

ALUMINIUM

Atomic number 13

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^1$

Occurrence

It is found in ores such as bauxite (impure hydrated aluminium oxide), $Al_2O_3 \cdot 2H_2O$ and cryolite (impure sodium hexafluoroaluminate), Na_3AlF_6 . It is found widely in the form of hydrated aluminium silicates in the rocks such as clays, micas and feldspars.

An ore is a naturally occurring substance from which an element is extracted.

EXTRACTION OF ALUMINIUM

Bauxite is the only ore from which it is profitable to extract aluminium. The extraction of aluminium from bauxite involves two stages namely

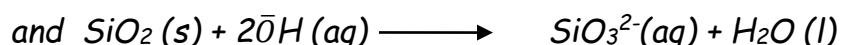
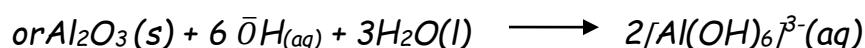
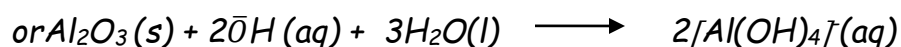
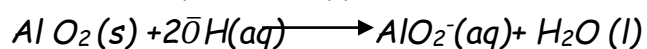
(i) Concentration (purification / dressing) of the ore. This involves removal of impurities from the ore. The main impurities in bauxite are iron(III) oxide, Fe_2O_3 and silicon(IV) oxide (silicon dioxide or silica), SiO_2 .

(ii) Reduction of purified ore to the metal by electrolysis

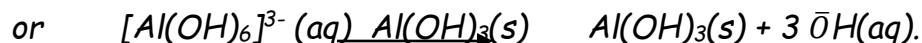
Purification (concentration) of the bauxite

Bauxite is first roasted in air to convert any iron(II) oxide to iron(III) oxide and to remove water from it.

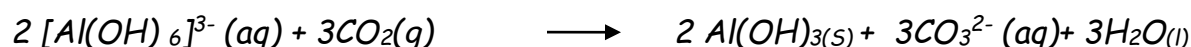
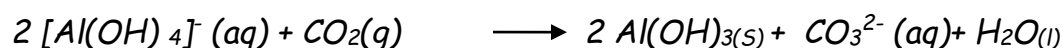
The roasted ore is then pulverized (ground or crushed into a fine powder) and heated with excess concentrated sodium hydroxide solution under pressure. Aluminium oxide and silicon dioxide impurity dissolve in the alkali to form sodium aluminate and sodium silicate in the solution. The iron (III) oxide impurity does not dissolve and so is filtered off.



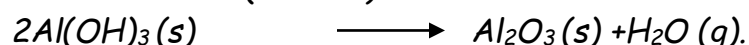
The filtrate which contains sodium aluminate and sodium silicate is then seeded with a little solid pure aluminium hydroxide (ie a little aluminium hydroxide crystals are added to the filtrate) to precipitate out aluminium hydroxide leaving sodium silicate in solution.



Alternatively, aluminium hydroxide may be precipitated by bubbling carbon dioxide gas into the filtrate, leaving the sodium silicate in solution.



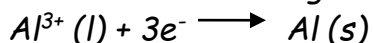
The aluminium hydroxide is filtered off and heated strongly to obtain pure aluminium oxide (alumina).



Reduction of the purified ore to the aluminium by electrolysis.

The pure aluminium oxide is then dissolved in molten cryolite and electrolysed at about 900 °C using graphite electrodes. The purpose of the cryolite is to lower the melting point of aluminium oxide which is very high (2045°C) that the use of the pure molten aluminium oxide as an electrolyte would be very expensive.

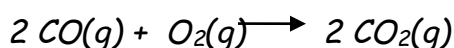
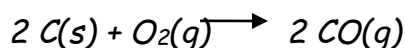
Aluminium ions are discharged at the cathode to form aluminum.



Oxide ions are discharged at anodes to form oxygen gas.



The oxygen burns away (reacts) with the anodes to form oxides of carbon (carbon monoxide and carbon dioxide). Therefore the anodes have to be replaced periodically (from time to time).



Note

1. The extraction of aluminium is only economic where cheap electricity is available from water power i.e. hydro electric power, because the electrolyte process consumes large quantities of electricity.
2. A low voltage is used (about 5V) to avoid decomposing the molten cryolite which acts as solvent and also to lower the rate at which the oxygen reacts with graphite to form oxides of carbon.
3. There is a problem of fluoride pollution in the vicinity of the works due to loss of cryolite.

Revision questions

1. (a) Write the formula of an ore of aluminium
(b) During the extraction of aluminium, the ore is first treated with sodium hydroxide, followed by aluminium hydroxide solution
(i) State the purpose of adding sodium hydroxide solution
(ii) write the equation for the reaction between the ore and sodium hydroxide
(iii) What is the purpose of adding aluminium hydroxide?
(c) Briefly explain how aluminium can be obtained after the ore has been treated as in (b)
(d) Carbon dioxide was used instead of aluminium hydroxide in (b). Write equation of reaction that took place.
2. During the extraction of aluminium from bauxite, the ore is first heated, powdered and then the powdered material is heated with sodium hydroxide solution and finally filtered.
(a) State why the
(i) ore is first heated before changing it to a powder
(ii) powdered ore is heated with sodium hydroxide solution and then filtered.
(b) Write equations of reactions between the powdered ore and sodium hydroxide
Solution
(c) Briefly describe how pure aluminium can be obtained from the products of the reactions in (b) above. (Your answer should include equations)

PHYSICAL PROPERTIES OF ALUMINIUM

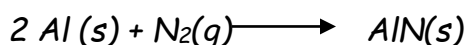
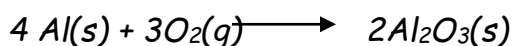
1. It is a silvery white metal
2. It is an excellent conductor of both electricity and heat
3. It has a density of 2.96 gcm^{-3}
4. It is very malleable and ductile so that aluminium sheet (or foil) and wire are easily produced.
5. It melts at 660°C

CHEMICAL PROPERTIES

Reaction with air.

When aluminium is exposed to air, it develops very thin layer (film) of aluminium oxide which prevents further reaction with most chemicals.

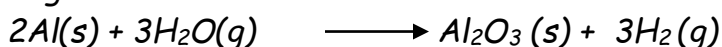
When aluminium is strongly heated in air, it burns brilliantly to form aluminium oxide and aluminium nitride.



Reaction with water.

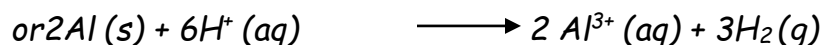
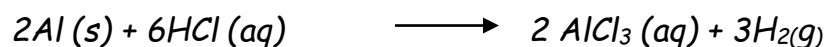
There is no reaction between cold water and aluminium because of the protective film of the oxide that forms at the surface of aluminium.

However strongly heated aluminium reacts with steam to form aluminium oxide and hydrogen.



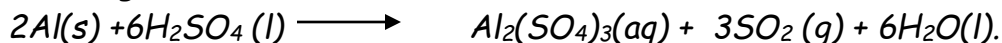
Reaction with acids.

Aluminium reacts slowly with cold dilute hydrochloric acid but more rapidly with hot concentrated hydrochloric acid to form aluminium chloride and hydrogen.



Aluminium does not readily react with dilute sulphuric acid because the oxide film on the aluminium is not soluble in dilute sulphuric acid. However hot concentrated

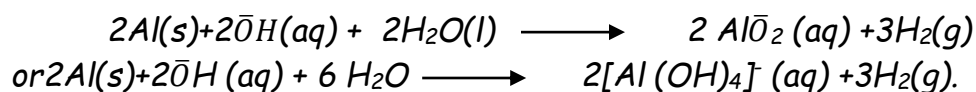
sulphuric acid oxidises aluminium to aluminium sulphate. The acid is reduced to sulphur dioxide gas and water.



Aluminium does not react with nitric acid of any concentration- i.e. nitric acid renders aluminium passive (unreactive) because the acid is an oxidising agent which favours build up (formation) of a protective oxide layer on the surface of aluminium.

Reaction with alkalis

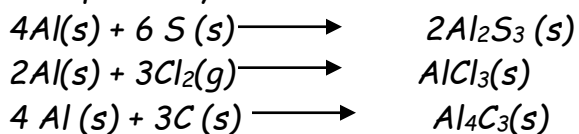
Aluminium reacts with hot concentrated sodium hydroxide solution to form sodium aluminate and hydrogen gas.



