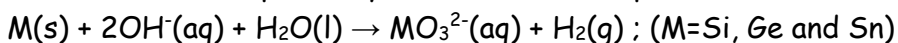




## B. Reaction with caustic alkalis

- Carbon has no reaction with alkalis at all conditions.
- The rest react with hot, concentrated aqueous alkali solution liberating hydrogen gas and the corresponding oxo-anions are left in solution.

Silicon, germanium and tin form silicate(IV) ions, germanate(IV) ions and stannate(IV) ions in solution respectively while, lead forms plumbate(II) ions in solution.



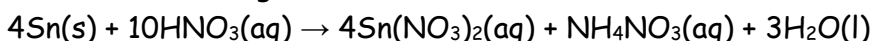
### Note:

- Silicon and germanium dissolve readily even in dilute alkali solutions, tin dissolves slowly only in hot concentrated solutions while, lead dissolves only very slowly in hot concentrated solutions. This is because the basic character of the metals decreases down the group.
- The elements except, carbon can also react with fused alkalis to give similar products.

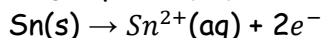
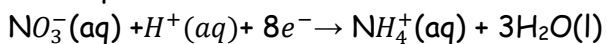
## C. Reaction with acids

### (a) Dilute acids

- Carbon, silicon and germanium do not react with dilute acids at all conditions.
- Cold, dilute nitric oxidises tin very slowly forming tin(II) nitrate. The acid is reduced to oxides of nitrogen and ammonium nitrate.

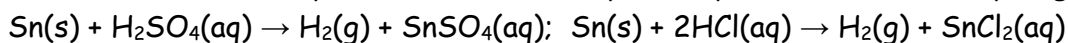


Half equations are:



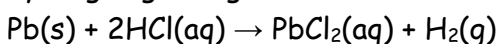
Overall equation is.....

- Tin reacts slowly with dilute hydrochloric acid and sulphuric acid **on warming**. Tin(II) chloride and tin(II) sulphate are formed respectively with evolution of hydrogen.

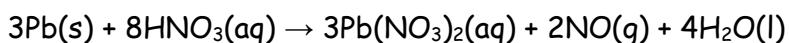


- Dilute sulphuric acid and cold dilute hydrochloric acid have no reaction with lead. This is due to formation of **insoluble** lead(II) sulphate or lead(II) chloride which **coat** the metal.

Hot dilute hydrochloric dissolves lead powder very slowly forming lead(II) chloride and hydrogen gas is given off.



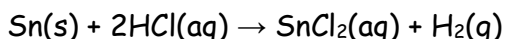
- Hot dilute nitric acid oxidises lead to form lead(II) nitrate and oxides of nitrogen.



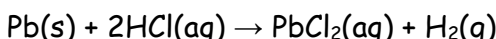
(b) Concentrated acids

- Silicon does not react with concentrated **mineral** acids at all conditions.
- Carbon and germanium do not react with concentrated hydrochloric acid at all conditions.

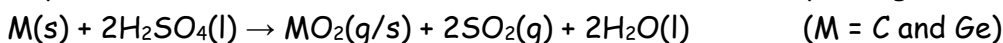
Hot, concentrated hydrochloric acid rapidly reacts with tin to liberate hydrogen gas and tin(II) chloride is left in solution.



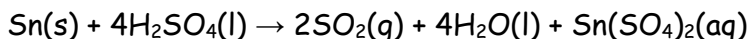
Hot, concentrated hydrochloric dissolves lead powder rapidly forming lead(II) chloride and hydrogen gas is given off. With cold concentrated acid, the reaction is very slow due to insoluble lead(II) chloride formed.



- Both carbon and germanium reduce hot, concentrated sulphuric acid to water and sulphur dioxide. The elements are oxidised to their corresponding dioxides.



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

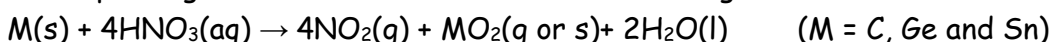


Hot, concentrated sulphuric acid very slowly oxidises lead to form lead(II) sulphate.

The acid is reduced to water and sulphur dioxide. Lead(II) sulphate formed is insoluble in water and retards the reaction.

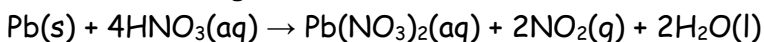


- Hot, concentrated nitric acid oxidises carbon, germanium and tin to their corresponding dioxides. The acid is reduced to nitrogen dioxide and water.



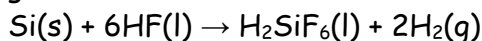
The tin(IV) oxide formed with tin is a **white precipitate**.

Hot, concentrated nitric acid oxidises lead to form lead(II) nitrate and the acid is reduced to nitrogen dioxide and water.

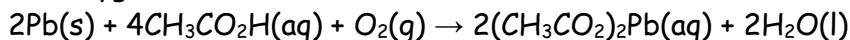


**Notes:**

- Silicon reacts with concentrated hydrofluoric acid contaminated with little concentrated nitric acid. The products are hexafluorosilicic acid and hydrogen gas.



- Lead is also attacked by organic acids such as ethanoic acid in the presence of air (oxygen).



#### D. Reaction with non-metals

- All elements react readily with dry fluorine at high temperatures.  
For example:  $C(s) + 2F_2(g) \rightarrow CF_4(g)$ ;  $Si(s) + 2F_2(g) \rightarrow SiF_4(g)$
- Carbon does not react with chlorine at all conditions.  
Heated silicon, germanium and tin react with dry chlorine to form the corresponding tetrachlorides.  
 $M(s) + 2Cl_2(s) \rightarrow MCl_4(l)$  ( $M = Si, Ge$  and  $Sn$ );  
Heated lead reacts with dry chlorine forming lead(II) chloride.  
 $Pb(s) + Cl_2(s) \rightarrow PbCl_2(s)$
- All the group elements **do not** react directly with hydrogen at all conditions, however a number of hydrides are known to exist (see pages 25-27 for details).
- All the elements react with sulphur on strong heating to form the corresponding disulphides. Lead forms lead(II) sulphide.  
 $M(s) + 2S(s) \rightarrow MS_2(l/s)$  ( $M = C, Si, Ge$  or  $Sn$ );  $Pb(s) + 2S(s) \rightarrow PbS(s)$

#### E. Reaction with water

- Carbon, silicon and tin are not affected by **cold** water.
- Germanium does not react with water at all conditions.
- Strongly heated carbon reacts with steam to form a mixture of carbon monoxide and hydrogen. A mixture of the gases formed is called **water gas**.  
 $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
- Heated silicon and tin react with steam to form the corresponding dioxides and hydrogen.  
 $M(s) + 2H_2O(g) \rightarrow MO_2(s) + H_2(g)$ ;  $M = Si$  or  $Sn$
- Lead reacts with soft water containing dissolved oxygen (aerated soft water) at room temperature to produce lead(II) hydroxide.  
 $2Pb(s) + 2H_2O(l) + O_2(g) \rightarrow 2Pb(OH)_2(s)$
- With hard water which contains carbonate ions or sulphate ions, insoluble lead(II) carbonate or lead(II) sulphate are formed. These form a protective layer so that further reaction is inhibited.
- Therefore, very soft water may be unsafe when carried in lead pipes because their continuous use may result into lead poisoning. Use of lead pipes is safer in areas with hard water.

