Group 4 Elements, carbon, Silicon, germanium, tin and lead

Members

<table>
<thead>
<tr>
<th>Elements</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>C</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
</tr>
<tr>
<td>Germanium</td>
<td>Ge</td>
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<tr>
<td>Tin</td>
<td>Sn</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
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</tbody>
</table>

Physical properties

- Carbon and silicon are nonmetals.
- Germanium is a metalloid
- Tin and lead are metal

Electron configuration

General electron configuration of group 4 elements is ns²np²

Oxidation states

The common oxidation state of group IV elements is +2 and +4

Stability of oxidation states

Oxidation state +2 become more stable down the group
Oxidation state +4 become less stable down the group.

For instance, carbon burns in oxygen to form carbon (IV) oxide (CO₂) whereas lead form Lead (II) oxide (PbO).

Secondly, CCl₄ is stable whereas PbCl₄ easily decomposes on heating giving lead (II) chloride and chlorine
PbCl₄ (g) (heat) → PbCl₂ (s) + Cl₂ (g)
**Reasons for variation of stability of oxidation states**

Down the group IV; +2 oxidation state become more stable due to inert pair effect i.e. the two s-electron do not participate in the bonding due to increase in the energy difference between ns and np electrons.

**Properties of compound with +2 and +4 oxidation states**

(i) Compounds in oxidation state +4 are predominantly covalent because formation of $M^{4+}$ requires a lot energy whereas compound in oxidation state +2 are ionic

This explains the fact that PbCl$_4$ is soluble in organic solvents like ethanol whereas PbCl$_2$ does not.

Note that

a. covalent compounds are soluble in organic solvents whereas ionic compounds do not.

b. Covalent compound have low melting and boiling points whereas ionic compounds have high melting and boiling point.

c. Covalent compounds do not conduct electricity whereas ionic compounds do. On this basis compound in oxidation state +4 show properties of covalent compounds because they are predominately covalent.

**Chemical properties**

(a) Reaction with water

Carbon does not react with cold water but reacts with steam to form water gas

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

Silicon, germanium and Tin do not react with water up to $100^\circ C$ because they are protected by thin layer of oxide. But they react with steam at very high temperatures to form dioxides

$$Ge(s) + 2H_2O(g) \rightarrow GeO_2(s) +2H_2(g)$$

Lead reacts with soft water (water that contains oxygen) to form lead II hydroxide.

$$Pb(s) + 2H_2O(g) + O_2(g) \rightarrow Pb(OH)_2(s)$$

**Reaction with acids**

(i) Dilute non oxidizing acid like HCl.

C, Si, and Ge do not react

Sn liberates hydrogen

$$Sn(s) + 2H^+(aq) \rightarrow Sn^{2+}(aq) + H_2(g)$$

Pb lead does not react with dilute hydrochloric acid and sulphuric acid due to formation of insoluble salts.
(ii) Nitric acid
With concentrated nitric acid.

C, Si, Ge and Sn react to form dioxide
\[ \text{C(s)} + 4\text{HNO}_3(aq) \rightarrow \text{CO}_2(g) + 4\text{NO}_2(g) + 2\text{H}_2\text{O}(l) \]

Pb reacts to form lead II nitrate and nitrogen dioxide.
\[ \text{Pb(s)} + 4\text{HNO}_3(aq) \rightarrow \text{Pb(NO}_3)_2(aq) + 2\text{NO}_2(aq) + 2\text{H}_2\text{O}(l) \]

With 50% nitric acid.
Pb reacts to form lead II nitrate and nitrogen monoxide.
\[ 3\text{Pb(s)} + 8\text{HNO}_3(aq) \rightarrow 3\text{Pb(NO}_3)_2(aq) + 2\text{NO}(aq) + 4\text{H}_2\text{O}(l) \]

(iii) With sulphuric acid
Dilute sulphuric acid
C, Si and Ge do not react.
Sn and Pb reacts dilute concentrated sulphuric acid liberating hydrogen.
\[ \text{Pb (s)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{PbSO}_4(s) + \text{H}_2(g) \]

With hot Concentrated sulphuric acid
C, Si and Ge react to form dioxides
\[ \text{C(s)} + 2\text{H}_2\text{SO}_4(aq) \rightarrow \text{CO}_2(g) + 2\text{SO}_2(g) + 2\text{H}_2\text{O}(l) \]