Aluminium utensils (e.g. sauce pans) are damaged through corrosion by alkaline solution. This is because the aluminium reacts with alkalis according to the equation above.

Reaction with non-metals.

When strongly heated, aluminium combines directly with oxygen, sulphur, nitrogen, halogens (e.g. chlorine) and carbon to form the oxide, sulphide, nitride, halides and carbide respectively

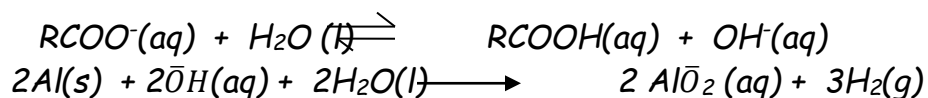


Revision question

1. Discuss the reactions of aluminium with hydrochloric, sulphuric and nitric acid
2. Explain why aluminium utensils should not be washed using soap solution.

Solution

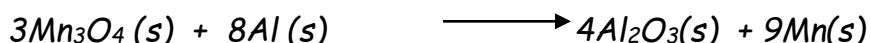
Soap solution undergoes hydrolysis to form an alkaline solution which reacts with (or corrodes) the aluminium utensils hence wearing out the utensils which eventually develop holes hence becoming useless.



USES OF ALUMINIUM

The wide spread use of aluminium is due to a number of physical and chemical properties of the element which make it particularly attractive compared with other metals.

1. Aluminium is used to make overhead tension or electrical cables for conveying electrical power, because of its lower density and good electrical conductivity. (Al is actually lighter and a better conductor than copper making it favourable for overhead electrical cables (power lines))
2. It is used to make domestic cooking utensils such as sauce pans and kettles because of bright appearance, lightness, resistance to attack by solutions used in cooking and the non-poisonous (or non-toxic nature) of aluminium.
3. Making light but strong alloys such as duralumin (Al, Mg, Cu, Fe, Si) and Magnalium (Al, Mg, Ca) used in the construction of aircraft and ships because they are light.
4. Aluminium is used to make door and window frames because it does not corrode (resists corrosion)
5. It is used for handling or holding nitric acid because it is rendered passive by the acid.
6. Aluminium foil is used as packing material for sweets, biscuits, chocolates and cigarettes because it is non-toxic.
7. It is used to make heat exchangers in the chemical, oil and other industries because it is a good conductor of heat.
8. Aluminium is used in roofing to insulate buildings because it is an excellent reflector of radiant energy.
9. It is used as a reducing agent in the extraction of some metals such as chromium, because of its high affinity for oxygen. It will reduce oxides of chromium, iron and manganese on strong heating.





COMPOUNDS OF ALUMINIUM

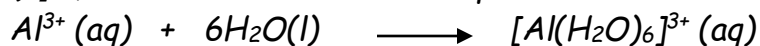
Aluminium forms both ionic and covalent compounds. However its ionization energy is high. Furthermore, the Al^{3+} ion has a very small radius and has a high charge of +3. Therefore its charge density (i.e. the charge-to-radius ratio) is very high compared with other metal ions of period 3.

Cation	Charge	Ionic radius /nm	Charge to radius ratio (charge density)
Na^+	+1	0.095	10.5
Mg^{2+}	+2	0.065	30.8
Al^{3+}	+3	0.050	60.0

Consequently, the Al^{3+} ion is able to strongly polarize most anions -ie its able to distort the electron clouds of anions(especially anions with large radii) to form bond with a high degree of covalent character. This explains why most compounds of aluminium are predominantly covalent.

Aluminium fluoride AlF_3 and aluminium oxide Al_2O_3 are predominantly ionic, however, this is so because the fluoride ion, F^- and oxide ion, O^{2-} have very small ionic radii, so they are weakly polarized by the aluminium ions Al^{3+} resulting into a high degree of ionic character in these compounds. However, the chloride, bromide and iodide of aluminium (AlCl_3 , AlBr_3 and AlI_3) are predominantly covalent, because the chloride, bromide and iodide ions have large radii, so they are strongly polarized by the aluminium ion resulting into a large degree of covalency.

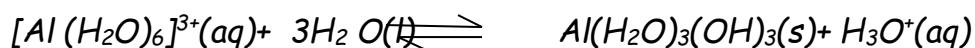
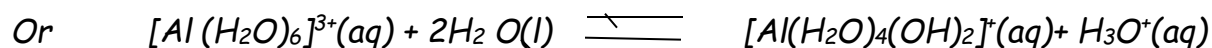
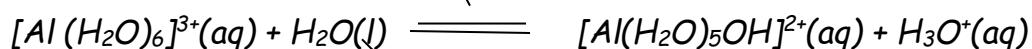
In aqueous solution, the Al^{3+} is stabilized by the coordination of six water molecules or exists as a hydrated ion to form the hexaaquaaluminium(III) complex ion, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, which is octahedral in shape.



Due to the high charge density and high polarizing power of the aluminium ion, it polarizes the lone pair of electrons on the water molecules, releasing hydrogen ions in solution that exist a hydroxonium ions.

The above solution, is acidic -ie is a proton donor and so aqueous solution containing the complex ion are acidic -ie have a PH less than 7.

Explanation: The hexaaquaaluminium ion undergoes hydrolysis to form hydroxonium ions which make the solution acidic.



The hydrolysis of complex ion is due to very small radius and high charge (triple charge) of the central aluminium cation which give it a high charge density so it strongly polarises the coordinated water molecules thus weakening the oxygen-hydrogen bonds so much that other water molecules in solution are able to abstract protons to form hydroxonium ions making the resultant solution acidic.

Revision questions

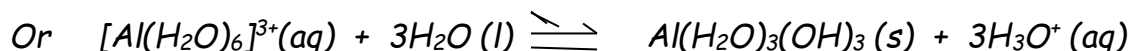
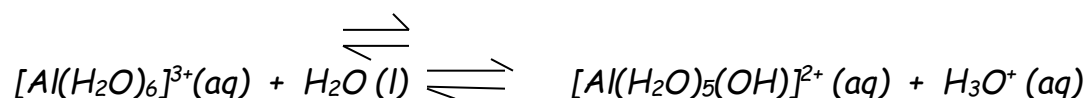
1. Aluminium chloride was dissolved in water and the solution tested with litmus. State what

was observed and explain your answer.

Observation: Blue litmus turned red (or pink).

Explanation: When dissolved in water aluminium sulphate forms hydrated aluminium ions

which undergo hydrolysis to form hydrogen (or hydroxonium ions) which make solution acidic hence turning blue litmus paper red (or pink)



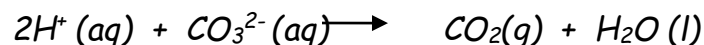
2. Sodium carbonate solution was added to solution an aqueous solution of aluminium nitrate.

(a) State what was observed

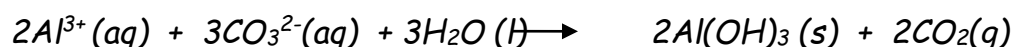
Effervescence (or bubbles) of a colourless gas and a white precipitate

(b) Explain your observation in (a)

Aluminium nitrate solution contains hydrated aluminium ions which undergo hydrolysis to form hydrogen ions (or hydroxonium ions) which react with the carbonate ions in sodium carbonate solution to form carbon dioxide which bubbles out as a colourless gas and insoluble aluminium hydroxide as a white precipitate.



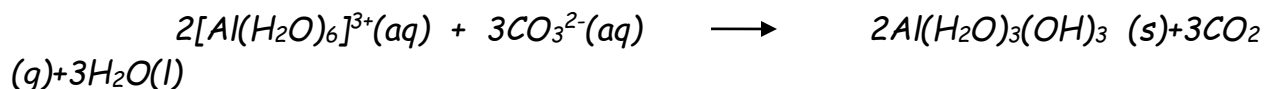
Or: the overall equation below may be given instead of the two equations above.



Alternative equations for reactions.



Or: the overall equation below may be given instead of the two equations above



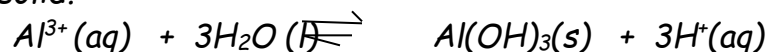
3. Magnesium ribbon was added to an aqueous solution of aluminium chloride solution

(a) State what was observed.

The silvery grey solid (the ribbon) dissolved with effervescence of a colourless gas, and a white solid.

