GROUP IV (A2)

General.

- electronic configuration ns^2np^2
- metallic properties increases down the group.
- stability of +4 oxidation state decreases down the group – the 'inert pair' effect.

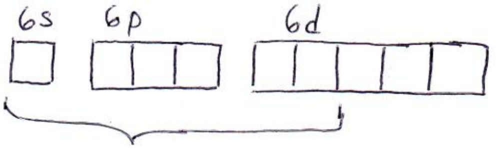
(inert pair effect – two outer s electrons are unwilling to be involved in bonding)

Element	C	Si	Ge	Sn	Pb
atomic no.	6	14	32	50	82
electron config.	$[He]\,2s^2 2p^2$	$[Ne]\,3s^2 3p^2$	$[Ar]\,4s^2 4p^2$	$[Kr]\,5s^2 5p^2$	$[Xe]\,6s^2 6p^2$
atomic radius/nm	0.077	0.177	0.122	0.140	0.154
electronegativity	2.5	1.8	1.8	1.8	1.8
1st I.E. (kJ mol^{-1})	1086	786	760	710	720
description	non-metal	metalloid	metalloid	metal	metal
bonding & structure	giant covalent	giant covalent	giant covalent	metallic	metallic
Tm/°C	3550 (diam)	1410	940	232	328
Tb/°C	4830 (diam)	2680	2830	2690	1751
electrical conductivity	graphite-good diamond-poor	semi-conductor	semi-conductor	good	good

Bonding and Expansion of the Octet.

- Elements of Group IV all have 4 electrons in their outermost electron shell.
- In covalent compounds, all four of these electrons can be used in bonding. Forming 4 covalent bonds, shape of molecule - tetrahedral
- However, all Group IV elements (except carbon). can make more than 4 bonds. This is due to possess of d orbitals. (C - 2 d orbitals not exist)
- Empty d orbitals can be used for dative bonding.
- This allows the elements to hold more than 8 electrons. = Expansion of the octet.
- Egs: octahedral complex ions SiF_6^{2-} and $PbCl_6^{2-}$

Pb^{4+} ion: [Xe]



6 Cl^- ions form 6 dative bonds by using 6 empty orbitals in the outer shell of lead ion.

(catenation - the unique ability of carbon to form stable compounds containing long chains and rings of carbon atoms)

Melting Point of Group IV elements

- down the group, change from giant molecular structure to metallic structure.
- vast number of covalent bonds to be weaken therefore high melting points (giant molecular structure)
- carbon has 2 main allotropes – graphite and diamond. (covered in Topic 4 States of Matter (AS)

  (allotropes are different structural modifications of an element; the atoms of the element are bonded together in a different manner.)
- Silicon and Germanium have diamond-type structure. T_b : Ge < Si < C (diamond). because bond strength decreases C–C > Si–Si > Ge–Ge. due to size of atom increases C < Si < Ge.
- Tin and lead have metallic bonding, metallic bonding is weaker compared to covalent bonding.

(Tin has 2 allotropes
- white tin (metallic)
- grey tin (giant molecular structure – diamond-type structure, only exist at low temperature))

Electrical Conductivity of Group IV elements

- Descending the group IV, electrical conductivity increases
- Diamond is poor conductor because no free electrons (all valence electrons involved in covalent bonds).
- Graphite is good conductor because one electron per carbon atom is not used for bonding and joins delocalised cloud.
- Both Silicon and Germanium (when pure) do not conduct electricity.
- Tin and Lead have a giant metallic structure. A delocalised sea of electrons allows electrical conductivity.

Si and Ge can be made to conduct electricity if doped to make semiconductors.
This properties arises because of the energy difference (or band gap) between the bonding orbitals and the conduction band is small.

Doping is adding a small quantity of similar size atom to the semiconductor, such that the doping atoms fit neatly into the semiconductor structure.

Germanium doped with arsenic (n-type conductor)

- An arsenic atom has one extra electron than a germanium atom.
- This electron occupies a conduction band.
- When a potential difference is applied across the doped germanium, it can conduct electricity.