## Compounds of group IV elements

- The elements form **two** classes of compounds i.e. compounds in +2 and +4 oxidation states. The relative stabilities of the two classes of the compounds vary from one element to the other.
- For carbon and silicon; compounds in +4 oxidation state are more stable than those in +2 oxidation state while for tin and lead; compounds in +2 oxidation state are more stable than those in +4 oxidation state. Germanium forms compounds of similar stability in both oxidation states.

### A. Oxides of group IV elements

- The elements form two types of oxides; monoxides,  $MO$ , in which the oxidation state is +2 and dioxides,  $MO_2$  in which the oxidation state is +4.
- The oxides formed by group IV elements are summarised as follows:

Element	Monoxides, $MO$	Dioxides, $MO_2$
Carbon, $C$	$CO(g)$	$CO_2(g)$
Silicon, $Si$	$SiO(s)$	$SiO_2(s)$
Germanium, $Ge$	$GeO(s)$	$GeO_2(s)$
Tin, $Sn$	$SnO(s)$	$SnO_2(s)$
Lead, $Pb$	$PbO(s)$	$PbO_2(s)$

### Monoxides of group IV elements, $MO$

#### (a) State, appearance and nature

Oxide	$CO$	$SiO$	$GeO$	$SnO$	$PbO$
Colour and state	Colourless gas	Brown powder	Yellow solid when hydrated and black powder when anhydrous	Dark grey or brown solid	Yellow solid when cold and reddish-brown when hot
Nature	Weakly acidic		Amphoteric		

#### (b) Preparation

- Carbon monoxide can be prepared by:
  - (i) reducing carbon dioxide using heated coke in a combustion tube.  
 $CO(g) + C(s) \rightleftharpoons 2CO(g)$
  - (ii) dehydration of formic (methanoic) acid, sodium methanoate or crystals of oxalic acid by use of hot concentrated sulphuric acid.  
 $HCOOH(l) \rightarrow CO(g) + H_2O(l)$  ;  $H_2C_2O_4(s) \rightarrow CO(g) + CO_2(g) + H_2O(l)$   
 $HCOONa(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + CO(g) + H_2O(l)$   
Its preparation should be done in an open place or in a fume cupboard because the gas is very poisonous.
- Silicon monoxide exists at very high temperatures of about  $2000^\circ C$ . It is made by heating silica (silicon dioxide) with silicon.  
 $Si(s) + SiO_2(s) \rightarrow 2SiO(s)$

- Germanium(II) oxide is made by action of water on germanium(II) chloride in absence of air.  

$$\text{GeCl}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{GeO}(\text{s}) + 2\text{HCl}(\text{g/aq})$$
- Tin(II) oxide is obtained by heating tin(II) oxalate or tin(II) hydroxide or tin(II) nitrate, in the absence of air.  

$$\text{SnC}_2\text{O}_4(\text{s}) \rightarrow \text{SnO}(\text{s}) + \text{CO}(\text{g}) + \text{CO}_2(\text{g}); 2\text{Sn}(\text{NO}_3)_2(\text{s}) \rightarrow 2\text{SnO}(\text{s}) + 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
- Lead(II) oxide is formed by heating lead(II) hydroxide, lead(II) carbonate or lead(II) nitrate.  
 For example; 
$$\text{PbCO}_3(\text{s}) \rightarrow \text{PbO}(\text{s}) + \text{CO}_2(\text{g})$$

### (c) Properties

#### 1. Carbon monoxide

- The gas has no smell, is insoluble in water and extremely poisonous.
- It burns readily in air with a pale blue flame forming carbon dioxide and a lot of heat is produced. Thus, it is a useful fuel.  

$$2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$$
- The oxide shows slight acidity by reacting with hot concentrated sodium hydroxide solution under high pressure. Sodium methanoate is formed.  

$$\text{CO}(\text{g}) + \text{NaOH}(\text{aq}) \rightarrow \text{HCOO}^-\text{Na}^+(\text{aq})$$
- At red heat, the gas, reduces oxides of lead, copper, and iron to the corresponding metals. This explains why it is widely used in metal extraction.  
 For example, iron from haematite,  $\text{Fe}_2\text{O}_3$  in the blast furnace
- The oxide is used in industrial preparation of methanol.  

$$\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \xrightarrow{\text{ZnO/Cr}_2\text{O}_3 \text{ catalyst}} \text{CH}_3\text{OH}(\text{l})$$
- The presence of the lone pair of electrons on the carbon atom enables the molecule to act as a ligand to form carbonyl complexes such as  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{CO})_8$  and  $\text{Fe}(\text{CO})_5$ .

#### 2. Silicon monoxide and germanium(II) oxide

- Both silicon monoxide and germanium(II) oxide are very unstable and disproportionate.  $\text{SiO}$  disproportionates on cooling and  $\text{GeO}$  disproportionates on heating in the absence of air.  

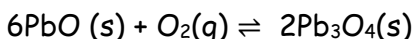
$$2\text{MO}(\text{s}) \rightarrow \text{M}(\text{s}) + \text{MO}_2(\text{s}); \text{M} = \text{Si or Ge}$$
- Germanium(II) oxide is amphoteric; it slowly dissolves in acids and also in alkalis.  

$$\text{GeO}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ge}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}); \text{GeO}(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{GeO}_2^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$$

#### 3. Tin(II) oxide and lead(II) oxide

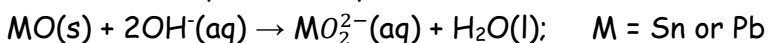
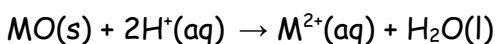
- On exposure to air, tin(II) oxide is rapidly oxidised to tin(IV) oxide,  $\text{SnO}_2$ .

- Lead(II) oxide is the most stable of all the monoxides. The oxide is readily reduced to metallic lead if heated with a variety of reducing agents such as carbon, carbon monoxide, hydrogen and ammonia.
- Lead(II) oxide undergoes a physical change on slight warming and on strong heating in excess air at about 670K to 720K for some hours, it yields red lead oxide (trilead tetraoxide).



Red lead oxide

- Both oxides are amphoteric although tin(II) oxide is less amphoteric; forming tin(II) salts or lead(II) salts with acids and stannate(II) or plumbate(II) ions in solution with alkalis.



- Lead(II) oxide is more basic than any other monoxide of group IV elements. Thus, the basicity (basic character) of the monoxides increases from CO to PbO.