(b) Explain your observation in (a)

The hydrated aluminium ions in aluminium chloride solution undergo hydrolysis to form hydrogen ions which react with magnesium ribbon to form hydrogen gas which bubbles out as a colourless gas and insoluble aluminium hydroxide as a white solid.

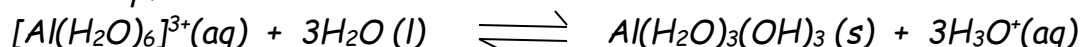




Or: the overall equation below may be written instead of the two equations above.



Alternative equations



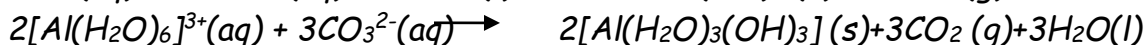
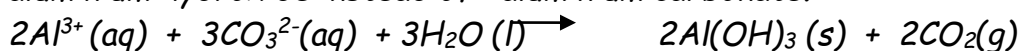
Or: the overall equation below may be written instead of the two equations above.



4. Explain why aluminium carbonate does not exist.

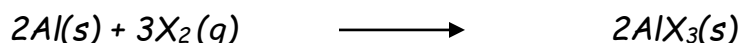
Most metal carbonates are insoluble and so are prepared by precipitation. Therefore the preparation of aluminium carbonate would involve mixing aqueous solutions of a soluble aluminium salt with an aqueous solution of a soluble metal carbonate. However, aqueous solutions of aluminium salts contain hydrated aluminium ions which undergo hydrolysis to form hydrogen ions (or hydroxonium ions) which make the solution acidic.

The hydrogen ions (or hydroxonium ions) would then react with the carbonate ions liberating carbon dioxide and precipitation of insoluble aluminium hydroxide instead of aluminium carbonate.



The halides (AlF_3 , AlCl_3 , AlBr_3 and AlI_3)

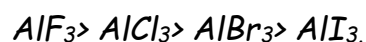
The anhydrous halides are prepared by passing the halogen gas (fluorine and chlorine) or vapour (bromine and iodine) over the heated metal



(X = F, Cl, Br, I)



Aluminium fluoride is predominantly ionic while the rest of the halides are predominantly covalent. The ionic character hence melting point of the aluminium halides decreases in the order;



Explanation

The radius of the halide ions increases from fluoride to iodide ion. Thus the polarisability of the halide ions by the aluminium cation increases from the fluoride to the iodide ion resulting into an increase in covalent character (or decrease in ionic character) from aluminium fluoride to aluminium iodide, hence decrease in melting points of the halides.

The structure and properties of anhydrous AlCl_3 , AlBr_3 , AlI_3 are very similar, but different from those of AlF_3 .

For instance, are covalent solids that dimerise in the gaseous state and readily hydrolysed by water forming aluminium hydroxide and the corresponding hydrogenhalides (hydrogen chloride, hydrogen bromide and hydrogen iodide) which fume in moist air.



Exercise:

1. Explain why aluminium fluoride is ionic while aluminium chloride is covalent.

The fluoride ion has a smaller radius than the chloride ion. The valency (outer most electrons) of the fluoride ion are strongly attracted by the nucleus. Therefore the fluoride ion

is weakly polarized by the aluminium ion, so aluminium fluoride is ionic.

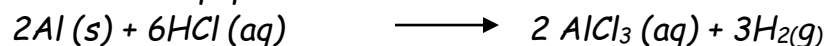
The chloride ion has a bigger ionic radius than the fluoride ion. The valency electrons of the

chloride are weakly attracted by the nucleus thus the chloride ion is strongly polarized by the

aluminium cation. This makes aluminium chloride covalent.

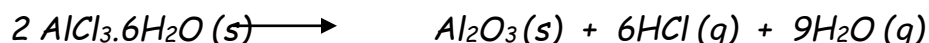
2. (a) Briefly describe how hydrated aluminium chloride $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ can be prepared from aluminium.

Aluminium is reacted with warm concentrated hydrochloric acid. The resultant solution is heated to the point of crystallization and cooled to form crystals of hydrated aluminium chloride. The crystals are filtered, washed with a little cold distilled water and dried by pressing them between filter paper.



(b) State what would be observed when hydrated aluminium chloride is strongly heated and write equation for the reaction that takes place.

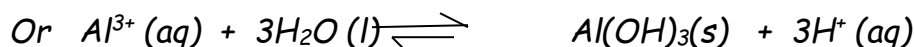
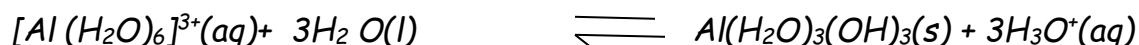
Observation: White (misty) fumes evolved and white crystals turn to a white powder.



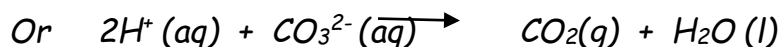
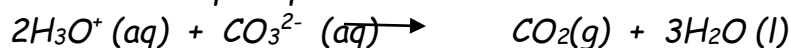
(c) Explain what would be observed when sodium carbonate solution is added to a concentrated solution of aluminium chloride.

Observation: Bubbles (effervescence) of a colourless gas and a white precipitate.

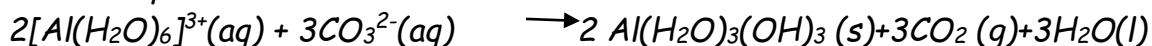
Explanation: Aluminium chloride hydrolyses in aqueous solution forming an acidic solution containing hydroxonium ions (hydrogen ions).

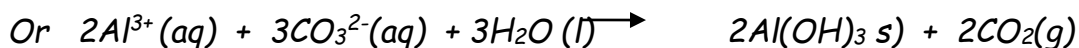


The hydroxonium ions (or hydrogen ions) react with carbonate ions in sodium carbonate solution to form carbondioxide gas and insoluble aluminium hydroxide as a white precipitate.



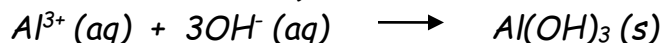
Overall equations of reactions





Aluminium hydroxide

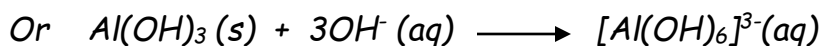
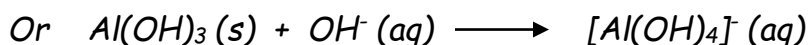
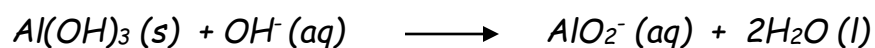
It is formed as a white precipitate when ammonia solution or a little sodium hydroxide solution is added to a solution containing aluminium ions (eg an aqueous solution of soluble aluminium salt).



Aluminium hydroxide is amphoteric. It reacts with mineral dilute acids to form aluminium salts and water



It also reacts with alkalis (sodium hydroxide and potassium hydroxide solutions) to form an aluminate.



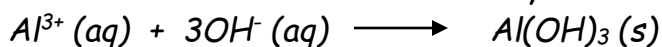
Exercise:

(a) State what would be observed when dilute sodium hydroxide solution is added drop-wise until in excess to aluminium sulphate solution.

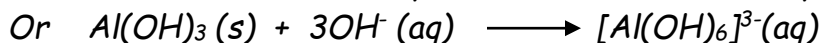
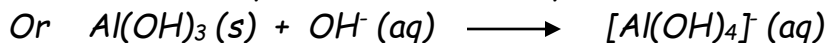
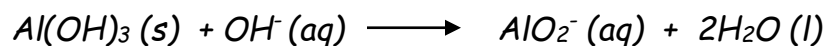
A white precipitate dissolves in excess to form a colourless solution

(b) Explain the observation in (a) above.

Aluminium ions in aluminium sulphate solution react with hydroxide ions in alkali to form insoluble aluminium hydroxide as a white precipitate.

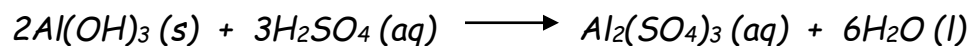


Being amphoteric, aluminium hydroxide reacts with hydroxide ions in the excess alkali to form soluble aluminate ions which are colourless.



Aluminium Sulphate

This is manufactured by reacting aluminium hydroxide or aluminium oxide with hot concentrated sulphuric acid.



And $\text{Al}_2\text{O}_3 (\text{s}) + 3\text{H}_2\text{SO}_4 (\text{aq}) \longrightarrow \text{Al}_2(\text{SO}_4)_3 (\text{aq}) + 3\text{H}_2\text{O} (\text{l})$
 It crystallizes from water with 18 molecules of water of crystallization.

