

The Periodic Table - Group 4

To succeed in this topic you need to:

- Understand atomic structure (Factsheet 01), bonding (Factsheet 05) and structure of elements and compounds (Factsheet 06)
- Understand oxidation numbers (Factsheet 11)

After working through this Factsheet you will:

- Know the trends in physical properties of the Group 4 elements
- Know the relative stabilities of the +2 and +4 oxidation states of the Group 4 elements
- Know key characteristics of Group 4 oxides and chlorides

Group 4 Elements

The electron configurations of Group 4 are shown below:

Element	Electronic Structure	
carbon	2.4	[He] 2s ² 2p ²
silicon	2.8.4	[Ne] 3s ² 3p ²
germanium	2.8.18.4	[Ar] 3d ¹⁰ 4s ² 4p ²
tin	2.8.18.18.4	[Kr] 4d ¹⁰ 5s ² 5p ²
lead	2.8.18.32.18.4	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²

Group 4 elements are part of the **p-block**.

Trends within the group

As we go down Group 4:

- **Atomic radius increases** - as electrons go into higher energy levels
- **Density increases** - density depends on structure, atomic radius and atomic mass. Larger atomic masses usually produce higher densities, since the atomic radius does not increase as fast as the atomic mass.
- **Melting point decreases** - due to the change in structure from giant molecular to metallic
- **Ionisation energy generally decreases** - since the atomic radius increases, meaning the outer electrons are further away from the nucleus, and there is an increased shielding effect due to the greater number of electrons between outer electrons and the nucleus
- **Metallic character increases** - since an explanation of this requires knowledge of oxide characteristics, further details are given at the end of this Factsheet

Exam Hint: Questions on trends, their explanations and consequences are common. Candidates need to be able to explain the reasons for the trends in atomic radius, ionisation energy and metallic character.

Table 1. Elements of Group 4

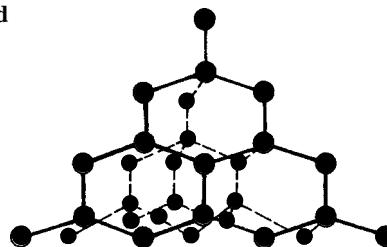
Element	Symbol	Appearance	Melting pt (°C)	Density (gcm ⁻³)	Conductivity	1 st I.E. (kJ mol ⁻¹)	Bonding	Metallic character
carbon (graphite)	C	shiny black solid	3652	2.26	fairly good	1086	giant molecular	non-metal
carbon (diamond)	C	colourless solid	3730	3.51	non-conductor	1086	giant molecular	non-metal
silicon	Si	shiny grey solid	1410	2.33	semi-conductor	787	giant molecular	non-metal
germanium	Ge	shiny grey solid	937	5.32	semi-conductor	760	giant molecular	metalloid
tin	Sn	silver solid	232	7.3	good	707	giant metallic	metal
lead	Pb	silver solid	327	11.4	good	715	giant metallic	metal

Structure

Carbon exists as two common allotropes (fig 1):

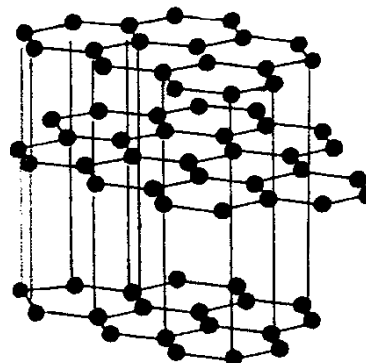
Fig 1. Allotropes of carbon

Diamond



- Giant covalent molecule.
- One of the hardest substances known, due to **strong covalent** bonds.
- Insulator.

Graphite



- Giant covalent layer lattice.
- Lubricant due to ability of layers to 'slide' across each other.
- High melting point due to strong covalent interatomic bonds.
- Conductor (in plane of layers) due to presence of delocalised electrons.

Silicon and **Germanium** have a structure similar to diamond.

Tin has three allotropes, whose stability depends on the temperature. The allotrope stable at room temperature (white tin) has a metallic structure. However, the other allotropes, which are stable at other temperatures, have different structures.

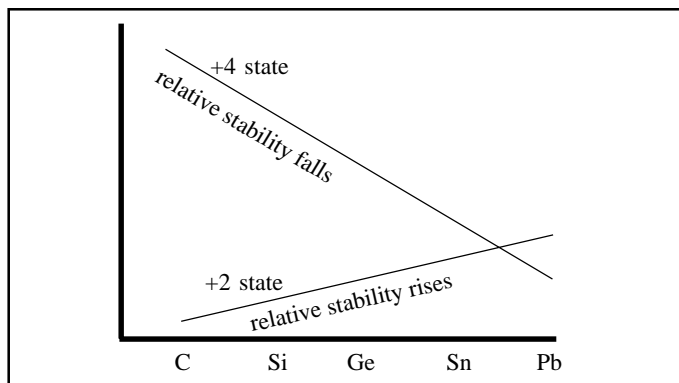
Lead has a metallic structure.