Sn and Pb reacts hot concentrated sulphuric acid liberating sulphur dioxide.
\[ \text{Pb(s)} + 2\text{H}_2\text{SO}_4(aq) \rightarrow \text{PbSO}_4(s) + \text{SO}_2(g) + 2\text{H}_2\text{O}(l) \]
\[ \text{Sn(s)} + 2\text{H}_2\text{SO}_4(aq) \rightarrow \text{SnSO}_4(s) + \text{SO}_2(g) + 2\text{H}_2\text{O}(l) \]

(iv) With acetic or ethanoic acid
C, Si Ge and Sn do not react.
Pb reacts ethanoic acid in presence of air giving lead II ethanoate and water
\[ \text{Pb (s)} + 4\text{CH}_3\text{COOH(aq)} + \text{O}_2(g) \rightarrow \text{Pb(CH}_3\text{COO^-)}_2(aq) + 2\text{H}_2\text{O}(l) \]

Reaction with sodium hydroxide
C does not react.
Si Ge and Sn react liberating hydrogen and silicate (IV), germates (IV) and stannates (IV) respectively
\[ \text{Si (s)} + 2\text{NaOH(aq)} + \text{H}_2\text{O}(l) \rightarrow \text{Na}_2\text{SiO}_3(aq) + 2\text{H}_2(l) \]
Lead reacts to form plumbates (II).
\[
Pb(s) + 2NaOH(aq) \rightarrow Na_2PbO_2(aq) + 2H_2(g)
\]

**Unique characteristics of carbon**

1. Forms gaseous oxides, the rest form solid oxides

Note that
a. Carbon dioxide is a gas because its molecules are bonded by weak van der Waal forces.

b. Silicon dioxide is a solid of high melting point because each silicon atom is bonded to four oxygen atom by strong covalent bonds.

2. Catenation: carbon forms chains, rings and branches with single, double and triple bonds while others do not

3. Forms compounds mainly with oxidation state (IV); other elements form compounds with oxidation states +2 and +4.


5. Carbon form CF_4 and not CF_6^-2

**Reason for uniqueness of carbon**
- Has a very small atomic radius
- Has high electronegativity
- Lacks easily accessible d-orbital in its valence shell.

**Allotropes of carbon**

**Allotropy** is the existence of two or more different physical forms in the same state of a chemical element.

An allotrope is any of the different physical form in the same state into which a chemical element can exist.

Carbon exists in two main allotropes, i.e. graphite and diamond.

a. Graphite
In graphite, each carbon atom is covalently bonded to 3 carbon atoms to form a layer of hexagons. Each layer is bonded to another by weak van der Waal forces.

Properties of graphite as a result of its structure

1. Has open structure and low density.
2. It is slippery and used as a lubricant.
3. Has unbonded π-electron that is free to move about making graphite a good conductor of electricity and heat

b. Diamond

Structure of diamond

Each carbon atom is bonded tetrahedrally to four carbon atoms to form a 3D compact structure by strong covalent bonds. As a result diamond has a high density, melting and boiling point. It is the hardest substance known.

Diamond is used as an ornament, and to drill and cut other substances.

Differences between diamond and graphite

1. The density of graphite (2.3 g cm\(^{-3}\)) that of diamond (3.5 g cm\(^{-3}\))
2. Diamond is very hard while graphite is soft
3. Graphite is slippery while diamond is not
4. Graphite conducts electricity while diamond does not.

Experiment to show that graphite and diamond are allotropes of carbon
When equal masses of graphite and diamond are burn in air, they give equal volume of carbon dioxide.

**Compounds of carbon**

1. **Hydrides:** they include alkanes, alkenes, alkyne and aromatic compounds studied in organic chemistry
2. **Halides of carbon**
   Carbon forms all the four tetrahalides: CF₄, CCl₄, CBr₄ and Cl₄
   **Comments**
   a. The melting points of halides increase with molecular. All tetrahalides are volatile liquids
   b. The stability of the halides decrease from CF₄ > CCl₄ > CBr₄ > Cl₄ due to decrease in the bond strengths as electronegativity of the halogen decrease.
   c. CCl₄ is a good solvent, being very stable and heavier than air; is used in fire extinguisher to protect the burning substance from oxygen.
   d. CCl₄ is not hydrolyzed by water due to lack of accessible d-orbital to accommodate the lone pair of electron from water and weaken the C-X bond.

