GROUP IV

General

- occurs in the middle of the periodic table
- contains metals and non-metals
- metallic properties increase down group
- stability of +4 oxidation state decreases down group - the 'inert pair' effect
- all have the electronic configuration **...** n**s²** n**p²** .

ELEMENTS

	C	Si	Ge	Sn	Pb
atomic number	6	14	32		
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	gaint covalent	giant covalent	giant covalent	metallic	metallic
melting point / °C	3550 (diam)	1410	940	232	328
boiling point / °C	4830 (diam)	2680	2830	2690	1751
electrical conductivity	graphite - good diamond - poor	semiconductor	semiconductor	good	good

TRENDS

Melting Point

General decrease down group	**C**	**Si**	**Ge**	**Sn**	**Pb**
Melting point / °C	*3550*	*1410*	940	232	328

- change from giant molecular to metallic bonding
- many bonds need to be broken to separate the atoms in giant molecules
- the larger the atoms the weaker the covalent bond

Electrical conductivity

C	diamond	poor	no free electrons - all used for bonding
	graphite	good	one electron per carbon is not used for bonding and joins delocalised cloud
Si		semiconductor	
Ge		semiconductor	
Sn		good	metallic bonding - delocalised electron cloud
Pb		good	metallic bonding - delocalised electron cloud

TETRACHLORIDES

	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
boiling point / °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
reaction with water	none	hydrolysed	hydrolysed	hydrolysed	hydrolysed

Bonding Covalency is favoured if the **cation is small** and has a **high charge**... therefore

- all should be covalent - in +4 oxidation state
- CCl_4 should be the most covalent - small size of carbon
- all will be tetrahedral - repulsion between 4 bond pairs of electrons

Hydrolysis

- CCl_4 isn't hydrolysed by water - no available space to accept a lone pair
- remainder are rapidly hydrolysed - not limited to a co-ordination number of 4
  - give an acidic solution due to HCl

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

DIOXIDES

	CO_2	SiO_2	GeO_2	SnO_2	PbO_2
melting point / °C	-56	1610	1116	1127	decomp 300
thermal stability	<——— stable to high temperatures ———>				decomposes
bonding	covalent	covalent	——— increasingly ionic ———>		
structure	molecular	giant molecule	< ——— giant structure ———>		
nature	acidic	acidic	amphoteric	amphoteric	amphoteric
solubility in water	slightly	insoluble	insoluble	insoluble	insoluble

Stability

- All except PbO_2 are thermally stable
- The +4 oxidation state gets less stable down the group

Bonding

- ionic character increases down the group as atomic size increases
- CO_2 is a simple molecule, the rest have giant structures

Acid-base character

CO_2
- **acidic** (non-metal oxide)
- **dissolves in water** to give a weak acidic solution

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

SiO_2
- **acidic** (non-metal oxide)
- insoluble in water
- **dissolves in conc alkali**

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

GeO_2
- **amphoteric**
- dissolves in acid

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

- dissolves in alkal**i**

$$GeO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightleftharpoons [Ge(OH)_6]^{2-}{}_{(aq)}$$

SnO_2, PbO_2
- **amphoteric**
- similar reactions to germanium
- acidic character decreases down the group

MONOXIDES

Stability
- The +2 oxidation state gets more stable down the group
- CO is a powerful reducing agent

Bonding
- ionic character increases down the group as atomic size increases
- CO is a simple molecule

Acid-base character

CO
- **neutral**
- **insoluble in water**

GeO, SnO, PbO
- **amphoteric**
- dissolves in acid

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

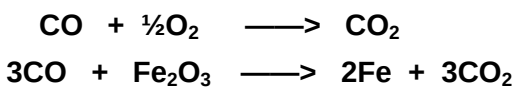
- dissolves in alkal**i**

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

STABILITY OF OXIDATION STATES

General
- +4 oxidation state stability decreases down the group
- +2 oxidation state stability increases down the group
- due to what is called the 'inert pair' effect

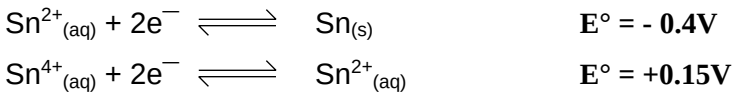
Examples
- CO is a powerful reducing agent

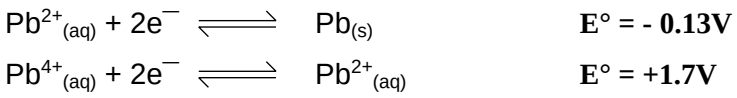


- PbO_2 is a powerful oxidision agent

- $PbCl_4$ is thermally unstable

E° values
- the E° value for the reduction of lead(IV) is very positive so it is a favourable reaction
- the value for tin(IV) is much lower so it isn't as good an oxidising agent





SILICON(IV) OXIDE - SiO_2

Properties Silica based ceramics are
- good electrical insulators
- good thermal insulators
- have great rigidity
- are hard

Uses
- furnace linings
- glasses for solar panels
- power line insulators
- parts of turbines

Q.1 *Why is graphite a better conductor of electricity than diamond or silica?*

Q.2 *What is the shape of the complex ion $[Ge(OH)_6]^{2-}$?*