Germanium doped with gallium (p-type conductor)

- Gallium atom has 1 less electron than germanium, the doped germanium has fewer electrons overall.
- This introduces a positive hole which enable electrons to move through.

Tetrachlorides of Group IV Elements

	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
T_b/°C	77	58	87	114	105 (explodes)
bonding	covalent	covalent	covalent	covalent	covalent
structure	molecular	molecular	molecular	molecular	molecular
shape	tetrahedral	tetrahedral	tetrahedral	tetrahedral	tetrahedral
rxn with water	none	hydrolysed	hydrolysed	hydrolysed	hydrolysed

- Group IV tetrachlorides (except lead) are volatile liquids at room temperature. Simple molecular structure with intermolecular forces Van der Waals (weak)

- T_b compounds increases down the group because molecules become larger (no electrons ↑) and Van der Waals forces become stronger.

- Thermal stability of compounds decreases down the group because :-
  a) the covalent bonds become weaker as the Group IV atom becomes larger.
  b) the inert pair effect makes the +IV oxidation state less stable down the group.

- CCl_4 is very stable to heat.

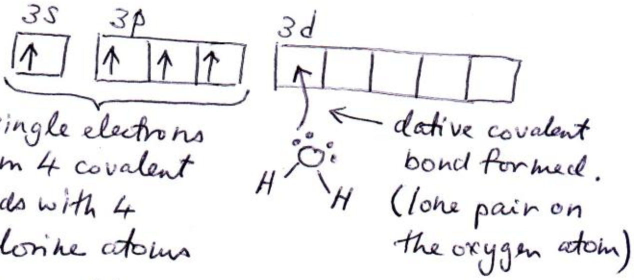
- $PbCl_4$ is a yellow liquid which decomposes when gently heated.

$$\underset{\text{Lead(IV) chloride (yellow liquid)}}{PbCl_{4(l)}} \longrightarrow \underset{\text{Ledd(II) chloride (white solid)}}{PbCl_{2(s)}} + Cl_{2(g)}$$

Reaction of Group IV Tetrachlorides with Water (hydrolysis)

- All Group IV tetrachlorides (except CCl_4) are readily hydrolysed and forming HCl (gives acidic solution).
- These rxns are strongly exothermic and produces white fumes ($HCl_{(g)}$)
- When $SiCl_4$ reacts with water, a water molecule can form a dative bond with the silicon atom by using an empty 3d orbital. (lone pair – oxygen atom of H_2O molecule)
- eg.

Si atom in $SiCl_4$: [Ne]



- Hydrolysis of $SiCl_4$ – the reaction can be regarded to take place in stages:

$$SiCl_4 + H_2O \longrightarrow Si(OH)Cl_3 + HCl$$
$$Si(OH)Cl_3 + H_2O \longrightarrow Si(OH)_2Cl_2 + HCl$$
$$Si(OH)_2Cl_2 + H_2O \longrightarrow Si(OH)_3Cl + HCl$$
$$Si(OH)_3Cl + H_2O \longrightarrow Si(OH)_4 + HCl$$
$$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O$$

Overall, $SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$

CCl_4 does not react with water.

2 reasons for CCl_4 unreactive toward H_2O molecule.

1. The outer shell for carbon atom is shell no 2. There are no 2d orbitals. Lone pair at oxygen atom of water molecule can not form dative covalent bond with C atom. The hydrolysis process cannot be initiated.
2. CCl_4 is the smallest molecule among the Group IV tetrachlorides. The C-Cl bond is the shortest and this makes no room for the H_2O molecule to get close enough to the carbon atom to initiate any reaction.