3. **Oxides of carbon**
   (a) **Carbon monoxide (CO)**

   **Preparation**
   By dehydation of methanoic acid with concentrated sulphuric acid.
   \[ \text{HCO}_2\text{H}(l) + \text{Conc. } \text{H}_2\text{SO}_4(l) \rightarrow \text{CO}(g) + \text{H}_2\text{O}(l) \]

   **Uses of carbon monoxide**
   (i) It reduces most metal oxides to metals.
   \[ \text{Fe}_2\text{O}_3 (s) + 3\text{CO} (g) \rightarrow 2\text{Fe} (s) + 3\text{CO}_2 (g) \]
   \[ \text{NiO} (s) + \text{CO} (g) \rightarrow \text{Ni} (s) + \text{CO}_2 (g) \]
   This property is employed industrially in the extraction of iron and nickel.

   It is used to purify nickel: it forms a volatile carbonyl that decompose to give a pure metal
   \[ \text{Ni} (s) + 4\text{CO}(g) \rightarrow 90^\circ \text{C} \rightarrow \text{Ni(CO)}_4(g) \]
   \[ \text{Ni(CO)}_4(g) \rightarrow 180^\circ \text{C} \rightarrow \text{Ni} (s) + 4\text{CO} (g) \]

   (ii) It is used preparation of carbonyl chloride that is used in the production of polyurethane form of plastics and pesticides.
   \[ \text{CO} (g) + \text{Cl}_2 (g) \rightarrow \text{COCl}_2 (g) \]
   [carbonyl chloride]

   (iii) It reacts with fused NaOH under pressure to give sodium methanoate. Methanoic
acid is produced from this salt by the addition of dilute HCl.

\[
\text{NaOH (l) + CO (g) } \rightarrow \text{HCOONa (s)} \\
\text{then } \text{HCOO}^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{HCOOH (l)}
\]

Methanoic acid is used to produce insecticides and for dyeing, tanning, and electroplating.

(b) Carbon dioxide (CO₂)

**Preparation**

By decomposition of calcium carbonate

\[ \text{CaCO}_3 (\text{s}) \text{ (heat)} \rightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g}) \]

Limestone quick lime

**Uses of carbon dioxide**

a. Flavors fizzy drinks.

b. It is heavy and stable so is used in fire extinguishers to displace oxygen from burning objects.

**Carbonic acid**

**Preparation**

By reacting carbon dioxide and water. There is however, equilibrium in solution of carbonic acid, hydrogen ions, hydrogen carbonate and carbonate ions.

\[ \text{CO}_2 (\text{g}) + \text{H}_2\text{O (l)} \leftrightarrow \text{H}_2\text{CO}_3 (\text{aq}) \]

\[ \text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq}) \leftrightarrow 2\text{H}^+ (\text{aq}) + \text{CO}_3^{2-} (\text{aq}) \]

**Structure of carbonic acid**

Has 3 resonance hybrid whose bond lengths are intermediate between a C=O and C-O bonds

![Structure of carbonic acid](image)

Carbonates and hydrocarbonate

- Both react with acids to liberate carbon dioxide
  \[ \text{CO}_3^{2-} (\text{aq}) + 2\text{H}^+ (\text{aq}) \rightarrow \text{H}_2\text{O (l)} + \text{CO}_2 (\text{g}) \]
  \[ \text{HCO}_3^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{H}_2\text{O (l)} + \text{CO}_2 (\text{g}) \]

- CO₃²⁻ forms white ppt with Mg²⁺ whereas HCO₃⁻ does not.