Oxidation States of Group 4

We might expect group 4 to have a common oxidation state of +4 as it has 4 outer electrons.

However, there are two oxidation states for Group 4: +4 and +2

Going down the group, the stability of the +4 oxidation state falls, and the stability of the +2 oxidation state rises (fig 2).

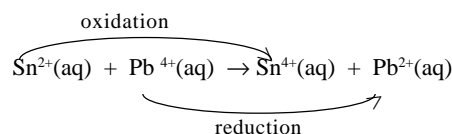
Fig 2. Relative stability of +2 and +4 oxidation states in Group 4


Only lead has a more stable +2 state than +4 state

Consequently:

- +2 oxidation state of C, Si, Ge, Sn are reducing agents (ie want to be oxidised and lose 2 electrons). In carbon and silicon, the +2 state is extremely unstable, so such compounds are rarely met.
- +4 oxidation state of Pb is an oxidising agent (ie wants to be reduced and gain 2 electrons)

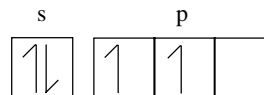
So tin(II) will reduce lead(IV) to lead(II):



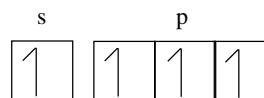
We will see examples of both oxidation states in the Group 4 elements when we look at their oxides and chlorides.

Valencies in Group 4 - an explanation

The ground state for the outer electrons of the Group 4 compounds is as shown below:



Hence, to achieve a valency of four, one s electron must be promoted to the vacant p orbital:



Promotion of this electron requires energy, but the energy released in forming the two extra bonds compensates for this.

As we go down the group, the bonding electrons are further from the nucleus, so the energy gained from forming the extra bonds becomes less. The s electron therefore becomes less likely to be promoted. This is known as the **inert pair effect**.

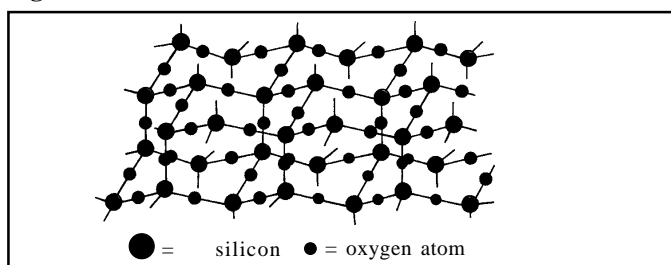
Since silicon and the elements below it have vacant d-orbitals, they can show a covalency of up to 6.

Oxides of Group 4
Monoxides (+2 oxidation state)

Monoxide	Reducing agent?	Bonding	Character
CO	Yes - important industrially	covalent	neutral
SiO	Yes	covalent	amphoteric - react with both acids and alkalis
SnO	Yes	some covalent character	With alkali: $\text{PbO}(\text{s}) + 2\text{OH}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Pb}(\text{OH})_4^{2-}(\text{aq})$
PbO	No	ionic	With acid: $\text{PbO}(\text{s}) + 2\text{H}^{+}(\text{aq}) \rightarrow \text{Pb}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Dioxides (+4 oxidation state)

Dioxide	State	Bonding	Structure	Character
CO ₂	gas	covalent	simple molecular	acidic - reacts with aqueous alkalis $\text{CO}_2(\text{g}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
SiO ₂	solid	covalent	macromolecular (Fig 3)	v. weakly acid - reacts with hot concentrated alkalis $\text{SiO}_2(\text{s}) + 2\text{OH}^{-}(\text{l}) \rightarrow \text{SiO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
GeO ₂ SnO ₂ PbO ₂	solid	some ionic character	giant structure	amphoteric - react with both acids and alkalis With alkali: $\text{SnO}_2(\text{s}) + 2\text{OH}^{-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Sn}(\text{OH})_6^{2-}(\text{aq})$ With acid: $\text{SnO}_2(\text{s}) + 4\text{H}^{+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

Fig 3. Structure of silicon dioxide


Acidity of the oxides decreases down the group

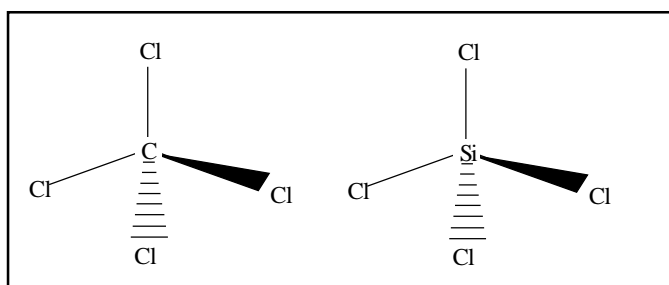
Exam Hint: Candidates must be able to recall suitable equations to demonstrate the amphoteric character of oxides.

