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TOPIC 11; PERIODICITY II

Competency; The learner analyses the trends in the physical and chemical properties of Group 14 elements, Group 17 elements and d-block elements and relates these trends to their applications in industrial and environmental contexts.

Sub-topic 11.1 TRENDS IN PROPERTIES OF GROUP 14 ELEMENTS AND THEIR COMPOUNDS.

Required; elements {
- *Physical properties — trends in melting points, metallic character, bond energy, structure and bonding)
- *Chemical Properties — Reactions with water, air and halogens.

Their chlorides {
- *Physical properties — Structure and bonding, Melting points
- *Chemical properties — thermal stability, reaction with water.

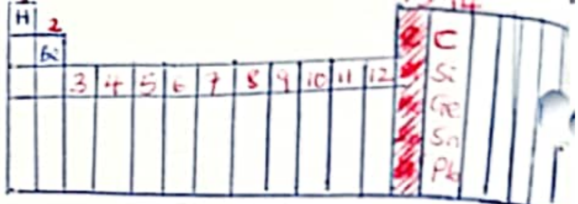
Their oxides {
- *Physical properties — structure and bonding, melting points
- *Chemical properties — bonding, thermal stability,
  - Rxn with water, acids, alkalis

Practical { Test tube experiments to identify Pb^{2+} and Sn^{2+} ions.

Project work { Applications and limitations of group 14 elements and compounds in technology and industry — In real life

End of sub-topic. #

— The Crystallogens —



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GROUP 14 ELEMENTS.

These are also called group 4 or group 4A or group IV elements. They are called Group 14 elements because they are located in the 14^{th} vertical column of the modern periodic table. The change from Group IV or 4A to Group 14 was adopted to count all the 18 columns consecutively, rather than splitting the table into A and B.

These are Carbon (C), Silicon (Si), Germanium (Ge), tin (Sn) and lead (Pb)

The general outer electronic configuration is ns^2np^2 where n = 2, 3, 4, 5, 6

PHYSICAL PROPERTIES OF GROUP 14 ELEMENTS.

1. Trends in melting points

Melting point; Is a constant temperature at which a solid changes to a liquid at constant pressure

Element	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Melting point (°C)	3550	1410	937	232	327

(Let learners plot a graph)

Trend; The melting points decrease from Carbon to tin and increase from tin to lead.

Explanation; Carbon has the highest melting point because it has a giant covalent structure with many, short and strong covalent bonds that require more energy to be broken.

True; Carbon, silicon and Germanium have giant covalent structures held by strong covalent bonds, however, from Carbon to germanium atomic radius increases, bond length between atoms of the elements increases but bond strength decreases/bond weakens hence less energy required to break the bond for melting to occur.

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Tin and lead have giant metallic structures held by strong metallic bonds. The melting point of tin is lower that of lead because tin forms a distorted cubic close-packed (tetragonal packing) structure in which the metallic bonds are weaker than in the regular cubic close-packed structure of lead. (face-centred cubic packing)

2. Metallic character.

Element	Carbon	Silicon	Germanium	Tin	Lead.
Character	Non-metal	Metalloid	Metalloid	metal	metal

Metallic character increases from Carbon to lead. This is because, as the atomic radius increases down the group, the nuclear attraction for the outermost electrons decreases thus the tendency of the atoms to lose electrons increase.

3. Bond energy.

Element	Carbon (C-C)	Silicon (Si-Si)	(Ge-Ge) Germanium	~~Sn-Sn~~
Bond energy ($kJmol^{-1}$)	346	222	188	

Bond energies in Group 14 decreases down the group. As atomic radius increases, bond length increases but bond strength decreases. Thus, less energy is required to break required to break one mole of covalent bonds into its constituent gaseous atoms.

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(b) With water;

Heated Carbon reacts with steam to form carbon monoxide and hydrogen gases. (water gas)

$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

Heated silicon slowly reacts with steam to form silicon dioxide and hydrogen gas.

$Si_{(s)} + 2H_2O_{(g)} \longrightarrow SiO_{2(s)} + 2H_{2(g)}$

Germanium does not react with water nor steam.