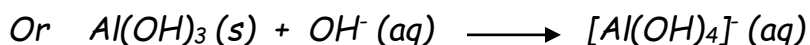
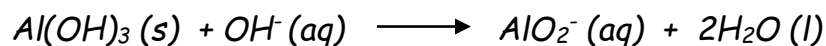
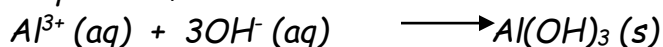
QUALITATIVE ANALYSIS OF ALUMINIUM IONS(Al^{3+}) IN AQUEOUS SOLUTION

1.Reagent: Sodium hydroxide solution (or aqueous sodium hydroxide)

Test: To a solution containing Al^{3+} ions is added sodium hydroxide solution drop-wise until in excess.

Observation: A white precipitate dissolves (soluble) in excess forming a colourless solution

Equations;

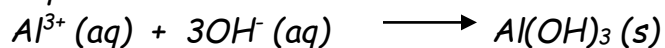


2. Reagent: Ammonia solution (or aqueous ammonia or ammonium hydroxide solution)

Test: To a solution containing Al^{3+} ions is added ammonia solution drop-wise until in excess.

Observation: A white precipitate insoluble in excess.

Equation



3. Reagent: Litmus solution

Test: To a solution containing Al^{3+} ions is added 1-2 drops of litmus solution followed by dilute hydrochloric acid and then ammonia solution until just alkaline.

Observation: A blue lake forms. This confirms presence of Al^{3+} ion

4. Reagent: Alizarin solution

Test: To a solution containing Al^{3+} ions is alizarin solution followed solution followed by ammonia solution until just alkaline.

Observation: A pink lake forms. This also confirms presence of Al^{3+} ion

5 Reagent: Aluminon reagent

Test: To a solution containing Al^{3+} ions is added dilute hydrochloric acid followed by ammonium ethanoate then aluminon reagent.

Observation: A red precipitate forms. This also confirms presence of Al^{3+} ion

GROUP IV ELEMENTS

The elements of group IV are carbon, silicon, germanium, tin and lead.

Element	Symbol	Atomic number	Electronic configuration
Carbon	C	6	$1s^2 2s^2 2p^2$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Tin	Sn	50	$[Kr] 4d^{10} 5s^2 5p^2$
Lead	Pb	82	$[Xe] 4f^{14} 5d^{10} 6s^2 6p^2$

ELECTRONIC CONFIGURATION

All the elements in this group have an outer general electronic configuration of $ns^2 np^2$.

OXIDATION STATES

All group (IV) elements have an outer general electronic configuration of $ns^2 np^2$. The elements have two oxidation states in their compounds - i.e. the +2 and +4 oxidation states. The +2 oxidation state corresponds to loss of two electrons in p-orbitals of the outermost energy level to form a divalent cation M^{2+} . The +4 state corresponds to the formation of four covalent bonds after promotion of an s-orbital electron into a p-orbital in the outermost energy level, and the formation of four sp^3 hybrid orbitals.

However, the stability of the +2 oxidation state increases down the group (from carbon to lead) while the stability of the +4 oxidation state decreases down the group.

The increase in stability of the +2 oxidation state down the group is due to inert pair effect -ie the inability of a pair of electrons in s-orbitals of the outermost energy level to take part in bonding.

The inert pair effect increase down group(IV) elements because from one element to the 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-orbital electrons to shield the outer most s-orbital electrons from the increasing nuclear charge

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

Thus, in carbon, silicon, germanium and tin compounds, the +4 oxidation state is very stable relative to the +2 oxidation state. Thus compounds of C, Si, Ge and Sn in +2 oxidation state behave as reducing agents, getting oxidized to compounds in the more stable +4 oxidation state.

However, the +2 oxidation state in lead compounds is more stable than the +4 state. Therefore, lead (IV) compounds behave as oxidizing agents getting reduced to the more stable lead (II) compounds.

Exercise

1.(a) (i) State the common oxidation states shown by elements in Group IV of the Periodic Table

+2 and +4

(ii) State how the stability of the oxidation states of group IV elements vary down the group (Illustrate your answer with chlorides of carbon and lead)

The +2 oxidation state becomes more stable down the group where as the +4 oxidation state becomes less stable down the group.

Lead(IV) chloride decomposes at room temperature to lead(II) chloride and chlorine



However, carbon tetrachloride is very stable at room temperature.

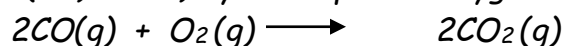
(c) Give a reason for your answer in (a) (ii)

As the radius of the atoms increases down the group, there is increasing tendency for the two bonding electrons in the *s*-sub-energy level in the outermost energy level to resist taking part in bonding a phenomenon referred to as inert pair effect.

2. (a) State two important oxidation states exhibited by group(IV) elements +2 and +4
- (b) Describe how the stability of the two oxidation states varies from carbon to lead. Use the oxides to illustrate your answer

Stability of the +2 state increases from carbon to lead, while stability of +4 oxidation state decreases from carbon to lead

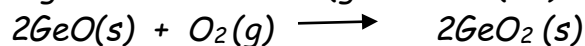
The monoxides of carbon, silicon, germanium and tin are unstable. Carbon monoxide (carbon(II) oxide) is readily oxidized to carbon dioxide (carbon(IV) oxide) by atmospheric oxygen



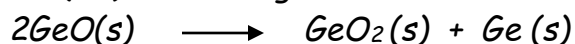
Silicon monoxide (silicon(II) oxide) disproportionates at room temperature to silicon dioxide (silicon(IV)oxide) and silicon.



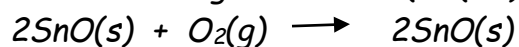
Germanium monoxide (germanium(II) oxide) is readily oxidized when heated in air to germanium dioxide (germanium(IV) oxide)



It also disproportionate when heated out of contact with air to germanium(IV)oxide and germanium.



Tin monoxide (tin(II)oxide) oxidizes rapidly if exposed to air at room temperature forming tin dioxide (tin(IV) oxide)



The dioxides of carbon, silicon, germanium and tin are more stable than the monoxides.

Lead dioxide (lead(IV) oxide) is **unstable**, decomposing on heating to form the more stable lead monoxide (lead(II) oxide) and oxygen gas.



Lead(IV)oxide is an **oxidizing agent**. For instance it oxidizes hot concentrated hydrochloric acid to chlorine and is itself reduced to the more stable lead(II) chloride



3. Explain each of the following statements

(a) The stability of the +2 oxidation state increases down group IV elements

Stability of the +2 oxidation state increases down the group due to **inert pair effect**-ie the inability of a pair of electrons in s-orbitals of the outermost energy level to take part in bonding. The inert pair effect increases down group(IV) elements because from one element to the 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-orbital electrons to shield the outer most s-orbital electrons from the increasing nuclear charge increases. The s-orbitals which are spherical in shape tend to penetrate and enter the atomic core, rendering the s-orbital electrons less available for bonding

(b) Carbon dioxide is more stable than carbon monoxide at room temperature.

(c) Carbon dioxide is more stable than lead(IV) oxide.

BONDING AND STRUCTURE

Carbon has giant covalent (or giant molecular) structures in its two crystalline allotropes - diamond and graphite

Structure of diamond (from o-level chemistry)

In diamond, each carbon atom is covalently bonded to four other atoms in a tetrahedral arrangement. The network of the strong covalent bonds continues in this way with an infinite number of carbon atoms giving rise to a three-dimensional giant molecular structure (or giant covalent structure).

Diamond does not conduct electricity because all the four valency electrons of each carbon atom in diamond are used to form covalent bonds leaving no delocalized electrons.

Diamond is extremely hard because of the strength and uniformity of the bonding. There are no planes of weakness in the crystal structure of diamond. For instance there are no weak van der Waals forces

Structure of graphite. (from o-level chemistry)

A graphite crystal consists of layers of hexagonal rings of carbon atoms. Each layer is a giant molecule in two dimensions only. Each carbon atom is at corner of a regular hexagon, bonded covalently to three other atoms in the same plane. The layers are held together by relatively weak van der Waals forces of attraction.

Graphite conducts electricity because each carbon atom in the layer uses three of its four valency electrons to form three covalent bonds with other carbon atoms, leaving one electron which is delocalized within the layer. It is these delocalised electrons that aid conduction of electricity.