**Silicon**
Existence
Exists as silica, SiO$_2$ or sand used for building or making glass.

Chemical properties of SiO$_2$

Reaction with NaOH

\[
\text{SiO}_2(s) + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{SiO}_3(aq) + \text{H}_2\text{O}(l)
\]

\[
\text{SiO}_2(s) + 2^\cdot \text{OH (aq)} \rightarrow \text{SiO}_3^{2-} (aq) + \text{H}_2\text{O (l)}.
\]

Germanium, tin and lead

Points to note

a. They form compounds with oxidation states +2 and +4. The stability of compounds with oxidation states +2 increases down the group due to ‘inert pair effect’ while those of oxidation states +4 decreases down the group.

b. Compounds with oxidation state +2 are reducing. For instance tin II ions reduce iron III ions to iron II ions.

\[
\text{Sn}^{2+}(aq) + \text{Fe}^{3+}(aq) \rightarrow \text{Sn}^{4+}(aq) + \text{Fe}^{2+}(aq)
\]

c. Compounds with oxidation state +4 are oxidizing. For instance lead IV oxide ions oxidizes HCl ions to chlorine

\[
\text{PbO}_2(s) + 4\text{HCl (aq)} \rightarrow \text{PbCl}_2(s) + 2\text{H}_2\text{O (l)} + \text{Cl}_2 (g)
\]

d. Compounds with oxidation state +4 are predominantly ionic whereas those in oxidation state +4 are predominantly covalent. This explains the fact that PbCl$_2$ is soluble in water but insoluble in ethanol whereas PbCl$_4$ is soluble in ethanol.

Chemical properties

The principal reactions of germanium and tin are similar, both elements exhibiting oxidation state of 4
The principal reactions of lead are summarized below

**a. Lead IV halide**
Lead forms ionic Pb\(^{4+}\)(F\(^{-}\))\(_4\), and covalent liquid PbCl\(_4\).
The tetra-bromide and tetra-iodide do not exist, presumably because bromine and iodine are not sufficiently strong oxidizing agents to convert Pb\(^{2+}\) to Pb\(^{4+}\).

**Lead IV chloride**
**Preparation**
By reacting lead IV oxide with cold concentrated hydrochloric acid.
PbO\(_2\) (s) + 4 HCl (aq) (conc. and cold) \(\rightarrow\) PbCl\(_4\) (aq) +2H\(_2\)O(l)

**Effect of Heat on Lead (IV) chloride**
Decomposes on heating liberating chlorine
PbCl\(_4\) (g) (heat) \(\rightarrow\) PbCl\(_2\) (s) + Cl\(_2\) (g)

**Hydrolysis of lead (IV) chloride**
Lead tetrachloride is readily hydrolyzed by water (white fumes of HCl and brown precipitate of PbO\(_2\) are observed)
PbCl\(_4\) (s) + 2H\(_2\)O (l) \(\rightarrow\) PbO\(_2\) (s) + 4HCl (aq)

**b. Lead II halide**
**Preparation**
By reacting soluble salt like lead nitrate with soluble halide
\[ \text{Pb}^{2+}(aq) + 2X^-(aq) \rightarrow \text{Pb}X_2(s) \; (X = \text{F}, \text{Cl}, \text{Br}, \text{I}). \]

E.g. \[ \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow \text{PbCl}_2(s) \]

Properties
Except the iodide, which is yellow, they are white solids. Lead (II) chloride forms chloro-complexes, e.g., \([\text{PbCl}_4]^{2-}\), with \(\text{Cl}^-\) ions and because of this, it is soluble in concentrated hydrochloric acid.

c. Lead IV oxide
Preparation
(i) Lead (IV) oxide, \(\text{PbO}_2\), is a brown solid obtained by oxidation of a soluble lead (II) salt with hot sodium chlorate (I).

\[ \text{Pb}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{ClO}^-(aq) \rightarrow \text{PbO}_2(s) + \text{Cl}^-(aq) + 2\text{H}^+(aq) \]

(ii) By action of nitric acid on trilead tetra oxide, \(\text{Pb}_3\text{O}_4\).

\[ \text{Pb}_3\text{O}_4(s) + 4\text{HNO}_3(aq) \rightarrow 2\text{Pb(NO}_3)_2(aq) + \text{PbO}_2(s) + 2\text{H}_2\text{O}(l) \]

Chemical properties of lead (IV) oxide
(i) Decomposes on heating

\[ 2\text{PbO}_2(s) + \text{heat} \rightarrow 2\text{PbO} (s) + \text{O}_2(g) \]

(ii) Reacts with cold concentrated hydrochloric acid to form lead (IV) chloride and water

\[ \text{PbO}_2(s) + 4\text{HCl}(aq) \rightarrow \text{PbCl}_4(s) + 2\text{H}_2\text{O}(l) \]