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

$Sn_{(s)} + 2H_2O_{(g)} \longrightarrow SnO_{2(s)} + 2H_{2(g)}$

Lead reacts very slowly with soft water in presence of oxygen to form lead(II) hydroxide

$Pb_{(s)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow Pb(OH)_{2(s)}$

(c) With halogens- (F_2, especially Cl_2, Br_2, I_2)

Carbon does not react with chlorine at any condition.

Heated silicon reacts with dry chlorine gas forming silicon tetrachloride

$Si_{(s)} + 2Cl_{2(g)} \longrightarrow SiCl_{4(l)}$

Heated germanium reacts with dry chlorine gas forming germanium-tetrachloride

$Ge_{(s)} + 2Cl_{2(g)} \longrightarrow GeCl_{4(l)}$

Heated tin reacts with dry chlorine gas forming tin(IV) chloride

$Sn_{(s)} + 2Cl_{2(g)} \longrightarrow SnCl_{4(l)}$

Heated lead reacts with dry chlorine gas forming lead(II) chloride

$Pb_{(s)} + Cl_{2(g)} \longrightarrow PbCl_{2(s)}$

Note: Same reactions for bromine and iodide forming a corresponding tetrahalide and lead(II) halide.

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OXIDATION STATES OF GROUP 14 ELEMENTS

Group 14 elements exhibit two oxidation states ie +2 and +4. Due to the high ionisation energy involved in removing all the 4 valence electrons from the atoms, the +4 oxidation state is exhibited in covalent compounds. while that of +2 is exhibited in ionic compounds. This is because the ionisation energy required to remove the two electrons from outermost p-orbital is not that high.

STABILITY OF +2 and +4 oxidation states

The stability of +2 oxidation states increases down a group from Carbon to lead while the stability of +4 oxidation state decreases from Carbon to lead.

This implies that lead(II) compounds are more stable than lead(IV) compounds.

Explanation; The increase in stability of the +2 oxidation state down the group is due to inert pair effect.

Inert pair effect is the inability of a pair of electrons in the outermost s-orbital of group 14 elements to participate in chemical bonding.

The inert pair effect increases from Carbon to lead because as the atomic radius increases from one element to next, the number of electrons in the d- and f-orbitals with a poor shielding effect increases. The ineffectiveness of the inner d- and f-orbitals electrons to shield the outermost s-orbital electrons from increasing nuclear charge increases.

The s-orbitals which are spherical in shape tend to penetrate and enter the atomic core, rendering them (s-orbital electrons) less available for bonding.

CHLORIDES OF GROUP 14 ELEMENTS.

These are two types depending on +2 and +4 oxidation states. They include; (i) Dichlorides (MCl_2)
(ii) Tetrachlorides (MCl_4)

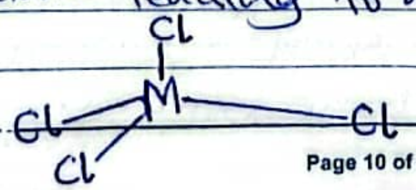
(a) TETRACHLORIDES (MCl_4)

Tetrachloride	State	Bonding	Shape	Boiling points (°C)
CCl_4	colourless liquids	Covalent	Tetrahedral	77
$SiCl_4$	colourless liquids	Covalent	Tetrahedral	58
$GeCl_4$	colourless liquids	Covalent	Tetrahedral	83
$SnCl_4$	colourless liquids	Covalent	Tetrahedral	114
$PbCl_4$	yellow liquid	Covalent	Tetrahedral	Decomposes at room temperature

PHYSICAL PROPERTIES OF TETRACHLORIDES

1. Structure and bonding. ✓ All are covalent non-volatile liquids at room temp

All tetrachlorides of group 14 elements are covalent in nature with a central atom forming 4 covalent single bonds with chlorine atoms leading to a tetrahedral shape.



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Although each bond is polar, the molecules as a whole are non-polar since the molecules are symmetrical and the dipole moments cancel out (net dipole moment zero)

Explanation: Chlorine being more electronegative than the atoms of the elements it attracts bonding electrons towards itself acquiring a partial negative charge and atom of the element gains a partial positive charge. This makes the bond polar. Consequently, the whole molecule is non-polar because the chlorine atoms are symmetrically distributed around the central carbon atom in a tetrahedral shape. This creats equal and opposite dipole-dipole moment cancellation hence no dipole moment in the molecule, thus molecules are non-polar.