#### Question

Explain the following observations. Illustrate your answers with relevant equations.

- The reaction of lead(II) oxide with both cold, dilute sulphuric acid and hydrochloric acid stops after a short period of time.
- Lead(II) oxide readily dissolves in hot dilute hydrochloric acid than in cold dilute hydrochloric acid.

### Dioxides of group IV elements, $\text{MO}_2$

#### (a) State, appearance and nature

Oxide	CO <sub>2</sub>	SiO <sub>2</sub>	GeO <sub>2</sub>	SnO <sub>2</sub>	PbO <sub>2</sub>
Colour and state	Colourless gas	White crystalline solid		White solid	Dark brown solid
Nature	Acidic		Amphoteric		

#### (b) Preparation

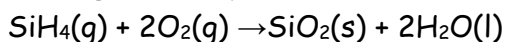
- Carbon dioxide can be prepared by:
  - the action of dilute acid on carbonates or hydrogencarbonates.  

$$\text{CO}_3^{2-}\text{(aq)} + 2\text{H}^+\text{(aq)} \rightarrow \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$$
  - heating strongly carbonates other than group I metal carbonates.  

$$\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$$
  - burning carbon in plenty of air.
  - fermentation.

- Silicon(IV) oxide (also known as silicon dioxide or silica) can be made by:

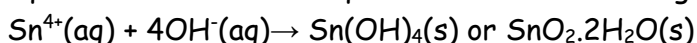
- hydrolysis of silicon tetrachloride,  $\text{SiCl}_4$ .
- heating silicon hydride (silane) or elemental silicon strongly in air.



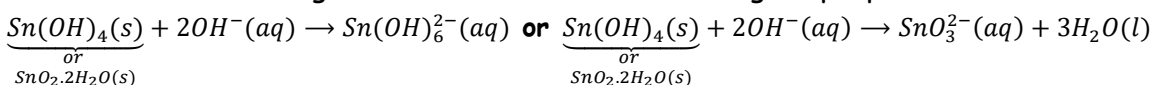
- Germanium(IV) oxide and tin(IV) oxide are made by:

- hydrolysis of their tetrachlorides,  $\text{GeCl}_4$  and  $\text{SnCl}_4$ .
- heating elements strongly in air.
- reacting the elements with hot, concentrated nitric acid.

Tin(IV) oxide naturally occurs as cassiterite/tinstone and can also be made by adding aqueous ammonia to an aqueous solution containing tin(IV) ions.

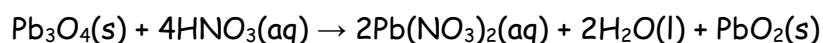


The precipitate is **amphoteric** and thus, dissolves in excess alkali (NaOH or KOH) solution form a colourless solution. This is due to formation of a soluble complex ion. Thus, the use of strong alkalis should be avoided during its preparation.

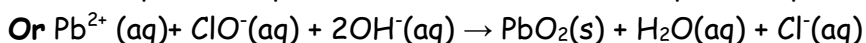
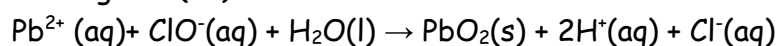


- Lead(IV) oxide is prepared by:

- the action of hot, concentrated or dilute nitric acid on red lead oxide.



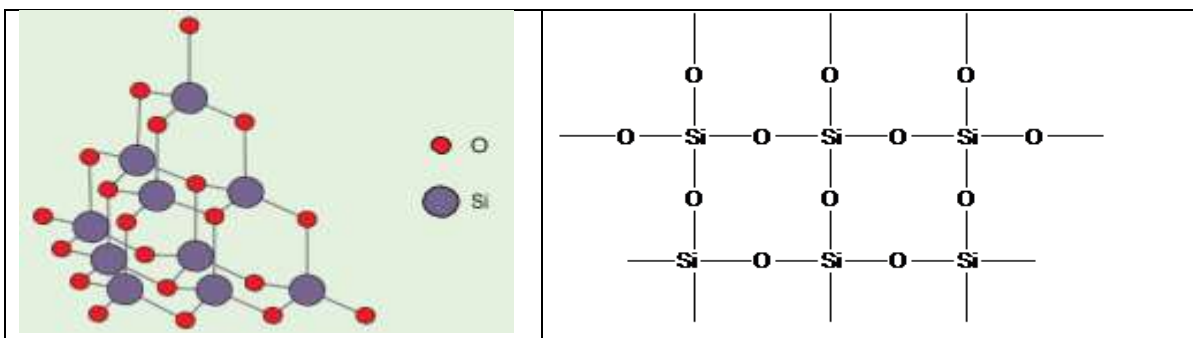
- heating lead(II) nitrate/ethanoate solution with bleaching powder.



### (c) Bonding and structure

Oxide	$\text{CO}_2$	$\text{SiO}_2$	$\text{GeO}_2$	$\text{SnO}_2$	$\text{PbO}_2$
Melting point ( $^{\circ}\text{C}$ )	-56.5	1700	1116	1827	752
Bonding	Covalent			Ionic	
Structure	Simple Molecular	Giant covalent		Giant ionic	

- The carbon dioxide molecule has a linear shape,  $\text{O} = \text{C} = \text{O}$ .
- Silicon(IV) oxide contains silicon atoms bonded tetrahedrally to four oxygen atoms by means of single silicon-oxygen covalent bonds. The bonds are extensive and strong, thus, this it possess a giant covalent (or molecular) structure.



- Explanation for trends in melting points of the dioxides is as follows:
  - Carbon dioxide has a simple molecular structure with the discrete molecules held by weak van der Waals forces of attraction. Little amount of heat energy is therefore required to melt the oxide.
  - Both silicon(IV) oxide and germanium(IV) oxide have giant covalent structures. In their structures, the atoms are held together by covalent bonds. The bonds are strong and extensive/many. A lot of heat energy is therefore required to melt the oxides.  
The atomic radius of germanium atom is larger/bigger than that of silicon atom. Hence, the germanium-oxygen bonds in germanium(IV) oxide are longer and weaker than silicon-oxygen bonds in silicon(IV) oxide.
  - Both tin(IV) oxide and lead(IV) oxide have giant ionic structures with strong ionic bonds between the oppositely charged ions. The ionic radius of tin(IV) ion is smaller than that of lead(IV) ion. Thus, the ionic bonds in tin(IV) oxide are stronger than those in lead(IV) oxide. A lot of heat is therefore required to melt tin(IV) oxide than to melt lead(IV) oxide.

#### (d) Properties

##### 1. Stability

- The dioxides of carbon, silicon, germanium and tin are stable even at higher temperatures.
- Lead(IV) oxide on the other hand is unstable. It decomposes readily on warming to form a more stable lead(II) oxide with liberation of oxygen.  

$$2\text{PbO}_2(\text{s}) \rightarrow 2\text{PbO}(\text{s}) + \text{O}_2(\text{g})$$

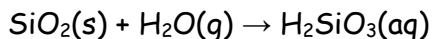
##### 2. Reaction with water

- Carbon dioxide slightly dissolves in cold water and react with it to form a weak carbonic acid.  

$$\text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$$
**Or** 
$$\text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$
 Solubility of the gas in water increases rapidly with increase in pressure.