(iii) Oxidizes hot concentrated hydrochloric acid to chlorine

\[ \text{PbO}_2(s) + 4\text{HCl}(aq) \rightarrow \text{PbCl}_2(s) + 2\text{H}_2\text{O}(l) + \text{Cl}_2(g) \]

Qualitative analysis of \(\text{Pb}^{2+}\)
1. Forms a white precipitate with sodium hydroxide soluble in excess

\[ \text{Pb}^{2+}(aq) + 2\text{OH}^-(aq) \rightarrow \text{Pb(OH)}_2(s) + 2\text{OH}^-(aq) \rightarrow \text{Pb(OH)}_4^{2-}(aq) \]

2. Forms white precipitate with ammonia solution insoluble in excess

\[ \text{Pb}^{2+}(aq) + 2\text{OH}^-(aq) \rightarrow \text{Pb(OH)}_2(s) \]

3. Forms yellow precipitate with potassium iodide

\[ \text{Pb}^{2+}(aq) + 2\text{I}^-(aq) \rightarrow \text{PbI}_2(s) \]

4. Forms white precipitate hydrochloric acid soluble on warming

\[ \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow \text{PbCl}_2(s) \]

5. Forms white precipitate with sulphate ions

\[ \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) \]
Revision questions

Trial 1
Explain the following observation:
(a) Graphite and copper are both good conductors of electricity. (4 marks)
(b) Lead (II) chloride is insoluble in water whereas lead (IV) chlorides readily dissolve in the same solvent. (2 marks)
(c) Carbon which is in the same group as lead in the periodic table shows one valence of 4 in its compounds but lead shows two valences of 2 and 4.
(d) Lead IV chloride readily decomposes to lead (ii) chloride when heated but lead II chloride is not affected by heat. (2 marks)
(e) The solubility of lead (II) halides increase in order PbI₂<PbBr₂<PbCl₂.
(f) When dilute hydrochloric acid is added to a solution of lead ethanoate, a white precipitate is formed. The precipitate is soluble in excess concentrated hydrochloric acid. (4 marks)
(g) Crystals of lead (II) chloride can be prepared in the laboratory by heating lead (II) oxide with dilute hydrochloric acid and cooling. When lead (II) oxide is treated with concentrated hydrochloric acid under the same conditions, no crystals form. Give a reason for this observation and illustrate your answer with equations.

Trial 2
(a) (i) Define the term allotrope.
   (ii) Give evidence that shows that graphite and diamond are allotropes of carbon.
(b) b. Explain the following:
   (i) Graphite conducts heat and electricity yet it is a non-metal.
   (ii) Diamond is a very hard element.
   (c) Some properties of graphite and diamond are shown in the table below:

<table>
<thead>
<tr>
<th>Allotrope</th>
<th>Density g/cm³</th>
<th>Heat of combustion at 298K (KJ/mol.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>2.25</td>
<td>-393.5</td>
</tr>
<tr>
<td>Diamond</td>
<td>3.51</td>
<td>-395.4</td>
</tr>
</tbody>
</table>

(i) Calculate the heat of conversion of graphite to diamond and state the allotrope that is more stable at room temperature (298 K). Give your reasoning.
(ii) State what would happen to the total volume of the system if a given mass of diamond is converted completely into graphite. Explain your answer.
(iii) Suggest, with a reason, one condition required for the converting of graphite to diamond.
(iv) Calculate the change in volume when one gram of graphite is converted completely into diamond.
(iv) Give one use of diamond and graphite.
Trial 3
State four properties in which carbon differs from the rest of members in group (IV). (4 marks)