Note; These are non-volatile liquids at room temperature held ~~together by weak Van der Waals forces of attraction whose~~ magnitude depends on molar mass of the compound

2. Trends in Boiling point

Trend: Boiling point decreases from Carbon tetrachloride to silicon tetrachloride and then increases to tin tetrachloride; with lead tetrachloride that decomposes even at room temperature

Explanation: This is explained by changes in strength of Van der Waal's forces in the molecules. The strength of the forces increases with an increase in molecular weight/molar mass and increase in the total number of electrons in the molecules that can be polarised

Lead(IV) chloride is unstable in +4 oxidation state hence decomposes at even room temperature to lead(II) chloride (in +2 oxidation state that is more stable) and chlorine gas

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CHEMICAL PROPERTIES

1. THERMAL STABILITY OF THE TETRACHLORIDES.

Trend. Thermal stability decreases from Carbon tetrachloride to lead(IV) chloride.

Carbon tetrachloride, Silicon tetrachloride and $GeCl_4$ do not decompose because they are thermally stable.

Tin tetrachloride decomposes on strong heating to form tin(II) chloride and Chlorine

Lead(IV) chloride decomposes slowly at room temperature to form Lead(II) chloride and chlorine gas

CCl_4, $SiCl_4$, $GeCl_4$ } thermally stable hence No decomposition.

$$SnCl_4(l) \xrightarrow{heat} SiCl_2(s) + Cl_2(g)$$

$$PbCl_4(l) \xrightarrow{room\ temp} PbCl_2(s) + Cl_2(g)$$

Explanation; The decrease in thermal stability is because atomic radius increases from Carbon to lead, element–chlorine bond length increases. however the bond strength decreases, requiring less energy to break the bonds.

2. Reaction with Water (Hydrolysis)

Apart from Carbon tetrachloride, all other tetrachlorides hydrolyse in water forming a corresponding dioxide and hydrogen chloride gas.

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~~Explanations~~

Illustration;

- C ...... $2s^2 2p^2$ — No vacant d-orbital
- Si ...... $3s^2 3p^2 (3d^0)$ — Available
- Ge ...... $4s^2 4p^2 (4d^0)$ — Present
- Sn ...... $5s^2 5p^2 (5d^0)$ — Present
- & Pb ...... $6s^2 6p^2 (6d^0)$ — present

Explanation;

The Carbon atom in CCl_4 lacks vacant d-orbital to accomodate the lone pair of electrons from oxygen atom of water molecule hence does not undergo hydrolysis.

In $SiCl_4$, $GeCl_4$, $SnCl_4$ and $PbCl_4$, the central atom (Si or Ge or Sn or Pb) has vacant d-orbital to accommodate the lone pair of electrons from oxygen atom of water molecules, hence they undergo hydrolysis in water forming a corresponding dioxide and hydrogen chloride gas

ie

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$$

$$GeCl_{4(l)} + 2H_2O_{(l)} \longrightarrow GeO_{2(s)} + 4HCl_{(g)}$$

$$SnCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SnO_{2(s)} + 4HCl_{(g)}$$

$$PbCl_{4(l)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4HCl_{(g)}$$

(b) Dichlorides of Group 14 elements.

MCl_2 ; M = Ge, Sn, Pb

Dichloride	State	Bonding	Shape (in vapour phase)	Boiling point (°c)
$GeCl_2$	white Solid	Covalent	Bent shape	165
$SnCl_2$	white Solid	Mainly Covalent	Bent shape	2[illegible]
$PbCl_2$	Solid (white)	Ionic	Bent shape	500

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4. PHYSICAL PROPERTIES OF DICHLORIDES.

Tin(II) chloride and lead(II) chloride are white crystalline solids.

Tin(II) chloride is highly soluble in water forming a colourless solute while ~~T~~ lead(II) chloride is sparingly soluble in cold water but soluble in warm water.

1. Structure and bonding.

Dichlorides of Carbon and silicon donot exist due to a decrease in stability of the +2 oxidation state down the group from Carbon to lead.