Group IV Dioxides

	CO_2	SiO_2	GeO_2	SnO_2	PbO_2
Tm/°C	−56	1610	1116	1127	decompose at 300
thermal stability	stable at high T	stable at high T	stable at high T	stable at high T	decomposes
bonding	covalent	covalent	→ increasingly ionic		→
structure	simple molecule	giant molecule	giant structure	giant structure	giant structure
nature	acidic	acidic	amphoteric	amphoteric	amphoteric
solubility in water	slightly soluble	insoluble	insoluble	insoluble	insoluble

Stability of Group IV Dioxides

- The +IV oxidation state becomes less stable down the group.
- Group IV Dioxides are thermally stable (except PbO_2)
- $$\underset{\text{Lead(IV) oxide}}{2PbO_{2(s)}} \xrightarrow{heat} \underset{\text{Lead(II) oxide}}{2PbO_{(s)}} + O_{2(g)}$$
- therefore $PbO_{2(s)}$ is a powerful oxidising agent.
- oxidised [O]
  $$PbO_2 + 2I^- + 4H^+ \longrightarrow Pb^{2+} + I_2 + 2H_2O$$
  reduced [R]

Bonding and structure of Group IV dioxides

- CO_2 is simple molecule. The molecule is non-polar. The intermolecular forces are weak Van der Waals forces. CO_2 sublimes at very low temperatures and is a gas under room conditions.
- SiO_2 has a giant molecular structure. Vast no. of covalent bonds to overcome leads to high T_b.
- ionic character increases down the group as atomic size increases. GeO_2, SnO_2 and PbO_2 have intermediate between giant molecular and ionic structure.

Acid/base nature of Group IV dioxides

- Group IV Dioxides become less acidic when going down the group.
- CO_2 (non-metal oxide) is acidic. It dissolves in water to give a weak acidic solution.
- $$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + H^+_{(aq)}$$
- SiO_2 (non-metal oxide) is acidic. But SiO_2 is insoluble in water.
- SiO_2 dissolves in hot, concentrated alkali:

$$SiO_{2(s)} + 2OH^-_{(aq)} \longrightarrow \underset{\text{silicates.}}{SiO_3^{2-}{}_{(aq)}} + H_2O_{(l)}$$

- GeO_2 is amphoteric and dissolves in both acid and alkali.
  - dissolves in acid

    $$GeO_{2(s)} + 4HCl_{(aq)} \longrightarrow GeCl_{4(aq)} + 2H_2O_{(l)}$$
  - dissolves in alkali

    $$GeO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightleftharpoons [Ge(OH)_6]^{2-}_{(aq)}$$
- Both SnO_2 and PbO_2 are amphoteric and they have similar rxns when disolve in acid and alkali.

Group IV Monoxides

	CO	SiO	GeO	SnO	PbO
T_b/°C	−191				1470
Structure	simple moleculer	simple molecular	→ increasing ionic →		
Nature	acidic oxide	neutral oxide	amphoteric	amphoteric	amphoteric
Thermal Stability	← Readily oxidised to dioxide → ←(SiO, GeO, and SnO revert to dioxide on standing in air)→				Stable

Stability of Group IV Monoxides

- The +II oxidation state gets more stable down the group.
- SiO exist only at high temperature
- CO has triple covalent bond and the molecules is thermally stable.
- CO is a powerful reducing agent.
- SiO and GeO have relatively weak covalent bonding and they decompose on heating in a disproportionation rxn.

  egs. $2GeO_{(s)} \longrightarrow GeO_{2(s)} + Ge_{(s)}$

Acid/base nature of Group IV monoxides

- CO is insoluble in water. However CO reacts with hot concentrated NaOH.
- GeO, SnO & PbO are amphoteric,
- Reacts with concentrated HCl solution (GeO, SnO & PbO react with conc HCl in a similar way).

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

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

- Reacts with $NaOH_{(aq)}$

$$PbO_{(s)} + 2OH^-_{(aq)} \longrightarrow \underset{\text{plumbate(II) ion}}{PbO_2^{2-}{}_{(aq)}} + H_2O_{(l)}$$

GeO and SnO reacts in a similar manner to form germinate(II) and stannate(II) ions.

Relative stability of the +II and +IV oxidation states

- In general, +IV oxidation state stability decreases down the group.
- +II oxidation state stability increases down the group.
- Eg.