Trial 4
Carbonates are salts of carbonic acid which its self is obtained when carbon dioxide dissolves in water.
(a) Write the structural formulae of carbon dioxide and carbonate ions. On the structure you have written, indicate the type of bonding.
(b) The bond length of carbon-oxygen single bond and carbon-oxygen double bond are 0.143 nm and 0.122 nm respectively. (2 marks)
(i) Estimate the bond lengths in carbonate ions and carbon dioxide. Give reason for your answers. (4 marks)
(ii) Write the structural formula of carbonic acid and estimate the oxygen-carbon bond length. (2 marks)
(iii) Give approximate value of the OCO bond angle in the structure you gave in (ii) and explain your answer.
(c) Write the formulae of two ions which are isoelectric (contain equal number of electrons) with carbonate ions (2 marks)
(d) The solubility of carbon dioxide in water is $0.51 \text{ cm}^3/\text{g}$ at s.t.p. Assuming the density of water is $1 \text{ g cm}^{-3}$, calculate the solubility of carbon dioxide in mol dm$^{-3}$ at s.t.p (1 mole of a gas occupies $22.41 \text{ at s.t.p}$). (3 marks)
(e) A sample of potassium carbonate was dissolved in water and the pH of solution determined. Was the pH of solution greater or less than 7? Explain your answer. (2 marks)
(f) Explain why it’s possible to get two end-points when carbonate ions are titrated against an acid. (2 marks)

Trial 5
Write an ionic equation for the reaction between sodium hydroxide and silicon (IV) oxide.

Trial 6
Carbon, silicon, tin and lead are elements of group (IV) of the periodic table.
(i) How do these elements react with sodium hydroxide?

Trial 7
Carbon, silicon, tin and lead are elements of in group IV of the periodic table.
(a) State:
(i) the common oxidation states shown by elements in group IV of the P.T. (1 marks)
(ii) how the stability of the oxidation states of group (IV) elements varies down the group.
    (illustrate your answer with the chlorides of carbon and lead). (03 marks)
(b) Give a reason for your answer in (a) (ii). (01 mark)
Trial 8
(a) When red lead Pb₃O₄ was reacted with nitric acid, a solid was formed.
   Write the equation for the reaction. (2 marks)
(b) The mixture from (a) was filtered and the residue warmed with concentrated hydrochloric acid,
   (i) What was observed? Explain your answer. (1 marks)
   (ii) Write the equation for the reaction. (1½ mark)
(c) The filtrate from (a) was divided into two parts.
   (i) To the first part was added aqueous potassium iodide. State what was observed and write the equation for the reaction. (2 marks)
   (ii) The second part was evaporated to dryness and heated strongly. Explain what was observed and write the equation for the reaction that took place. (2½ marks)

Trial 9
A sample of lead (IV) oxide was treated with warm concentrated hydrochloric acid.
(i) State what was observed. (1½ marks)
(ii) Write the equation for the reaction. (02 marks)

Trial 10
Write down the equations for the reactions between:
   i. The oxides of group (IV) elements and sodium hydroxide. (06 marks)
   ii. Lead IV oxide and concentrated hydrochloric acid. (1½ marks)

(b) Write the ionic equation for the reaction between sodium hydroxide and lead (II) oxide. (1 ½ marks)

Trial 11
a. State two industrial uses of tin.
   b. Tin is said to be enantiotropic, explain what this means.
   (c) How would you convert a solution containing tin (II) ions into a solution containing tin (IV) ions?
   (d) Pure tin was reacted with chlorine to give a colorless liquid that fumed in moist air. A solution of 0.162 g of the liquid in water was equivalent to 24.00 cm³ of exactly 0.1 M sodium hydroxide solution using methyl orange as the indicator. Calculate the percentage purity of the liquid in tin compound.

Trial 12
Give a comparative account of the Chemistry of the oxides and chlorides of silicon, germanium, tin and lead, paying particular attention to:
(a) the formation, composition and stability of oxides.
(b) the formation, hydrolytic behavior and stability of chlorides.

Trial 13
7. Give a concise account of the Chemistry of elements of group 4 of the periodic table (carbon, silicon, germanium, tin and lead) referring your answer to all the following aspects:
(a) The variation in the first ionization energy.
(b) The hydrolysis of the tetrachloride.
(c) The acid-base character of the oxides of the elements in the oxidation states II and IV.
(d) The relative stabilities of II and IV oxidation states of elements in oxides and chlorides.
(e) Show how the electron pair repulsion theory can be used to predict the shape of the silicon tetrachloride molecule.

Trial 14
(a) Carbon, silicon, germanium, tin and lead are elements of group IV in the periodic table.
   (i) Describe the types of chlorides formed by these elements.
   (ii) Show how the chlorides of these elements react with water.
(b) Describe the trends in the basicity of the oxides of group IV elements and write equations to show how the oxides of carbon, silicon and germanium react with sodium hydroxide.
(c) When a mixture of carbon and an oxide of a group II element was heated to a very high temperature, a compound X was formed. X reacted with cold water to give a gas Y that decolourised chlorine water.
   (i) Identify the element in group (II) and substances X and Y.
   (ii) Write equations leading to the formation of Y.