From germanium to lead, the bonding in these dichlorides become more ionic.

In vapour phase, $SnCl_2$ and $PbCl_2$ consist of mainly discrete molecules of tin(II) chloride and lead(II) chloride that are bent-shaped.

2. Trend in Melting point.

Trend: Melting point increases from $GeCl_2$ to lead(II) chloride.

Explanation: Cationic radius increases from germanium(II) to lead(II) hence an decrease in charge density and polarising power making lead(II) chloride predominantly ionic ~~a~~ while germanium(II) chloride and tin(II) chloride ~~mos~~ mainly covalent. Consquently, more energy is required to break the ionic bonds in lead(II) chloride than in tin(II) chloride and germanium(II) chloride.

CHEMICAL PROPERTIES OF DICHLORIDES

1. THERMAL STABILITY.

~~Germ~~ Thermal stability increases from germanium(II) chloride to lead(II) chloride.

Germanium(II) Chloride decomposes on heating to form germanium(IV) chloride and germanium. This is a disportionation reaction.

$$2GeCl_{2(s)} \overset{heat}{\rightleftharpoons} GeCl_{4(l)} + Ge_{(s)}$$

Tin(II) chloride and lead(II) chloride are thermally stable hence do not decompose. (Remember concept of stability +2 oxidation state)

2. Reaction with water

Germanium(II) Chloride is readily hydrolysed in water to form germanium(II) oxide and hydrogen chloride gas

$$GeCl_{2(s)} + H_2O_{(l)} \rightarrow GeO_{(s)} + 2HCl_{(g)}$$

Tin(II) chloride is partially hydrolysed by water forming basic tin(II) chloride and hydrogen chloride gas.

$$SnCl_{2(s)} + H_2O_{(l)} \longrightarrow Sn(OH)Cl_{(s)} + HCl_{(g)}$$

In hot excess water; $SnCl_{2(s)} + 2H_2O_{(l)} \rightarrow Sn(OH)_{2(s)} + 2HCl_{(aq)}$

Lead(II) chloride is sparingly soluble in water hence does not undergo hydrolysis. Thus it's solubility in water increases with increase in temperature. $PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

OR $PbCl_{2(s)} + aq \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

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OXIDES OF GROUP 14 ELEMENTS

These include ;- Monoxides (in +2 oxidation state)
- Dioxides (in +4 oxidation state)
- Trilead tetraoxide (Pb_3O_4)

(a) DIOXIDES. (MO_2)

Dioxide	State	Bonding	Structure	Shape	Melting point (°c)
CO_2	Gas	Covalent	Simple molecular	Linear	−78
SiO_2	Solid	Covalent	Giant covalent	Tetrahedral	2590
GeO_2	Solid	Covalent	Giant Covalent	Tetrahedral	1200
SnO_2	Solid	Ionic	Giant ionic		1900
PbO_2	Solid.	Ionic	Giant ionic		Decomposes even at room temp.

(i) Structure and bonding

CO_2 has a simple molecular structure with weak van der Waal's forces of attraction between its molecules

SiO_2 and GeO_2 have giant covalent structures with strong covalent bonds.

SnO_2 and PbO_2 have giant ionic structures with strong ionic bonds.

(b) Trend in Melting point

Carbon dioxide has a simple molecular structure with weak van der Waal's forces of attraction between its molecules, that require less energy to be broken hence the lowest Melting point

SiO_2 and GeO_2 have giant covalent structures with strong covalent bonds that require more energy to be broken hence higher melting points. However from germanium to tin, atomic radius increases, bond length increases but bond strength decreases, hence covalent bonds in GeO_2 are weaker than those in SiO_2, thus a decrease in melting point.

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SnO_2 and PbO_2 have giant ionic structures with strong ionic bonds. However, the ionic radius of tin(IV) ion in SnO_2 is smaller than that of lead(IV) ion in PbO_2 making bonds in PbO_2 weaker than those of SnO_2.

PbO_2 decomposes on heating forming lead(II) oxide and oxygen gas.

$$2PbO_{2(s)} \xrightarrow{heat} 2PbO_{(s)} + O_{2(g)}$$

CHEMICAL PROPERTIES

(a) Reaction with Water:

Carbon dioxide reacts with water forming Carbonic acid

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

All other dioxides donot react with water.