		Oxidation state			
		+II	+IV		
increasing stability.	↓	CO	CO_2	↑	increasing stability
		SiO	SiO_2		
		GeO	GeO_2		
		SnO	SnO_2		
		PbO	PbO_2		

- The trend is due to the inert pair effect. An increasing tendency for the two s electrons not to take part in the bonding as the atomic size increases.
- The two p-electrons are lost to form a +2 ion and give the bonding characteristic of a metal.
- CO is a powerful reducing agent,

$$\overset{+3}{Fe_2O_{3(s)}} + \overset{+2}{3CO_{(g)}} \xrightarrow{heat} \overset{0}{2Fe_{(s)}} + \overset{+4}{3CO_{2(g)}}$$

iron(III) oxide   oxidised to +4 (more stable)   Iron

$$\overset{+2}{2CO_{(g)}} + \overset{+2}{2NO_{(g)}} \xrightarrow[\text{at calalytic converter}]{\text{high } T} \overset{0}{N_{2(g)}} + \overset{+4}{2CO_{2(g)}}$$

- At the other end of Group IV, the +II oxidation state in lead compounds is more stable than the +IV state.

- PbO_2 is a powerful oxidising agent,

$$\overset{+4}{Pb}O_{2(s)} + 4H\overset{-1}{Cl}_{(aq)} \longrightarrow \overset{+2}{Pb}Cl_{2(aq)} + \overset{0}{Cl}_{2(g)} + 2H_2O_{(l)}$$

lead(IV) oxide   lead(II) chloride

- $PbCl_4$ is thermally unstable,

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

- Between these extremes, there is a gradual change in stability of the +II compared with the +IV state.

- The +IV state of germanium compounds is more stable than the +II state. Germanium(II) compounds are good reducing agents.

- The +IV state of tin is slightly more stable than the +II state. So tin(II) compounds generally act as weak reducing agent.

Redox reactions in Group IV

- At the top of the group, a compound with the oxidation state of +II can be a good reducing agent because it will tend to be oxidised to +IV.
- At the bottom of the group, a compound with oxidation state of +IV will be a good oxidising agent because it will tend to be reduced to +II
- Eg.

	Oxidation state		
	+IV	+II	
↓	CO_2	CO	↑
better oxidising agent	SiO_2	SiO	better reducing agent.
	GeO_2	GeO	
	SnO_2	SnO	
↓	PbO_2	PbO	

- Oxidation from +II state to +IV state,

$$Fe_2O_3 + 3\overset{+2}{C}O \xrightarrow{[O]} 2Fe + 3\overset{+4}{C}O_2$$

$$\overset{+2}{Sn^{2+}} + I_2 \xrightarrow{[O]} \overset{+4}{Sn^{4+}} + 2I^-$$

$$5\overset{+2}{Sn^{2+}} + 2MnO_4^- + 16H^+ \xrightarrow{[O]} 5\overset{+4}{Sn^{4+}} + 2Mn^{2+} + 8H_2O$$

- Reduction from +IV state to +II state,

$$\overset{+4}{Pb}Cl_4 \xrightarrow{[R]} \overset{+2}{Pb}Cl_2 + Cl_2$$

$$2\overset{+4}{Pb}O_2 \xrightarrow{[R]} 2\overset{+2}{Pb}O + O_2$$

$$\overset{+4}{Pb}O_2 + 4H\overset{-1}{Cl} \xrightarrow{[R]} \overset{+2}{Pb}Cl_2 + \overset{0}{Cl_2} + 2H_2O$$

$E^\ominus$ values of Group IV ions

$$Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)} \qquad E^\ominus = +0.15V$$

$$Pb^{4+}_{(aq)} + 2e^- \rightleftharpoons Pb^{2+}_{(aq)} \qquad E^\ominus = +1.69V$$

- The $E^\ominus$ value for the reduction of lead(IV) is very positive, so it is a favourable reaction.
- Therefore Lead(IV) oxide is a powerful oxidising agent.
- The value for tin(IV) is much lower, so it isn't as good an oxidising agent.

$$Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)} \qquad E^\ominus = -0.14V$$

$$Pb^{2+}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)} \qquad E^\ominus = -0.13V$$

- In general, metals are good reducing agents. Both $E^\ominus$ values are negative, tin and lead tend to oxidise to tin(II) ion and Pb(II) ion respectively.

- Both tin and lead ready to displace hydrogen ion from acids,