Trial 15
(a) Illustrate the transition from non metallic to metallic character of carbon, silicon and tin by describing the structure of and giving one chemical property of, any one type of these elements.
(b) One of the products of the reaction between magnesium silicide (Mg$_2$Si) and sulphuric acid is a gas X. A 0.620 g sample of X occupied 224 cm$^3$. When hydrolysed, this sample yielded 1568 cm$^3$ of hydrogen and a residue (SiO$_2$) which, after it had been strongly heated, weighed 1.200 g. (All gas volumes corrected to S.T.P.)
   (i) What is the molecular formula of X?
   (ii) Write an equation for the hydrolysis of X.

Trial 16
(a) (i) State two important oxidation states exhibited by carbon, silicon, tin and lead.
   (ii) Describe how the stability of the two states varies from carbon to lead. Use the oxides of the elements to illustrate your answer.
(iii) Explain the inert pair effect in group (IV) elements.

(b) State what would happen if tetrachloromethane, silicon (IV) chloride, tin(IV) chloride and lead (IV) chloride are separately shaken with water. Write equations to illustrate your answer where necessary.

(c) (i) Write equations to show how lead (II) chloride can be prepared in the laboratory. State the conditions for the reaction.
(ii) What type of bonding exists in lead (II) chloride?
(iii) State two physical properties that show that lead (II) chloride exhibits the type of bonding you have stated in (ii) above.

Trial 17
12. C, Si, Ge, Sn and Pb are elements of group (IV) of the periodic table.
   (a) Explain the following trends among the group (IV) elements:
      (i) electropositivity.  
      (ii) stability of +2 oxidation state.  
      (4 marks)
   (b) State four properties in which carbon differs from the rest of the members of group (IV).  
      (4 marks)
   (c) Explain why carbon tetrachloride molecule is nonpolar yet the bonds in carbon tetrachloride are polar.  
      (3 marks)
   (d) A sample of lead (IV) oxide was treated with warm concentrated hydrochloric acid  
      (i) State what was observed.  
      (1.5 marks)
      (ii) Write an equation for the reaction.  
      (2 marks)

Trial 18
13. Carbon, silicon, tin and lead are elements of in group (IV) of the periodic table
   (a) State  
      (i) The common oxidation state shown by the elements of group (IV).  
      (1 mark)
      (ii) How the stability of the oxidation states of group (IV) elements varies down the group.  
      (Illustrate your answer with the chlorides of carbon and lead).  
      (03 marks)
   (b) Give a reason for your answer in (a)(i)  
      (01 mark)
   (c) Discuss the reactions of the chlorides of each element with water  
      (06 marks)
   (d) Write down equations for the reactions between:  
      i. The oxide of each element and sodium hydroxide.  
      (06 marks)
      ii. Lead (IV) oxide and concentrated hydrochloric acid.  
      (1½ marks )
Suggested answers

Trial 1

(a) Both copper and graphite conduct electricity because they both possess mobile electrons. The mobile electrons of copper are the delocalized valence electrons whereas those of graphite are those of unbounded p-electrons.

(b) Lead (II) chloride is ionic whereas lead (IV) chloride is covalent. Lead (IV) chloride is formed by sharing electrons because the amount of energy required to form Pb$^{4+}$ is too much.

(c) Carbon form compound with oxidation state $+4$ because there is very little difference between $2s^2$ and $2p^2$ electron is small. The energy difference between $6s^2$ and $6p^2$ is big that sometimes lead form Pb$^{2+}$ ions by inert pair effect when only $6p^2$ electron take part in the chemical reaction.

(d) Lead (II) oxidation state is more stable due to inert pair effect.