(b) Thermal Stability:

CO_2, SiO_2 and GeO_2 are thermally stable hence donot decompose.

PbO_2 decomposes on heating forming lead(II) oxide and oxygen gas

$$2PbO_{2(s)} \xrightarrow{heat} 2PbO_{(s)} + O_{2(g)}$$

(c) Reactions with alkalis.

CO_2 reacts with cold dilute alkalis forming a carbonate and water

$$CO_{2(g)} + 2\bar{O}H_{(aq)} \longrightarrow CO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$

SiO_2 reacts with hot concentrated alkalis forming a silicate and water

$$SiO_{2(s)} + 2\bar{O}H_{(aq)} \longrightarrow SiO_3^{2-}{}_{(aq)} + H_2O$$

GeO_2 reacts with hot concentrated alkalis forming germanate(IV) ions and water

$$GeO_{2(s)} + 2\bar{O}H_{(aq)} \longrightarrow GeO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$

SnO_2 reacts with hot concentrated alkalis forming Stannate(IV) ions and water

$$SnO_{2(s)} + 2\bar{O}H_{(aq)} \longrightarrow SnO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$

PbO_2 reacts with hot concentrated alkalis forming Plumbate(IV) ions and water

$$PbO_{2(s)} + 2\bar{O}H_{(aq)} \longrightarrow PbO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$

(d) Reaction with acids.

(i) With dilute acids.

CO_2 does not react with acids since it's acidic.

GeO_2, SnO_2 and PbO_2 do not react with dilute acids.

However; Silicon dioxide reacts with only one acid, Hydrofluoric, ~~a~~ forming silicon tetrafluoride or Hexafluorosilicic acid (with excess acid)

$$SiO_{2(s)} + 4HF_{(aq)} \longrightarrow SiF_{4(g)} + 2H_2O_{(l)}$$

OR $$SiO_{2(s)} + \underset{\text{excess}}{6HF_{(aq)}} \longrightarrow H_2SiF_{6(aq)} + 2H_2O_{(l)}$$

(ii) With concentrated acids.

CO_2, GeO_2, SiO_2 ~~and SnO_2~~ do not react with concentrated acids.

Tin(IV) oxide reacts with concentrated sulphuric acid forming tin(IV) sulphate and water

$$SnO_{2(s)} + 2H_2SO_{4(l)} \longrightarrow Sn(SO_4)_{2(s)} + 2H_2O_{(l)}$$

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Lead(IV) oxide reacts with hot concentrated sulphuric acid forming lead(II) sulphate, Oxygen gas and water.

$PbO_{2(s)} + 2H_2SO_{4(l)} \longrightarrow 2PbSO_{4(s)} + O_{2(g)} + 2H_2O_{(l)}$

Lead(IV) oxide reacts with hydrochloric acid under the following conditions

- Cold conc. HCl; $PbO_{2(s)} + 4HCl_{(aq)} \longrightarrow PbCl_{4(l)} + 2H_2O_{(l)}$
- Excess Conc. HCl; $PbO_{2(s)} + 4H^+_{(aq)} + 6Cl^-_{(aq)} \longrightarrow PbCl_6^{2-}{}_{(aq)} + 2H_2O_{(l)}$ (Hexachloroplumbate(IV))
- Hot Conc. HCl; $PbO_{2(s)} + 4HCl_{(aq)} \longrightarrow PbCl_{2(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$

(b) MONOXIDES.

PHYSICAL PROPERTIES:

Monoxide	State	Bonding	Structure	Melting pt	Character
CO	Gas (colourless)	Covalent	Simple molecular	−205.02	Neutral
SiO	Solid (Brown)	Covalent	Simple molecular	2000°C	Neutral
GeO	Solid (Yellow)	Ionic	Giant Covalent	Sublimes	Amphoteric
SnO	Solid (Blue-black)	Ionic	Giant ionic	1080	Amphoteric
PbO	Solid (Yellow)	Ionic	Giant ionic	888	Amphoteric

Structure and bonding.