Graphite is soft and slippery (greasy) because of the weak van der Waals forces between the layers which enable the layers to slide (slip) over each other easily.

Silicon and germanium are non- allotropic and both adopt giant molecular structures similar to that of diamond.

The most common allotrope of tin is white tin. It has a giant metallic structure - with its atoms held by metallic bonds. The structure is a distorted cubic close-packed arrangement in which each atom is surrounded by 12 near-neighbouring atoms.

Lead is non-allotropic and adopts a giant metallic structure with a regular cubic-close packed structure.

ATOMIC AND PHYSICAL PROPERTIES OF GROUP IV ELEMENTS

Element	C	Si	Ge	Sn	Pb
Atomic radius(nm)	0.077	0.117	0.122	0.142	0.154
Melting point($^{\circ}\text{C}$)	3730	1410	937	232	327
Boiling point($^{\circ}\text{C}$)	4830	2680	2830	2270	1730
1 st IE(KJmol ⁻¹)	1086	786	760	708	715
2 nd IE (KJmol ⁻¹)	2352	1577	1537	1411	1452
Electronegativity	2.5	1.8	1.8	1.8	1.0
Type of structure	Giant molecular	Giant molecular	Giant molecular	Giant metallic	Giant metallic

Atomic radius

Generally atomic radius increases down the group, because the increase in screening effect due to addition of extra energy levels of electrons outweighs the increase in nuclear charge due to addition of protons to atomic nuclei of the elements. Thus the effective nuclear charge decreases leading to decrease in nuclear attraction for the outermost electrons hence increase in atomic radius.

However, the increase in atomic size from silicon to germanium is less than expected because germanium has a full inner 3d sub-energy level of electrons which poorly shield the the valency electrons from the nuclear charge. Consequently the valence electrons experience a stronger nuclear attraction than expected resulting into slight increase in atomic radius from silicon to germanium. In a similar way, the small increase in atomic radius between tin and lead is because of the filling of the inner 4f sub-energy level of electrons in lead which are poorest at shielding the valency electrons from the nuclear attraction.

Melting and boiling points

Generally, the melting points decrease down the group. This is because down the group, atomic radius increases and so covalent bonds between atoms of elements carbon, silicon and germanium increasingly become longer and weaker such that the energy required breaking them for melting to occur also decreases.

Increase in atomic radius through metallic elements tin and lead results into decrease in nuclear attraction for the delocalized electrons (ie decrease in strength of metallic lattice) hence decrease in amount of energy required to break the metallic bonds.

The low value of tin's melting point compared with lead is due to tin forming a distorted cubic close-packed structure in which the metallic bond is weaker than in the regular cubic close-packed structure of lead.

Ionisation energies

Generally the ionization energies decrease down the group because the increase in shielding effect due to addition of extra energy levels of electrons outweighs the increasing nuclear charge due to addition of protons to atomic nuclei. This leads to decrease in effective nuclear charge, hence decrease in nuclear attraction for the outermost electron, so the energy required removing it decreases.

However, there is little decrease in ionization energies from silicon to germanium and tin to lead due to filling up of d- and f-orbitals with electrons which poorly (weakly) shield the valency electrons from the nuclear charge.

Electrical conductivity

Carbon diamond does not conduct electricity because there are no delocalized electrons in it, since all the four valency electrons per carbon atom are used to form covalent bonds.

In carbon graphite, only three out of the four valency electrons are used by each carbon atom to form three covalent bonds. The fourth electron is delocalized over all carbon atoms in the layer. It is these delocalized electrons which aid conduction of electricity in graphite.

Silicon and germanium are semi-conductors in which a few of the valency electrons in the atoms gain enough energy to become delocalized and so their conductivity increases with increase in temperature.

Tin and lead are metals which have delocalized electrons in their crystals which enable them to conduct electricity.

Metallic and non-metallic character

Carbon is non-metal, silicon and germanium are semi-metals while tin and lead are metals.

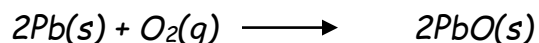
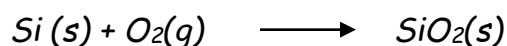
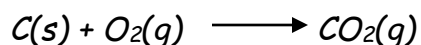
Thus, the metallic nature (character) increases down the group. This is because atomic radius increases down the group. Therefore, the nuclear attraction for the outermost electron decreases hence the tendency for atoms to lose electrons increases down the group.

CHEMICAL PROPERTIES OF GROUP IV ELEMENTS

The chemical reactivity of the elements generally increases down the group from carbon to lead.

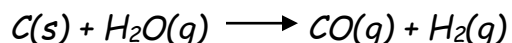
Reaction with air

When heated in air, all the elements react with oxygen in air to form dioxides except lead which forms a monoxide.



Reaction with water

Heated carbon reacts with steam to form carbon monoxide and hydrogen.



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

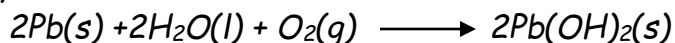


Germanium does not react with water or steam.

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



Lead reacts very slowly with soft water containing dissolved oxygen to form lead (II) hydroxide.

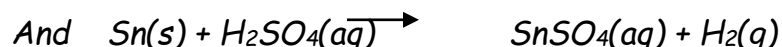
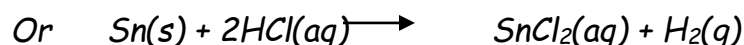


Reaction with mineral acid

(a) Reaction with dilute acid

Carbon, silicon and germanium do not react with dilute mineral acids .

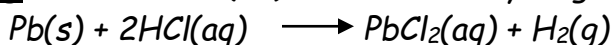
Tin slowly reacts with dilute hydrochloric acid and dilute sulphuric acid (non-oxidising acids) to form tin(II) salts (ie tin(II) chloride and tin(II) sulphate) and hydrogen gas..



Tin is slowly oxidized by dilute nitric acid to tin(II) nitrate. The acid is reduced ammonium nitrate and water.

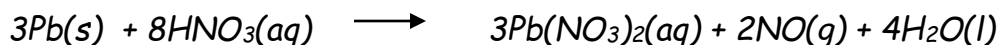


Lead is rendered passive by cold dilute hydrochloric acid due to formation of insoluble lead(II) chloride. However, lead reacts with dilute hydrochloric acid on heating to form lead (II) chloride and hydrogen gas.



Lead is rendered passive by dilute sulphuric acid due to formation of insoluble lead (II) sulphate.

Lead is readily oxidized by dilute nitric to lead(II) nitrate while the acid is reduced nitrogen monoxide and water.



(b) Reaction with concentrated acids

Carbon is oxidized by hot concentrated sulphuric acid to carbondioxide. The acid is reduced to sulphurdioxide and water.



Carbon is oxidized by hot concentrated nitric acid to carbondioxide. The acid is then reduced to nitrogen dioxide and water.



Silicon does not react with concentrated acids except hot concentrated hydrofluoric acid to form hexafluorosilicic acid and hydrogen gas.



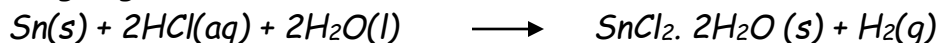
Germanium is oxidized by hot concentrated sulphuric acid to germanium(IV) oxide. The acid is reduced to sulphurdioxide and water.



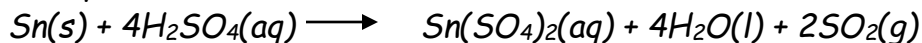
Germanium is also oxidized by hot concentrated nitric acid to form germanium (IV) oxide. The acid is reduced to nitrogen dioxide and water.



Tin reacts with concentrated hydrochloric acid to form hydrated tin (II) chloride and hydrogen gas.



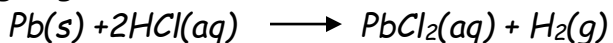
Tin is oxidized by hot concentrated sulphuric acid to tin(IV) sulphate. The acid is reduced sulphur dioxide and water



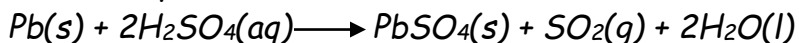
Tin is oxidized by hot concentrated nitric to tin(IV) oxide. The acid is reduced to nitrogen dioxide and water.



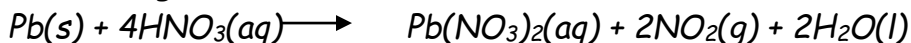
Lead reacts with hot concentrated hydrochloric acid to form lead (II) chloride and hydrogen gas.