(e) Because the lattice energy decrease in order PbI$_2$>PbBr$_2$>PbCl$_2$ and the ionic charater increase in order PbI$_2$<PbBr$_2$< PbCl$_2$ because electrogativity of chloride is in order Cl$>$ Br$>$ I

(f) A white precipitate of PbCl$_2$ is formed with dilute HCl which dissolves in concentrated HCl due to formation of a soluble complex.

\[
Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)
\]

\[
PbCl_2(s) + 2Cl^-(aq) \rightarrow PbCl_4^{2-}(aq)
\]

(g) Lead (II) oxide forms insoluble lead (II) chloride with dilute hydrochloric acid which dissolves in concentrated hydrochloric acid to form a soluble complex.

\[
Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)
\]

\[
PbCl_2(s) + 2Cl^-(aq) \rightarrow PbCl_4^{2-}(aq)
\]

Trial 2 (b)

(i) Graphite has mobile unbounded p-electrons that conduct heat and electricity

(ii) Each carbon atom is bonded to four carbon atoms by strong covalent bonds to form a compact solid

(c)(i) +1.9kJmol$^{-1}$

(ii) graphite is more stable because it contains less energy.
(iii) heat or pressure
(iv) volume decrease by 0.16 cm$^3$

**Trial 4**

(a)

(b) (i) Bond length in CO$_2$ = 0.122 nm
    Bond length in CO$_3^{2-}$ = 0.136 and average between two single bond and 1 double bond

(ii)

(iii) Bond angle = 120° due to uniform repulsion between the bonds

(c) SO$_3^{2-}$

(d) 0.0446 mol dm$^{-3}$

(e) pH will be more than 7 due to hydrolysis of carbonate ions to form hydroxide ions

\[
\text{CO}_3^{2-} + \text{H}_2\text{O(l)} \leftrightarrow \text{HCO}_3^{-} + \text{OH}^{-} \]

(f) The first end point occurs due to formation of hydrogen carbonate ions (HCO$_3^{-}$) and the second one due to formation of carbon dioxide and water.

**Trial 8**

(a) Pb$_3$O$_4$ (s) + 4HNO$_3$(aq) → PbO$_2$ (s) + 2Pb(NO$_3$)$_2$(aq) + 2H$_2$O(l)

(b) Green gas and white solid that dissolve in excess acid to form colorless solution

\[
PbO_2(s) + 4\text{HCl(aq)} \rightarrow Pb\text{Cl}_2(s) + Cl_2(g) + 2\text{H}_2\text{O(l)}
\]

Then

\[
Pb\text{Cl}_2(s) + 2\text{Cl}^{-}(aq) \rightarrow Pb\text{Cl}_4^{2-}(aq)
\]

(c) (i) yellow ppt
\[
Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s) 
\]
(ii) orange residue and brown fumes
\[
2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g) 
\]

Trial
(b) Tin exists in more than one crystal (allotropic) form that can be inter-converted by temperature changes, i.e., the white form is the normal form at room temperature.

\[
\begin{array}{c|c|c|c|c}
\text{ α-tin} & 13.2^\circ C & \beta-\text{tin} & 161^\circ C & \gamma-\text{tin} \\
\text{Grey} & & \text{White} & & \text{Grey} \\
\end{array}
\]

Trial 11
(c) By oxidation with acidified potassium permanganate or dichromate solution or iron (III) salt.
(d) \( \text{SnCl}_4(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{SnO}_2(s) + 4\text{HCl}(aq) \)

Moles of HCl produced = moles of NaOH = \( \frac{24 \times 0.1}{1000} = 0.0024 \text{ moles} \)

Moles of \( \text{SnCl}_4 \) = \( \frac{0.0024}{4} = 0.0006 \text{ moles} \)

Mass of pure \( \text{SnCl}_4 \) = 0.0006 \( x (119 + 35.4 \times 4) = 0.15636 \)

\% of \( \text{SnCl}_4 \) = 96.5\%

Trial 14 (c)
(i) Element is calcium, X is \( \text{CaC}_2 \) and Y is \( \text{HC}≡\text{CH} \).
(ii) \( \text{Ca} (s) + 2\text{C} (s) \rightarrow \text{CaC}_2 (s) \)
then \( \text{CaC}_2 (s) + 2\text{H}_2\text{O} (l) \rightarrow \text{Ca(OH)}_2 (aq) + \text{Y} (\text{HC}≡\text{CH}) (g) \)

Trial 15 (b)
(i) \( \text{SiH}_4 \)
(ii) \( \text{SiH}_4 (g) + 2\text{H}_2\text{O} (l) \rightarrow \text{SiO}_2 (s) + 4\text{H}_2 (g) \)