SiO & CO; have simple molecular structures with weak van der waals forces between molecules

GeO; has a giant covalent structure with covalent bonds.

SnO & PbO; have giant ionic structure with strong ionic bonds.

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(b) Trend in Melting point

Carbon monoxide has the lowest melting point due to simple molecular structure with weak van der waal's forces between the molecules. These require less energy to be broken. The strength of these forces ~~increase~~ depends ~~with~~ with increase in molar mass, thus Silicon (II) oxide having a higher melting point. From Silicon to tin, ~~at~~ atomic radius increases, bond length increases however bond strength decreases, thus ~~dec~~ less energy required to break the bonds.

SnO. and PbO. have giant ionic structures with strong ionic bonds However, the ionic radius of tin(II) ion in SnO_2 is smaller that of lead(II) ion in lead(II) oxide making bonds in lead(II) oxide weaker than those of tin(II) oxide. ~~thus~~

= CHEMICAL PROPERTIES =

(a) With water

All the monoxides donot react with water.

(b) Thermal stability

Thermal stability of these monoxides increases ~~down~~ from Carbon monoxide to ~~e~~ lead(II) oxide.

Silicon(II) oxide and germanium(II) oxide disp~~ro~~portionate in vapour phase to respective element and a dioxide of the element

$$2SiO_{(s)} \rightleftharpoons Si_{(s)} + SiO_{2(s)}$$

$$2GeO_{(s)} \rightleftharpoons Ge_{(s)} + GeO_{2(s)}$$

lead(II) oxide is thermally stable hence does not decompose since in +2 oxidation state, lead(II) oxide is stable.

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(c) Reaction with alkalis.

Carbon monoxide reacts with fused sodium hydroxide solution on heating under pressure forming ~~Sodiu~~ Sodium methanoate

$$NaOH_{(aq)} + CO_{(g)} \longrightarrow HCOONa_{(s)}$$

Silicon(II) oxide does not react with alkalis.

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

$$SnO_{(s)} + 2\bar{O}H_{(aq)} \longrightarrow SnO_2^{2-}{}_{(aq)} + H_2O_{(l)}$$

Lead(II) oxide reacts with hot concentrated alkalis to form plumbate(II) ions and water

$$PbO_{(s)} + 2\bar{O}H_{(aq)} \longrightarrow PbO_2^{2-}{}_{(aq)} + H_2O_{(l)}$$

(d) Reaction with acids

(i) With Dilute acids.

Carbon monoxide and silicon(II) oxide donot react with dilute acids

Germanium (II) oxide ~~and~~, tin(II) oxide and lead(II) oxide react with dilute acids (since these oxides are amphoteric) forming a corresponding salt and water

$$GeO_{(s)} + 2H^+_{(aq)} \longrightarrow Ge^{2+}_{(aq)} + H_2O_{(l)}$$

$$SnO_{(s)} + 2H^+_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + H_2O_{(l)}$$

$$PbO_{(s)} + 2H^+_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + H_2O_{(l)}$$

↑ for nitric acid

Lead(II) oxide reacts with hot hydrochloric acid forming lead(II) chloride and water. $PbO_{(s)} + 2HCl_{(aq)} \longrightarrow PbCl_{2(aq)} + H_2O_{(l)}$

~~PbO~~ $_{(s)}$ + ~~HCl~~

The reaction of lead(II) oxide with cold dilute Hydrochloric/and Sulphuric acids is slow due to formation of an insoluble salts ($PbCl_2$ and $PbSO_4$) that prevents further reaction.

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(ii) With Concentrated acids

Most monoxides donot react with with concentrated acids.
Lead(II) oxide reacts with excess concentrated hydrochloric acid forming tetrachloroplumbate(II) ions and water

$$PbO_{(s)} + 2H^+_{(aq)} + 4Cl^-_{(aq)} \longrightarrow PbCl_4^{2-}{}_{(aq)} + H_2O_{(l)}$$

(3). TRILEAD TETRAOXIDE (Pb_3O_4)

PHYSICAL PROPERTIES.