- Silicon dioxide too slightly reacts with water at its boiling point and under pressure to form 'silicic acid'.



- The rest are insoluble in water and thus, no reaction occurs.

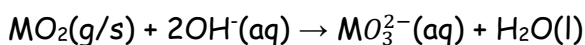
**Note:**

The above reactions show that the dioxides of carbon and silicon are acidic.

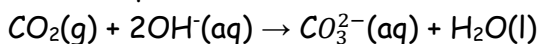
### 3. Reaction with alkalis

- All react with hot, concentrated aqueous solution of caustic alkalis (or fused alkalis) forming the corresponding salts in solution.

Carbon dioxide also reacts with **cold, dilute** solution of the caustic alkalis forming the corresponding salts in solution. The rest do not react with **cold, dilute** solution of the caustic alkalis.



For example:



The reaction with alkalis occurs because carbon dioxide and silicon(IV) oxide are **acidic** while the rest are **amphoteric**.

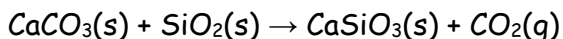
- The ease of reaction of the dioxides with alkalis decreases from carbon dioxide to lead(IV) oxide.

This is due to increase in basicity (decrease in acidity) of the dioxides in the same order.

- If carbon dioxide is bubbled into calcium hydroxide solution, a **white precipitate** is formed and in excess gas, the precipitate dissolves forming a **colourless solution** containing calcium hydrogencarbonate. This reaction is used to test for carbon dioxide.

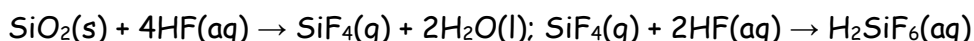


- Silicon(IV) oxide reacts with a mixture of sodium carbonate (or sodium sulphate) and calcium carbonate at 1500°C forming a mixture of sodium silicate and calcium silicate; also called soda glass. Carbon dioxide/sulphur dioxide is evolved.



### 4. Reaction with acids

- Carbon dioxide is acidic and thus, does not react with acids at all conditions.
- Silicon(IV) oxide is unaffected by any of the mineral acids at all conditions. It only reacts with hot **dilute** or **concentrated** hydrofluoric acid forming silicon tetrafluoride, and with excess acid, hexafluorosilicic is formed.



- The tin(IV) oxide forms no salts dilute acids however it also reacts with concentrated sulphuric acid to form tin(IV) sulphate and water. The salt readily hydrolyses to form back tin(IV) oxide on dilution with water.  

$$\text{SnO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Sn}(\text{SO}_4)_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- Lead(IV) oxide **only** reacts with concentrated acids as follows:
  - With hot/warm concentrated sulphuric acid, it forms lead(II) sulphate, water and oxygen.  

$$2\text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{l}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$$
  - With ice-cold hydrochloric acid, a yellow oil liquid is formed. The liquid decomposes immediately to form a white crystalline solid and greenish-yellow gas on **slight warming**. This reaction is used in the lab preparation of chlorine.  

$$\text{PbO}_2(\text{s}) + 4\text{HCl}(\text{aq}) \xrightarrow{0^\circ\text{C}} \text{PbCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}); \text{PbCl}_4(\text{l}) \xrightarrow{\text{warming}} \text{PbCl}_2(\text{s}) + \text{Cl}_2(\text{g})$$
 In **excess** concentrated hydrochloric acid, the lead(IV) chloride formed dissolves due to formation of a **soluble** complex ion.  

$$\text{PbCl}_4(\text{l}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_6^{2-}(\text{aq})$$

**Note:**

The other dioxides are acidic and thus, do not react with **dilute** acids at all conditions.

## 5. Other reactions:

- Unlike other dioxides, lead(IV) oxide is a powerful oxidising agent. The oxide oxidises sulphur dioxide, hot concentrated hydrochloric acid, hydrogen peroxide and manganese(II) salts. (**See previous chapters for details**)
- Hot magnesium reduces carbon dioxide or silica.  
 For example;  

$$\text{SiO}_2(\text{s}) + 2\text{Mg}(\text{s}) \rightarrow \text{Si}(\text{s}) + 2\text{MgO}(\text{s}); \text{SiO}_2(\text{s}) + \underbrace{4\text{Mg}(\text{s})}_{\text{excess}} \rightarrow \underbrace{\text{Mg}_2\text{Si}(\text{s})}_{\text{magnesium silicide}} + 2\text{MgO}(\text{s})$$
- Hot carbon reduces all the dioxides to the corresponding metals with formation of carbon monoxide.  
 For example;  

$$\text{SiO}_2(\text{s}) + 2\text{C}(\text{s}) \rightarrow \text{Si}(\text{s}) + 2\text{CO}(\text{s}); \text{SnO}_2(\text{s}) + 2\text{C}(\text{s}) \rightarrow \text{Sn}(\text{s}) + 2\text{CO}(\text{s})$$

## Trends in basicity (basic character) of the dioxides

The basicity of the dioxides increases from carbon dioxide to lead(IV) oxide. Carbon dioxide and silicon dioxide are acidic and dissolve in caustic alkalis to form carbonates and silicates respectively. The dioxides of germanium, tin and lead are all amphoteric though the acidic character predominates. They form salts with acids and solutions containing complex germanates(IV), stannates(IV) and plumbates(IV) respectively with excess alkalis.

### Uses of the dioxides

- (a) Carbon dioxide has a wide number of uses which include: In making aerated waters and soft drinks. Dry ice (solid carbon dioxide) is used as a refrigerant; the ice sublimates leaving no residue and this makes it a better preservative. It's also used in large scale production of sodium carbonate by Solvay process, ammonium sulphate and urea. The gas is used in fire extinguishers because it does not burn neither does it support combustion and is dense than air.
- (b) Silica in form of quartz and sand is used in building industries for making mortar, cement, concrete and silica-bricks. Silica is also used in making glass. Finely divided silica is used as a white re-enforcing for rubber. Quartz glass is used to make laboratory glass wares like tubes, flasks, dishes, etc.
- (c) Cassiterite is the chief ore of tin. Tin(IV) oxide is used in glazing white tiles and for making milk-glass.
- (d) Lead(IV) oxide is use in the manufacture of matches and in lead-acid accumulators.