Note that **lead(IV) oxide** is an oxidising agent, and will decompose on heating to give lead(II) oxide and oxygen.

Chlorides of Group 4

Element	dichlorides (+2 oxidation state)		tetrachloride (+4 oxidation state)	
	bonding	stability & hydrolysis	bonding	stability & hydrolysis
carbon	covalent	extremely unstable	CCl ₄ and SiCl ₄ have tetrahedral structures (Fig 4) All tetrachlorides covalent liquids with simple molecular structures	unreactive
silicon	covalent	extremely unstable		hydrolyses
germanium	covalent	hydrolyses with oxidation GeCl ₂ (s) + 2H ₂ O(l) → GeO ₂ (s) + 4HCl(aq)		reversible hydrolysis
tin	partially ionic	reversible hydrolysis SnCl ₂ (s) + H ₂ O(l) → SnClOH(s) + HCl(aq)		reversible hydrolysis
lead	ionic	stable, insoluble		unstable, rapidly hydrolysed

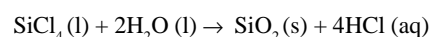
Fig 4. Structure of carbon and silicon tetrachlorides



Note: the dichlorides become increasingly ionic down the group as the "inert pair effect" (page 2) becomes more pronounced.

Exam Hint: Candidates must describe the inert pair effect in full; just saying "because of the inert pair effect" will not gain full marks.

Unlike the other tetrachlorides, CCl₄ will not hydrolyse in water. The reason for this can be seen by examining the mechanism for hydrolysis of SiCl₄. The reaction between silicon tetrachloride and water is:



This reaction can occur because a lone pair of electrons on the oxygen in water is allowed to approach the central silicon atom in SiCl₄ and form a dative bond, starting this reaction.

Tetrachloromethane, CCl₄, does not hydrolyse in water, as carbon is smaller than silicon, causing:

- C - Cl bonds to be shorter than Si - Cl bonds
- C - Cl bonds to be stronger than Si - Cl bonds
- Cl atoms to be more closely packed around central C atom, not allowing water molecule to approach it.
- Carbon, unlike silicon, has no available d - subshell to accept electrons and form a new active bond.

Exam Hint: Explaining the stability of carbon tetrachloride is a common examination question.

Metallic Character in Group 4 - Summary and Explanation

"Metallic character" is judged from a set of properties:

Metals	<ul style="list-style-type: none"> • Good conductors of electricity. • Form ionic compounds by losing electrons to produce positive ions • Form basic oxides.
Non-Metals	<ul style="list-style-type: none"> • Non-conductors of electricity (insulators) except graphite • Form ionic compounds by gaining electrons to produce negative ions, or form covalent compounds • Form acidic oxides.

So metallic character in Group 4 is measured by:

Electrical conductivity - this depends on the structure of the element. With the exception of graphite, conducting solids (as opposed to semiconductors) have a metallic giant structure, with free electrons. Tin and lead are the only group 4 elements with such a structure.

Covalent or ionic nature of compounds. Since +4 compounds are covalent (with the exception of a small number of lead(IV) compounds), the change in metallic character is best shown by examining:

- the relative stability of +2 and +4 compounds
This depends on the "inert pair effect" as described on page 2.
- the ionic or covalent nature of +2 compounds
This depends on ionisation energy, which decreases down the group.

Nature of oxides. Although no Group 4 oxides are basic, a change in character can be seen from acidic to amphoteric - i.e. becoming more basic in character. This is due to the increasingly ionic bonding in the oxides.

Questions

1. Explain the trend in first ionization energies down Group 4.
2. State the two oxidation states exhibited by Group 4 elements in their compounds, and indicate which is the most common.
3. Describe the trend in acidity of the Group 4 oxides.
4. Give examples to show that lead(II) oxide is amphoteric.
5. Use the electronic structure of carbon and silicon to explain why carbon tetrachloride does not hydrolyse.

Answers

1. First ionisation energies decrease going down Group 4. This is due to: increase in atomic radius; less attraction between outer electrons and nucleus; increased shielding effect as more electrons exist between outer electrons and nucleus. Consequently outer electrons are easier to remove from larger atoms such as lead.
2. Oxidation states of group 4 are +2 and +4. +4 is more common.
3. Acidity of the oxides decreases down the group.
4. $\text{PbO}(\text{s}) + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Pb}(\text{OH})_4^{2-}(\text{aq})$
 $\text{PbO}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Pb}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
5. Hydrolysis of SiCl₄ can occur because a lone pair on an oxygen atom in water forms a dative bond to the Si atom. This is possible because Si has the 3d subshell which can accept electrons. The outer electrons of carbon are in the second energy level, which has no d subshell, so the dative bond cannot be formed.

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