Lead is oxidized by hot concentrated sulphuric acid to lead (II) sulphate. The acid is reduced to sulphurdioxide and water .



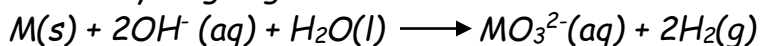
Lead is oxidized by hot concentrated nitric to lead (II) nitrate. The acid is reduced to nitrogen dioxide and water.



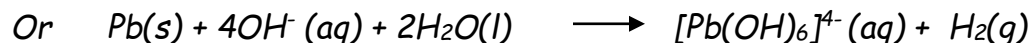
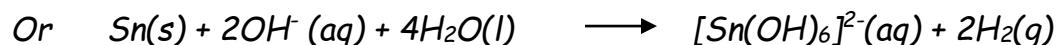
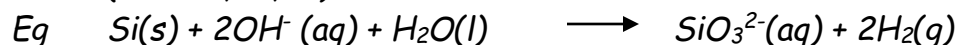
Reaction with alkalis;

Carbon does not react with alkalis.

Silicon, germanium, tin and lead reacts with hot concentrated sodium hydroxide solution to form a silicate, germanate, stannate and plumbate respectively with liberation of hydrogen gas.



(M = Si, Ge, Sn)



COMPOUNDS OF GROUP IV ELEMENTS

THE OXIDES

The Group (IV) elements form monoxides in which the elements have an oxidation state of +2 and dioxides in which their oxidation state is +4. The ability to form stable dioxides decreases down the group where as the ability to form stable monoxides increases.

(a) The Monoxides (MO)

Appearance

Carbon monoxide (carbon(II) oxide), CO is a colourless and poisonous gas

Silicon monoxide (silicon(II) oxide), SiO is a brown powder

Germanium monoxide (germanium(II) oxide), GeO is yellow solid when hydrated and black powder when anhydrous

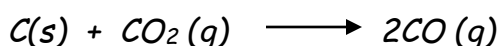
Tin monoxide (tin(II) oxide) SnO is dark grey or brown powder

Lead(II) oxide, PbO is a yellow solid when cold and brown (or reddish-brown) solid when hot.

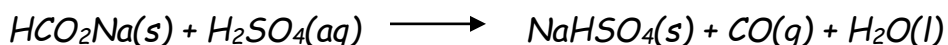
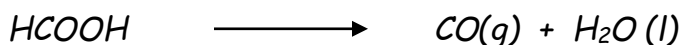
Preparation

Carbon monoxide is prepared by passing carbon dioxide over red hot carbon (coke).

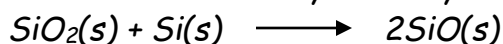
The carbon reduces the carbon dioxide to carbon monoxide.



It can also be made by heating concentrated sulphuric acid with methanoic acid, sodium methanoate or sodium oxalate (also called sodium ethanedioate)



Silicon monoxide is made by made by the strong heating silicon dioxide with silicon.

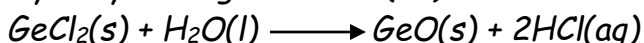


Germanium monoxide can be prepared by:

(a) Strong heating of germanium dioxide with germanium



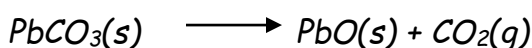
(b) Hydrolysis of germanium (II) chloride



Tin monoxide is most easily made by heating tin(II) oxalate out of contact with air.



Lead (II) oxide is prepared heating the hydroxide, nitrate or carbonate of the metal.



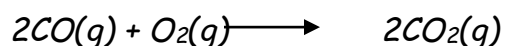
Bonding and structure in monoxides

Oxide	CO	SiO	GeO	SnO	PbO
Bonding	Covalent	Covalent	Ionic	Ionic	Ionic
structure	Simple molecular	Simple molecular	Giant ionic	Giant ionic	Giant ionic

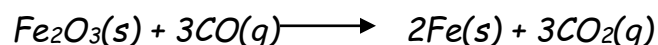
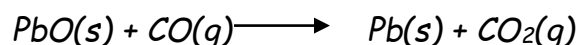
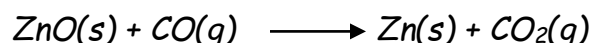
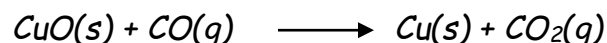
Stability of the monoxides.

The stability of the monoxides of group IV elements increases from carbon monoxide to lead monoxide because of increase in the stability of the +2 oxidation state down the group.

Carbon monoxide is very unstable. It is readily oxidized by oxygen in air to form carbon dioxide.



It is a reducing agent. It can reduce hot (heated) oxides copper, zinc, lead and iron and is itself oxidized to carbon dioxide.

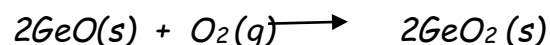


Thus carbon monoxide is used in the extraction of less reactive metals like iron and zinc from their respective ores.

Silicon monoxide is **unstable and disproportionates** at room temperature to silicon(IV)oxide and silicon



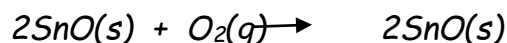
Germanium monoxide oxide readily oxidized when heated in air to germanium(IV) oxide



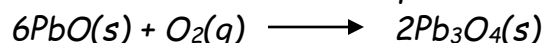
It also disproportionate when heated out of contact with air to germanium(IV)oxide and germanium.



Tin(II)oxide oxidizes rapidly if exposed to air at room temperature forming tin(IV) oxide

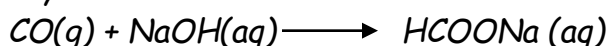


Lead(II) oxide is stable at room temperature. When it is heated very strongly in air , it oxidizes further to form a red powder of trileadtetraoxide



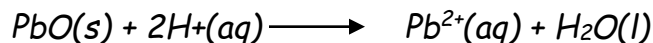
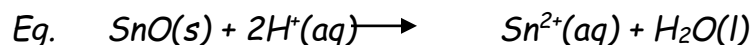
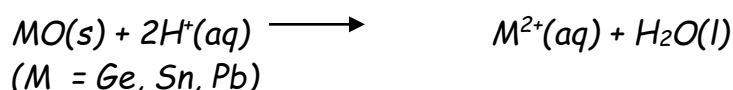
Acid -base properties of the monoxides

Carbon monoxide is very slightly acidic because it reacts with hot concentrated sodium hydroxide solution to form sodium methanoate.

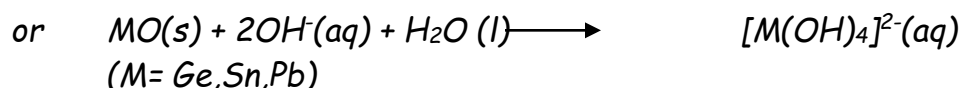
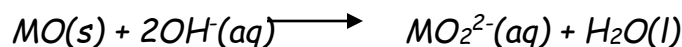


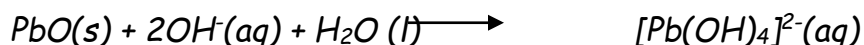
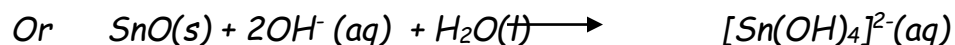
Silicon monoxide is a neutral oxide.

GeO , SnO and PbO are all amphoteric (becoming more basic in passing down the group, although without ever losing their acidic character completely). They react with acids to form salts and water.



They react with alkalis such as sodium hydroxide solution to form a germanate, stannate and plumbate respectively.





(b) **The Dioxides (MO_2)**

Appearance

Carbon dioxide (carbon(IV) oxide) CO_2 is a colourless gas

Silicon dioxide (silicon(IV) oxide) SiO_2 is a white crystalline solid

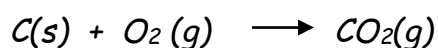
Germanium dioxide (germanium(IV) oxide) GeO_2 is a white crystalline solid

Tin dioxide (tin(IV)oxide) SnO_2 is a white solid

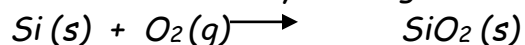
Lead dioxide (lead(IV)oxide) PbO_2 is a dark brown solid

Preparation

Carbon dioxide is made by action of a dilute mineral acid on a carbonate or by heating carbon strongly in excess air, or by heating carbonates other than group(I) metal carbonates

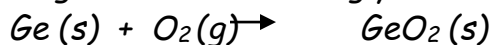


Silicon dioxide is made by heating silicon strongly in air

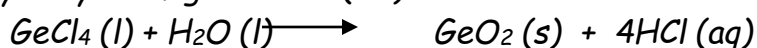


Germanium dioxide is made by:

(i) Heating the element strongly in air



(ii) Hydrolysis of germanium(IV) chloride

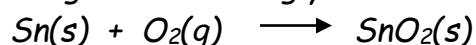


(iii) Heating germanium with concentrated nitric acid.