### Dilead(II) lead(IV) oxide, $\text{Pb}_3\text{O}_4$

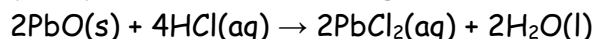
#### (a) Preparation

- Dilead(II) lead(IV) oxide is also called red lead oxide or trilead tetraoxide.
- It is obtained when lead(II) oxide is heated in air at 670-720K for some hours.  
(See page 8 for details)

#### (b) Properties

- The oxide is a dark-brown chocolate solid and is insoluble in water.
- It has properties which resemble both  $\text{PbO}$  and  $\text{PbO}_2$ . This is because it's a mixed oxide written as  $2\text{PbO} \cdot \text{PbO}_2$ .
- The oxide:

- (i) oxidises the warm concentrated hydrochloric acid to chlorine gas. A white precipitate forms on cooling. This is due to insoluble lead(II) chloride formed.



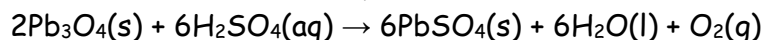
**Overall equation is:**



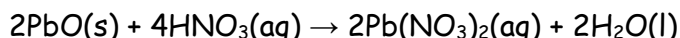
**Observations:**

Dark-brown solid dissolves with effervescence giving greenish-yellow gas.

- (ii) reacts with concentrated sulphuric acid on heating to evolves oxygen and a white solid of lead(II) sulphate is formed.

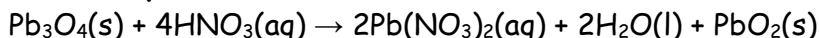


- (iii) reacts with warm/hot dilute nitric acid to form a dark brown solid of lead(IV) oxide. In addition water and lead(II) nitrate are also formed.



$\text{PbO}_2(s) \rightarrow \text{PbO}_2(s)$  no reaction occurs (**Both are oxidizing agents**)

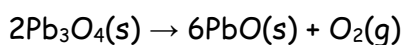
**Overall equation is:**



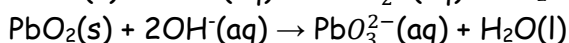
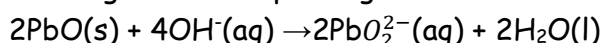
When the mixture is filtered, a colourless filtrate containing lead(II) nitrate and a dark brown solid residue are obtained.

- (iv) first turns black on strong heating and decomposes leaving lead(II) oxide which is reddish-brown when hot and yellow when cold. Oxygen is liberated.

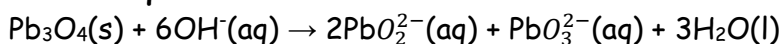
This again indicates that lead(II) oxide is much more stable than red lead oxide.



- (v) reacts with fused alkalis or hot, concentrated aqueous solution of caustic alkalis forming the corresponding salts in solution.



**Overall equation is:**



### (c) Uses

Red lead oxide is used as a pigment in oil paints, and in the making of glass and pottery-glazes. It is also used in the making of matches and in the production of lead(IV) oxide used in lead accumulators.

## B. Chlorides of Group IV Elements

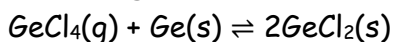
- The elements form **two** types of chlorides; tetrachlorides ( $\text{MCl}_4$ ) and dichlorides ( $\text{MCl}_2$ ).

### Dichlorides, $\text{MCl}_2$

- The stable dichlorides known are formed by germanium, tin and lead.
- $\text{GeCl}_2$  is a pale yellow solid with partial ionic character.
- Both  $\text{SnCl}_2$  and  $\text{PbCl}_2$  are white solids which are mainly ionic. The ionic character in the dichlorides is because:
  - (i) both are crystalline solids at room temperature.
  - (ii) both have relatively high melting points i.e. are non-volatile.
  - (iii) tin(II) chloride is an electrolyte in aqueous solution.
  - (iv) lead(II) chloride readily dissolves in hot water.

### (a) Preparation of the dichlorides

- Germanium(II) chloride ( $\text{GeCl}_2$ ) is made by passing a vapour of germanium(IV) chloride over hot germanium.

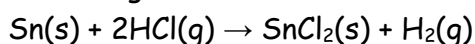


The chloride is very unstable and completely disproportionates at about 720K.

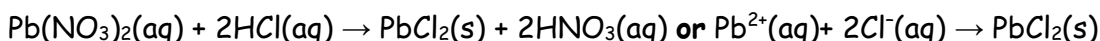
- Hydrated tin(II) chloride is obtained by heating tin or tin(II) oxide with moderately concentrated hydrochloric acid. The resultant solution is evaporated to dryness to obtain  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  crystals.



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



- Lead(II) chloride is prepared by the action of dilute hydrochloric acid (or any soluble chloride solution) on lead(II) nitrate/lead(II) ethanoate solution.

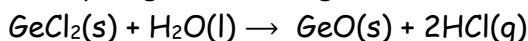


The precipitate is filtered off, washed with hot water to remove impurities and dried.

### (b) Properties of dichlorides

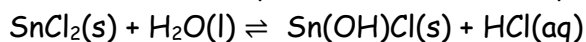
#### 1. Reaction with water

- Germanium(II) chloride readily hydrolyses in water forming germanium(II) oxide and hydrogen chloride gas is evolved.



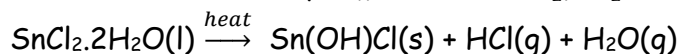
- Both hydrated and anhydrous tin(II) chloride hydrolyse in water to give products depending on the reaction conditions.

With **little cold** water, hydrolysis occurs to form a cloudy solution containing a basic chloride (tin(II) hydroxochloride) and hydrochloric acid.

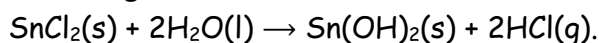


#### Note:

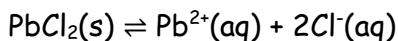
The basic salt is also formed when  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  crystals are heated.



With **large amounts of hot** water, tin(II) hydroxide is precipitated as a white solid.

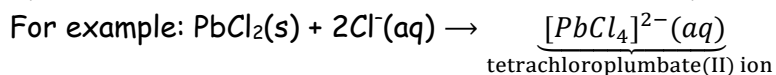


- Lead(II) chloride being ionic is only sparingly soluble in cold water but readily dissolves in hot water.



## 2. Reaction with hydrochloric acid

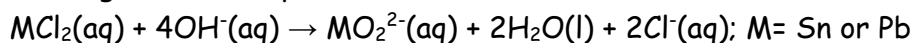
- Both tin(II) chloride and lead(II) chloride are readily soluble in concentrated hydrochloric acid due to formation of soluble complex ions.



- Lead(II) chloride less soluble in both in pure water and dilute hydrochloric acid. The limited solubility of the chloride in dilute hydrochloric acid is due to common ion effect and no soluble complex ion formation. Whereas, the limited solubility of the chloride in pure water is due to high lattice energy which cannot be offset by the low hydration energy of the ions produced.

## 3. With alkalis

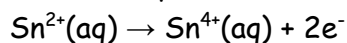
- Both tin(II) chloride and lead(II) chloride react with sodium hydroxide solution forming soluble complex ions in solution.