Trilead tetraoxide is a red or Bright-orange crystalline powder at room temperature with a density of $9.1gcm^{-3}$.
It's a mixed oxide consisting of lead(II) oxide and lead(IV) oxide thus contains both +2 and +4 oxidation states
The bond is primarily ionic but exhibits significant covalent character. This oxide is amphoteric in nature.
Melting point; Decomposes.

CHEMICAL PROPERTIES.

(a) With water
Trilead tetraoxide is insoluble in water; No reaction with water

(b) Thermal Stability;
Trilead tetraoxide decomposes readily at a temperature beyond 500°C forming lead(II) oxide and oxygen gas.

$$2Pb_3O_{4(s)} \xrightarrow{heat} 6PbO_{(s)} + O_{2(g)}$$

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(c) Reaction with alkalis

Trilead tetraoxide reacts with hot concentrated alkalis forming plumbate(II) and plumbate(IV) ions

$Pb_3O_4(s) + 4\bar{O}H(aq) \rightarrow 2PbO_2^{2-}(aq) + PbO_3^{2-}(aq)$

(d) Reactions with Acids

(i) Dilute nitric acid.

Trilead tetraoxide reacts with ~~d~~ hot dilute nitric acid forming lead(II) nitrate, lead(IV) oxide and water

$Pb_3O_4(s) + 4HNO_3(aq) \rightarrow 2Pb(NO_3)_2(aq) + PbO_2(s) + 2H_2O(l)$

(ii) Concentrated acids

~~Re Leads~~ Trilead tetraoxide reacts with hot concentrated hydrochloric acid forming lead(II) chloride, chlorine gas and water

$Pb_3O_4(s) + 8HCl(aq) \text{ (hot)} \rightarrow 3PbCl_2(aq)(s) + Cl_2(g) + 4H_2O(l)$

Trilead tetraoxide reacts with hot concentrated sulphuric acid forming lead(II) sulphate, Oxygen and water

$2Pb_3O_4(s) + 6H_2SO_4(l) \rightarrow 6PbSO_4(s) + O_2(g) + 6H_2O(l)$

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Practical work.

Test tube experiments to identify Pb^{2+} and Sn^{2+} ions.

For Pb^{2+} ions in a solution; (Carry out the expts and record observations in the table below.)

Divide the solution into 6 portions.

Test procedure	Observations
To the 1st portion, add sodium hydroxide solution dropwise until in excess.	
To the 2nd portion, add ammonia solution dropwise until in excess	
To the 3rd portion, add 2 drops of dilute sulphuric acid	
To the 4th portion, add 3 drops of potassium iodide solution	
To the 5th part, add 3 drops of dilute HCl and warm.	
Use the 6th part to confirm lead(II) ions	

For Sn^{2+}

Test	Observations
Add NaOH dropwise until in excess	
Add NH_3 solution dropwise until in excess	
Add acidified $KMnO_4$	
Add $FeCl_3$ solution	

More tests will be discussed in the lab.

— Psalms 44 —

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PROJECT WORK

Applications and Limitations of group 14 elements and Compounds.

Carbon as an element;
- graphite — electrodes, Lubricant, Lead pencils
- Diamond — Rock drillers, Jewelery.
- Amorphus — wood charcoal — fuel, masks; Animal charcoal — whiten sugar crystals; Coke — extraction of Iron, Zinc; Lamp black — Shoe polish & printer's ink.

Silicon — Semi-conductors in transistors.

Germanium — Semi-conductor in transistors

Tin and Lead — Alloys. — Solder,

CO_2 — Baking powder (solvay process); Refrigerant; Fire extinguisher

CO — making water gas when mixed with H_2

SiO_2 — glass; concrete; food-grade anticaking agent

SnO_2 — Component in gas sensor. Polishing powder for glass

GeO_2 — making fibre-optic cables

PbO_2 — used as a positive electrode

Pb_3O_4 — Paint; — Raw material in lead-acid battery making; — specialised glasses, ceramics

CCl_4 — dry cleaning; fire extinguishing agent

$SnCl_2$ — electroplating

$GeCl_4$/$SiCl_4$ — Solar panels; optical fibres

$PbCl_2$ — Precursor for synthesis of other lead compounds

$SnCl_4$ — Catalyst — in some organic rxns, glass surface treatment