Tin dioxide can be made by:

(i) Heating the tin strongly in air

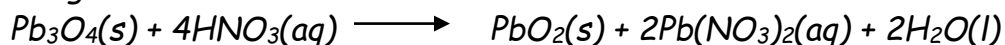


(ii) Heating tin with concentrated nitric acid

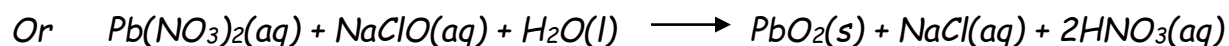
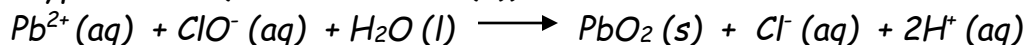


Lead dioxide can be made by

(i) heating trilead tetraoxide with dilute nitric acid.



(ii) Warming a soluble lead(II) salt solution (eg. lead(II) nitrate solution) with sodium hypochlorite (sodium chlorate(I)) solution.



Exercise

(a) State what would be observed when lead(II) ethanoate solution is warmed with sodium hypochlorite solution.

A brown precipitate

(b) Explain your observation in (a) above.

The hypochlorite ions in sodium hypochlorite solution oxidized lead(II) ions in lead(II) ethanoate solution to insoluble lead(IV) oxide as a black precipitate. The hypochlorite ions are reduced to chloride ions.

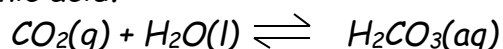


Bonding and structure

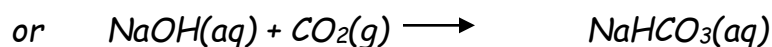
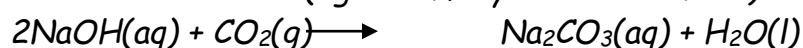
Oxide	CO ₂	SiO ₂	GeO ₂	SnO ₂	PbO ₂
Bonding	Covalent	covalent	Covalent	ionic	ionic
structure	Simple molecular	Giant molecular	Giant molecular	Giant ionic	Giant ionic

The acid-base nature of the dioxides

Carbon dioxide is acidic. It reacts with water to form weakly acidic solution of carbonic acid.



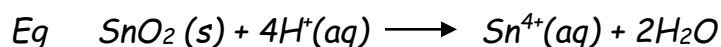
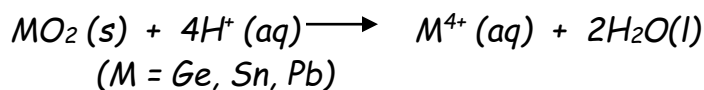
It also reacts with alkalis (eg sodium hydroxide solution) to form a salt and water



Silicon dioxide is also acidic reacting with hot concentrated sodium hydroxide solution to form sodium silicate and water.



The dioxides of germanium, tin and lead are amphoteric in nature. They react with acids to form a salt and water.



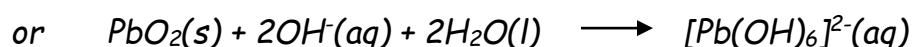
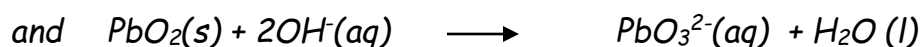
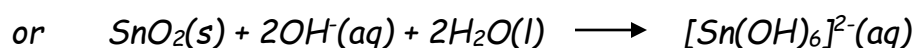
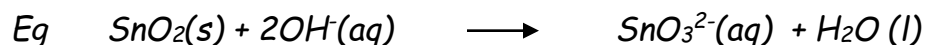
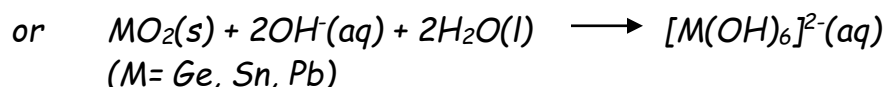
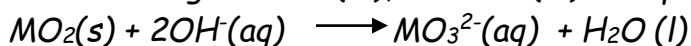
Lead(IV) oxide reacts oxidises hot concentrated hydrochloric acid to chlorine and itself reduced to lead(II) chloride and water.



Lead(IV) oxide reacts with cold concentrated hydrochloric acid (at 0°C) to form lead(IV) chloride (a yellow liquid) and water.



The dioxides of Ge, Sn and Pb also react with hot concentrated sodium hydroxide solution to form a germanate(iv), stannate(iv) and plumbate(iv) salt respectively.



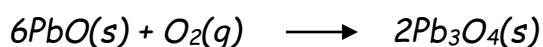
Thermal stability of the dioxides.

The stability of the dioxides of group IV elements decreases from carbon dioxide to lead dioxide because of decrease in the stability of the +4 oxidation state down the group.

The dioxides of C, Si, Ge and Sn are stable even at high temperatures. Lead (IV) oxide however, decomposes on warming to form the more stable lead (II) oxide with liberation of oxygen.

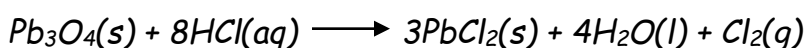


Tri-lead tetra-oxide (also called di-lead(II) lead(IV) oxide or red lead oxide) Pb_3O_4
Tri-lead tetra-oxide (also called dilead(II) lead(IV) oxide or red lead oxide) is a red powder made by heating lead(II) oxide in air at about $400^\circ C$. It is a mixed oxide.

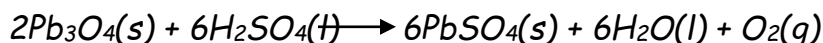


It is a mixed oxide which resembles lead(IV) oxide in some of its chemical properties as explained below.

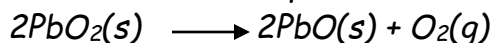
(a) Both oxides oxidize hot concentrated hydrochloric acid to chlorine, themselves being reduced to lead(II) chloride and water.



- (b) Both oxides react with hot concentrated sulphuric acid to form lead(II) sulphate, oxygen gas and water.



- (c) Both oxides decompose on heating to form lead(II) oxide and oxygen gas.



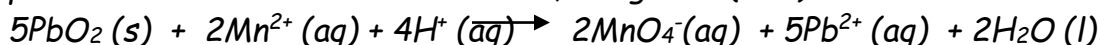
Lead (IV) oxide as an oxidizing agent

1. Lead(IV) oxide oxidizes the hot concentrated hydrochloric acid to chlorine and it's reduced to lead(II) chloride and water.



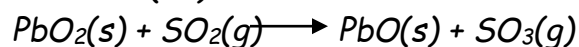
Observation: The brown solid dissolves with effervescence (bubbles) of a greenish-yellow gas to form a colorless solution..

2. lead(IV) oxide oxidized hot manganese(II) salts in aqueous solution in presence of concentrated nitric acid, manganate(VII) ions.

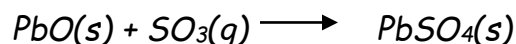


Observation: A purple solution forms.

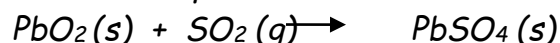
3. Hot lead(IV) oxide oxidizes sulphur dioxide to sulphur trioxide and it's self is reduced to lead(II) oxide.



The lead(II) oxide and sulphur trioxide then react to form lead(II) sulphate.



Thus the overall equation of reaction is



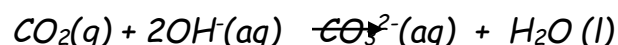
Observation: Brown solid turns into a white solid.

Exercise

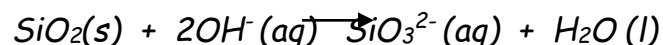
1. Using carbon dioxide, silicon(IV) oxide and lead(IV) oxide to illustrate your answer, explain the trend in the acidic nature of oxides of the group(IV) elements.

The acidic nature of the oxide decreases from carbon dioxide to lead(IV) oxide. Carbon dioxide and silicon(IV)oxide are acidic while lead(IV) oxide is amphoteric.