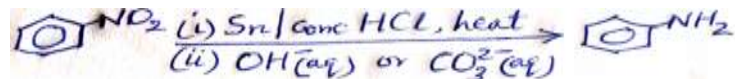
## 4. Reducing properties

- Tin(II) chloride solution in moderately concentrated hydrochloric acid, is a powerful reducing agent.

The half equation for its reducing action is:



- Thus, tin(II) chloride solution reduces:
  - (i) iron(III) salts to iron(II) salts, aqueous iodine solution to iodide ions, mercury(II) salts to metallic mercury, silver(I) salts to metallic silver, gold salts to gold, acidified potassium dichromate(VI) solution to chromium(III) ions and acidified potassium manganate(VII) solution to manganese(II) ions. **(Refer to the previous topics for details).**
  - (ii) many organic compounds particularly the nitro-compounds to primary amines. The best-known case is the reduction of nitrobenzene to aniline.



- Lead(II) chloride (lead(II) ion) is not a reducing agent. This is due to inert pair effect.

## (c) Uses of the dichlorides

- Tin(II) chloride is used as a reducing agent in qualitative and quantitative (volumetric) analysis, and also in the manufacture of organic compounds. The chloride is also used as a mordant in dye printing.
- Basic lead(II) chloride is used as a pigment in manufacture of paints.

### Questions

1. Explain the following observations. Illustrate your answers with relevant equations.
  - (a) Lead(II) oxide readily dissolves in concentrated hydrochloric acid than in dilute hydrochloric acid.
  - (b) Lead(II) chloride is more soluble in concentrated hydrochloric acid than in dilute hydrochloric acid.
  - (c) When concentrated hydrochloric acid is added to lead(II) ethanoate solution, a white precipitate is formed which dissolves in excess acid.
2. Concentrated hydrochloric acid was added to lead(II) nitrate solution drop wise until in excess. State what was observed and write equation(s) for the reaction(s) that took place.

### Tetrachlorides, $MCl_4$

- These include  $CCl_4$ ,  $SiCl_4$ ,  $GeCl_4$ ,  $SnCl_4$  and  $PbCl_4$ .
- All exist as covalent, colourless liquids except,  $PbCl_4$  which is a bright yellow oily liquid.

#### (a) Preparation of tetrachlorides

- Carbon tetrachloride can be prepared by:
  - (i) bubbling chlorine through boiling carbon sulphide in presence of iodine as a catalyst.
$$CS_2(l) + 3Cl_2(g) \rightarrow CCl_4(l) + S_2Cl_2(l)$$
  - (ii) reacting excess chlorine with methane in presence of ultraviolet light.
$$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g)$$
- The tetrachlorides of silicon, germanium and tin can all be prepared by heating the elements in dry chlorine.
$$M(s) + 2Cl_2(g) \rightarrow MCl_4(l)$$
- Lead(IV) chloride, is prepared as a bright oily yellow liquid by reacting lead(IV) oxide with concentrated hydrochloric acid at  $0^\circ C$ . (**See page 18 for details**)

#### Note:

The tetrabromides and tetraiodides of tin and lead don't exist.

This is because bromide and iodide ions have large ionic radii and thus, are strongly reducing. The ions therefore reduce the strongly oxidizing lead(IV) and tin(IV) ions to stable lead(II) and tin(II) ions respectively.

Thus, once the tetrahalides are formed they decompose to the corresponding dihalide and a halogen.

For example:  $Pb^{4+} + 2Br^- \rightarrow Pb^{2+} + Br_2$ ;  $Sn^{4+} + 2I^- \rightarrow Sn^{2+} + I_2$

Also bromine and iodine are not sufficiently strong oxidizing agents to convert  $Pb^{2+}$  or  $Sn^{2+}$  to  $Pb^{4+}$  or  $Sn^{4+}$  respectively.

## (b) Properties of tetrachlorides:

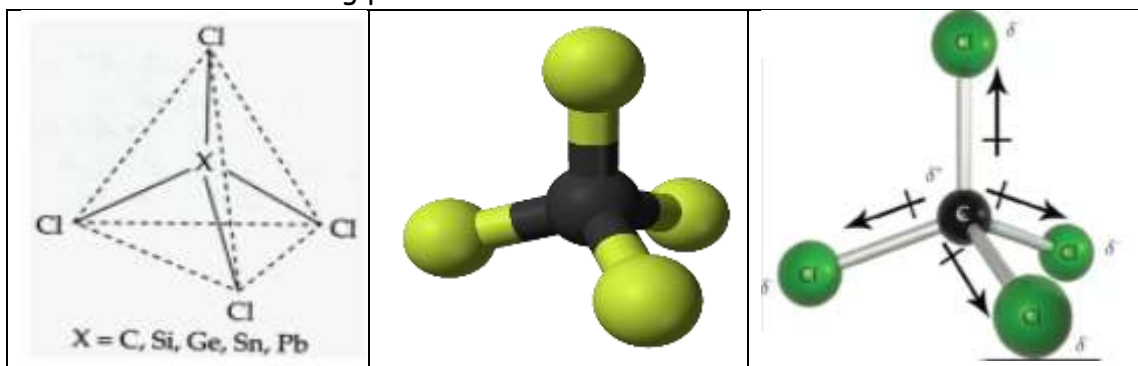
### 1. Bonding and structure

- All are covalent with simple molecular structures. Between the individual molecules are weak van der Waals forces of attraction. This explains why there are volatile liquids at r.t.p.
- The strength of van der Waals forces increases from  $\text{CCl}_4$  to  $\text{PbCl}_4$  due to increase in molecular mass. Thus, their boiling points increase in the order;  
 $\text{CCl}_4 < \text{SiCl}_4 < \text{GeCl}_4 < \text{SnCl}_4 < \text{PbCl}_4$ .
- The individual molecules adopt a **tetrahedral** structure. The individual bonds in the molecules are **polar** but the molecules are **non-polar**.

#### Explanation:

The individual bonds are polar because chlorine atom is more electronegative than the carbon atom. The chlorine atom attracts the bonding electrons more towards itself. As a result, the chlorine atom acquires partial negative charge and carbon atom acquires partial positive charge. This makes the individual bonds polar.

Since the chlorine atoms are symmetrically arranged around the carbon atom, the bond polarities in opposite directions (or dipole moments) cancel out. This gives rise to no net dipole moment and hence, the molecule becomes non-polar in spite of the individual bonds being polar.



### 2. Thermal stability

- Thermal stability decreases from  $\text{CCl}_4$  to  $\text{PbCl}_4$ .  
This is because atomic radius increases from carbon to lead; the element-chlorine bond becomes longer and weaker from  $\text{CCl}_4$  to  $\text{PbCl}_4$ . Thus, the amount of heat required to break the bonds decreases in the same order.
- $\text{CCl}_4$ ,  $\text{SiCl}_4$  and  $\text{GeCl}_4$  are stable even at higher temperatures.
- Both tin(IV) chloride and lead(IV) chloride are thermally unstable.  
Tin(IV) chloride decomposes on heating to tin(II) chloride and chlorine.  
Lead(IV) chloride readily decomposes to lead(II) chloride and chlorine even on slight warming and its melting point is  $-15^\circ\text{C}$ .  
 $\text{MCl}_4(\text{l}) \rightarrow \text{MCl}_2(\text{s}) + \text{Cl}_2(\text{g}); \quad \text{M} = \text{Sn or Pb}$



### 3. Hydrolysis of the tetrachlorides

- All tetrachlorides except, carbon tetrachloride are hydrolysed by water to give acidic solutions, misty/white fumes and the corresponding dioxides.  
$$MCl_4(l) + 2H_2O(l) \rightarrow MO_2(s) + 4HCl(g/aq)$$
  
 $SiO_2$ ,  $GeO_2$  and  $SnO_2$  are white solids while  $PbO_2$  is a dark brown solid  
The misty fumes are due to hydrogen chloride gas formed. The gas then dissolves in the water to form an acidic solution.
- Carbon tetrachloride is immiscible with water. Thus, two layers form when the compounds are mixed together in one container.
- The tendency to undergo hydrolysis decreases in the order:  $SiCl_4 > GeCl_4 > SnCl_4$ . This is due to increase in metallic character from silicon to tin/decrease in covalent character of the tetrachlorides in the same order.

### 4. Reaction with sodium hydroxide solution.

- Except carbon tetrachloride, the rest react with strong aqueous solution of an alkali forming soluble complex ions in solution. This is called **alkaline hydrolysis**.
- The equations can be written as:  
$$MCl_4(l) + 6OH^-(aq) \rightarrow MO_3^{2-}(aq) + 4Cl^-(aq) + 3H_2O(l); \text{ (where } M = Si, Ge \text{ or } Sn)$$
  
$$PbCl_4(l) + 4OH^-(aq) \rightarrow PbO_2^{2-}(aq) + 4Cl^-(aq) + 2H_2O(l)$$

### C. Hydrides of group IV elements

- All the elements form hydrides. The simplest being those with the general formula,  $MH_4$ .

Name	Formula	Other hydrides
Methane	$CH_4$	Alkanes, alkenes, alkynes and arenes
Silane	$SiH_4$	Silanes, $Si_nH_{2n+2}; n = 1 - 11$
Germane	$GeH_4$	Germanes, $Ge_nH_{2n+2}; n = 1 - 6$
Stannane	$SnH_4$	Do not exist
Plumbane	$PbH_4$	Do not exist

- Carbon forms numerous binary hydrides which are collectively called **hydrocarbons**. This due to its ability to catenate, form stable bonds with hydrogen atoms and stable multiple bonds with itself. From carbon to lead, ability to catenate decreases and atomic radius increases. The element-hydrogen bonds become longer and weaker/less stable.

### (a) Preparation

- Methane is made by hydrolysis of beryllium carbide or aluminium carbide.  
(See previous topics for details)
- Silane is made by treating magnesium silicide with dilute hydrochloric acid.  
 $Mg_2Si(s) + 4HCl(aq) \rightarrow 2MgCl_2(aq) + SiH_4(g)$
- Hydrides of germanium and tin can be made by action of lithium tetrahydridoaluminate(III) on the corresponding tetrachloride in dry ether at a low temperature.  
 $MCl_4(l) + LiAlH_4(s) \xrightarrow{\text{dry ether}} LiAlCl_4(s) + MH_4(g); \quad M = Ge \text{ or } Sn$
- The preparation of plumbane is quite difficult. This is because it is so unstable and cannot be isolated at room temperature.

### (b) Properties

#### 1. State at room temperature and structure

- All the hydrides are:
  - (i) volatile, colourless gases at room temperature and pressure.
  - (ii) covalent, have simple molecular structure and adopt a tetrahedral shape just like the tetrachlorides.

#### 2. Boiling points and decomposition temperatures of the hydrides

Hydride	CH <sub>4</sub>	SiH <sub>4</sub>	GeH <sub>4</sub>	SnH <sub>4</sub>	PbH <sub>4</sub>
Boiling point (°C)	-161	-112	-95	-52	-13
Decomposition temperature (°C)	800	450	285	150	0

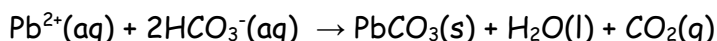
- Boiling point increases from methane to plumbane. All hydrides have simple molecular structures with weak van der Waals forces between their individual molecules.  
From carbon to lead, atomic mass increases and this leads to increase in the molecular mass of the hydrides in the same order. As a result, magnitude of van der Waals force also increases in that order. Thus, a relatively high amount of energy is required to successively overcome the increasing strength of van der Waals forces. Therefore, boiling point increases in that order.
- All the hydrides decompose on heating into their corresponding elements.  
 $MH_4(g) \xrightarrow{\text{heat}} M(s) + 2H_2(g)$   
The ease of decomposition increases from methane to plumbane. This is because atomic radius increases from carbon to lead and as a result, the element-hydrogen bonds become longer and weaker in the same direction. This results into decrease in the decomposition temperature and hence, thermal stability.  
Plumbane is so unstable that it can be isolated at room temperature.

### 3. Hydrolysis of the hydrides

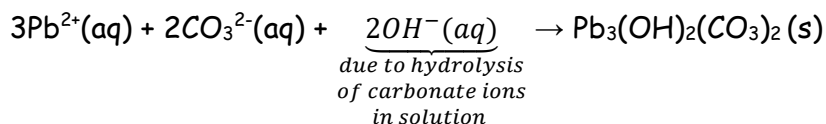
- Methane is unaffected by water, alkalis and acids.
- Silane is hydrolysed slowly by water containing traces of alkali.  
 $\text{SiH}_4(\text{g}) + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_3^{2-}(\text{aq}) + 4\text{H}_2(\text{g})$ .
- The rest are unexpectedly not hydrolyse by water, alkalis and acids.

### D. Carbonates and hydrogencarbonates of group IV elements

- The only important carbonate worth mentioning is lead(II) carbonate. No hydrogencarbonate is known to exist yet.
- Normal lead(II) carbonate can be obtained by precipitation method which involves addition of sodium hydrogencarbonate solution to an aqueous solution containing lead(II) ions.



- The use of usual sodium carbonate solution precipitates a basic carbonate ('white lead').



- The lead(II) carbonate is used in making oil paints.

## Chemical tests for carbonate, hydrogencarbonate, tin(II) and lead(II) ions in solution

- Tests for carbonate ions and hydrogencarbonate ions in solution.

Reagent used	Observations	Equations for the reactions taking place
Addition of dilute acid.	Bubbles of a colourless gas that turns limewater milky	$\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
Addition of barium nitrate solution (or barium chloride solution)	White precipitate	$\text{Ba}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{BaCO}_3(\text{s})$
Addition of lead(II) nitrate solution (or lead(II) ethanoate solution)	White precipitate	$\text{Pb}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{PbCO}_3(\text{s})$
Addition of silver nitrate solution	White precipitate	$2\text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{CO}_3(\text{s})$

Addition of magnesium solution (or magnesium chloride solution or magnesium nitrate solution)	Immediate white precipitate in the cold.	$\text{Mg}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{MgCO}_3(\text{s})$
	No observable change in the cold but on boiling white precipitate is formed	$\text{Mg}^{2+}(\text{aq}) + 2\text{HCO}_3^{-}(\text{aq}) \xrightarrow{\text{boil}} \text{MgCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

• Tests for tin(II) ions,  $\text{Sn}^{2+}$  in solution

Reagent used	Observations	Equations for the reactions taking place
Addition of sodium hydroxide solution.	White precipitate soluble in excess alkali to form a colourless solution	$\text{Sn}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Sn}(\text{OH})_2(\text{s})$ $\text{Sn}(\text{OH})_2(\text{s}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Sn}(\text{OH})_4^{2-}(\text{aq})$
Addition of dilute ammonia solution.	White precipitate insoluble in excess	$\text{Sn}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Sn}(\text{OH})_2(\text{s})$
Addition of excess sodium hydroxide solution followed by few drops of silver nitrate solution.	White precipitate dissolves in excess alkali to form a colourless solution that gives a grey precipitate on addition of silver nitrate solution.	$\text{Sn}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Sn}(\text{OH})_2(\text{s})$ $\text{Sn}(\text{OH})_2(\text{s}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Sn}(\text{OH})_4^{2-}(\text{aq})$ $\text{Sn}^{2+}(\text{aq}) + 2\text{Ag}^{+}(\text{aq}) \rightarrow 2\text{Ag}(\text{s}) + \text{Sn}^{4+}(\text{aq})$
Addition of acidified potassium manganate(VII) solution	Purple solution turns colourless	$2\text{MnO}_4^{-}(\text{aq}) + 5\text{Sn}^{2+}(\text{aq}) + 16\text{H}^{+}(\text{aq}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 5\text{Sn}^{4+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$
Addition of acidified potassium dichromate(VI) solution	orange solution turns green	$2\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{Sn}^{2+}(\text{aq}) + 14\text{H}^{+}(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Sn}^{4+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$

• Tests for tin(IV) ions,  $\text{Sn}^{4+}$  in solution

Reagent used	Observations	Equations for the reactions taking place
Addition of sodium hydroxide solution.	White precipitate soluble in excess alkali to form a colourless solution	$\text{Sn}^{4+}(\text{aq}) + 4\text{OH}^{-}(\text{aq}) \rightarrow \text{Sn}(\text{OH})_4(\text{s})$ $\text{Sn}(\text{OH})_4(\text{s}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Sn}(\text{OH})_6^{2-}(\text{aq})$
Addition of dilute ammonia solution.	White precipitate insoluble in excess	$\text{Sn}^{4+}(\text{aq}) + 4\text{OH}^{-}(\text{aq}) \rightarrow \text{Sn}(\text{OH})_4(\text{s})$

- Tests for lead(II) ions,  $\text{Pb}^{2+}$  in solution

<i>Reagent used</i>	<i>Observations</i>	<i>Equations for the reactions taking place</i>
Addition of sodium hydroxide solution.	White precipitate soluble in excess alkali to form a colourless solution	$\text{Pb}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Pb}(\text{OH})_2(\text{s})$ $\text{Pb}(\text{OH})_2(\text{s}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Pb}(\text{OH})_4^{2-}(\text{aq})$
Addition of dilute ammonia solution.	White precipitate insoluble in excess	$\text{Pb}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Pb}(\text{OH})_2(\text{s})$
Addition of sodium carbonate solution.	White precipitate	$\text{Pb}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{PbCO}_3(\text{s})$
Addition of dilute hydrochloric acid. Heat and leave the mixture to cool. Then add a few drops of concentrated hydrochloric acid.	White precipitate dissolves on heating and reforms (re-crystallises) on cooling. The precipitate dissolves in concentrated acid	$\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$ $\text{PbCl}_2(\text{s}) + 2\text{Cl}^{-}(\text{aq}) \rightarrow [\text{PbCl}_4]^{2-}(\text{aq})$
Addition of dilute sulphuric acid. Heat the mixture.	White precipitate insoluble on heating.	$\text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s})$
Addition of potassium chromate(VI) solution followed by excess sodium hydroxide solution.	Bright yellow precipitate dissolves in excess alkali to form a yellow solution.	$\text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightarrow \text{PbCrO}_4(\text{s})$
Addition of potassium iodide solution.	Bright yellow precipitate. The ppt is soluble in hot water.	$\text{Pb}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$

## Revision questions

1. The melting points of and atomic numbers of the elements of group IV of the Periodic Table are given in the table below.

Element	C	Si	Ge	Sn	Pb
Melting point (°C)	3730	1410	937	232	327
Atomic number	6	14	32	50	82

- (a) Draw a graph of melting point against atomic number for the elements of group IV of the Periodic Table. Explain the shape of your graph.
- (b) Compare the reactions of the elements with:
- water.
  - sulphur.
  - sodium hydroxide solution.
  - dilute acids.
- (c) Discuss the reactions of the chlorides with of each element with water.
- (d) State what would be observed and write equation for the reaction that would take place if:
- excess concentrated hydrochloric acid was mixed with lead(IV) oxide.
  - acidified solution of tin(II) chloride was added to potassium dichromate solution.
  - tin(IV) chloride was exposed to moist air.
  - tin was added to concentrated nitric acid and mixture heated.
  - bleaching powder was added to lead(II) ethanoate solution and mixture heated.
2. Explain the following observations.
- Silicon(IV) chloride is hydrolysed by water whereas carbon tetrachloride is not.
  - Lead(IV) chloride exists but lead(IV) bromide does not.
  - Silicon tetrahydride is hydrolysed by water whereas carbon tetrahydride is not.
3. (a) Draw the structure and name the shape of following species in the table below.

Species	Structure	Shape
CCl <sub>4</sub>		
SnCl <sub>2</sub>		
SiH <sub>4</sub>		

- (b) Write equation for the reaction between:
- water and tin(II) chloride.
  - silane and dilute sodium hydroxide solution.
  - tin(II) chloride and iron(III) ions.
4. Write equations for the reaction between:
- the oxides of each element and sodium hydroxide.
  - lead(IV) oxide with concentrated hydrochloric acid.
  - lead(IV) oxide with warm concentrated hydrochloric acid.
  - the chlorides of each element and water.
5. (a) Write equation for reaction leading to the formation of silicon(IV) chloride and tin(IV) chloride. State the conditions for the reactions in each case.
- (b) Compare the thermal stabilities of silicon(IV) chloride and tin(IV) chloride.