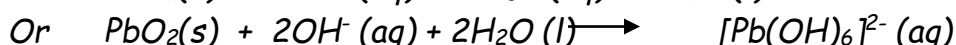
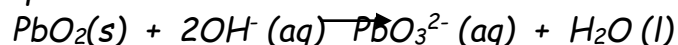
Carbondioxide reacts with sodium hydroxide solution to form sodium carbonate and water.



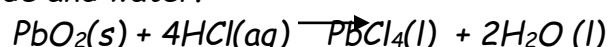
Silicon(IV)reacts with hot concentrated sodium hydroxide solution to form a silicate and water.



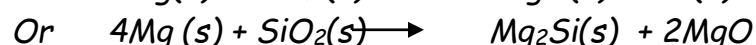
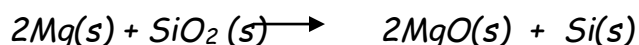
Lead(IV) oxide reacts with hot concentrated sodium hydroxide solution to form a plumbate and water.



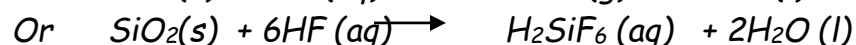
It also reacts with cold concentrated hydrochloric acid to form lead(IV) chloride and water.



2. Write equation(s) for the reaction between silicon(IV) oxide and
(i) magnesium



- (ii) hydrofluoric acid



3. Explain why carbon dioxide is a gas at room temperature while silicon dioxide is a solid with a very high melting point.

Carbon is very electronegative and has a very small atomic radius. Therefore carbon is capable of forming strong double bonds with oxygen to form discrete molecules carbon dioxide at room temperature with weak van der Waals of attraction of attraction between the molecules hence gaseous.

Silicon has a lower electronegativity and a larger atomic radius hence cannot form multiple (double) bonds with oxygen but forms single silicon-oxygen bonds with each silicon atom bonded to four oxygen atoms in a three-dimensional giant covalent structure which is strong, hence silicon dioxide is a solid with a high melting point.

4 (a) When red lead oxide Pb_3O_4 was reacted with nitric acid a solid was formed. Write

the equation for the reaction

(b) The mixture from (a) was filtered and the residue warmed with concentrated

hydrochloric acid. State what was observed. Explain your answer.

(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.

(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

THE CHLORIDES

The elements form two types of chlorides i.e the tetrachlorides MCl_4 in which the group IV elements are in the +4 oxidation state and the dichlorides, MCl_2 in which the elements are in the +2 oxidation state.

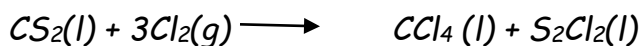
(a) The tetrachlorides (MCl_4)

Appearance

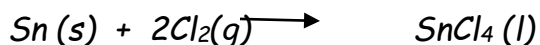
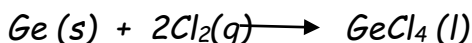
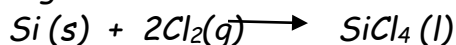
The tetrachlorides of carbon, silicon, tin and germanium are colourless liquids but lead tetrachloride (or lead(IV) chloride) is a yellow liquid.

Preparation

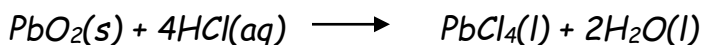
Carbon tetrachloride is prepared by passing chlorine gas through carbon disulphide.



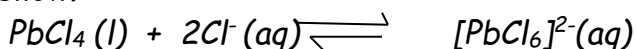
The tetrachlorides of Si, Sn and Ge can be prepared by heating the elements in dry chlorine gas.



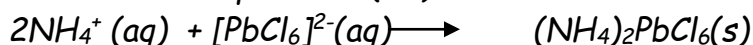
Lead (IV) chloride is prepared by reacting lead (IV) oxide with cold concentrated hydrochloric acid at 0°C.



However if the acid is in excess, some of the lead(IV) chloride reacts with chloride ions in excess the acid to form the hexachloroplumbate(IV) complex ion which is also yellow.



Addition of a concentrated solution of ammonium chloride to the solution containing the above complex ions gives an immediate pale yellow precipitate of ammonium hexachloroplumbate(IV)



When this solid is treated with concentrated sulphuric acid at about 0°C, lead(IV) chloride is formed as a yellow liquid.



Exercise

9.12g of an inorganic compound X contains 0.5g of nitrogen, 0.16g hydrogen, 4.14g of lead and 4.2g of chlorine. Given that 9.12g of X contains 0.02 moles at s.t.p

(a) Determine the molecular formula of X

(b) X is an ionic compound containing a complex anion of lead and a simple cation.

Name

(i) compound X

(ii) complex anion of lead in X

(c) The complex anion in b(ii) above can be prepared from lead(IV) oxide and hydrochloric acid.

(i) State the conditions for the reaction leading to the formation of the anion.

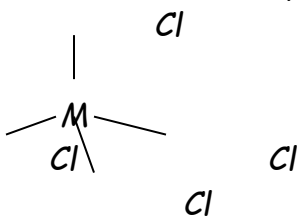
(ii) Write the formula and give the IUPAC name of any other complex ion formed by

lead in the same oxidation state as the anion in b(ii) above.

Bonding and structure of the tetrachlorides

The bonding in the tetrachlorides is covalent. They all have a simple molecular structure with weak van der Waals' forces of attraction binding molecules together. Therefore, all of them are volatile liquids at room temperature.

The individual molecules have a tetrahedral shape.



In the tetrachlorides MCl_4 , the chlorine atom is more electronegative than the central group IV atom M. Therefore, the chlorine atom attracts the bonding electrons more towards itself and acquires a partial negative charge while the group IV atom acquires a partial positive charge. This unequal distribution of bonding electrons establishes a dipole moment in the direction of the more electronegative chlorine atom, hence making the M-Cl bonds in the tetrachlorides MCl_4 polar.

However, the tetrachloride molecule is non-polar because of the symmetrical tetrahedral arrangement of the M-Cl bonds. Therefore, the effects of bond polarity in the opposite directions cancel out each other, so that the net dipole moment in the whole molecule, MCl_4 is zero, thus making the molecule to be non-polar.

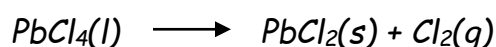
Thermal stability of the tetrachlorides

Thermal stability decreases from carbon tetrachloride to lead tetrachloride (or down the group)

Explanation:

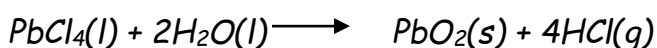
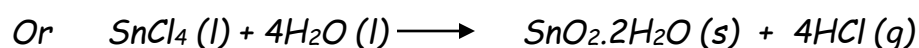
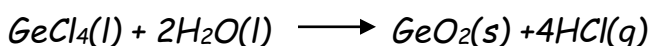
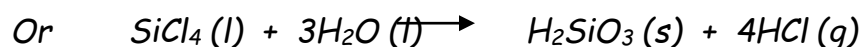
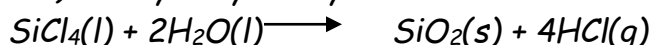
The atomic radius of group IV elements increases down the group (or from carbon to lead), so the covalent bond between group IV atom and chlorine becomes longer and weaker down the group. Thus amount of energy required to break the covalent bonds in the tetrachlorides decreases hence decrease in thermal stability.

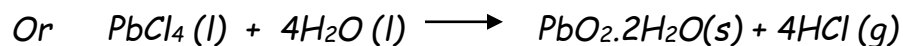
Thus CCl_4 , SiCl_4 and GeCl_4 are stable even at high temperatures, whereas SnCl_4 and PbCl_4 decompose readily - SnCl_4 decomposes on heating, whereas PbCl_4 decomposes even at room temperature to form the dichlorides and chlorine.



Hydrolysis of the tetrachlorides

All the tetrachlorides except for carbon tetrachloride (because carbon lacks a vacant d-orbital that accommodate the lone pairs of electrons from the water molecules) are hydrolysed by water to form the dioxides and hydrogen chloride.





The tetrachlorides of silicon, germanium, tin and lead are hydrolysed because these elements have empty (vacant) d-orbitals of the right energy which accommodate lone pairs of electrons from water molecules.

Carbon tetrachloride is not hydrolysed because the carbon atom in the molecule lacks vacant 2d-orbitals to accommodate lone pairs of electrons from water molecules.

Exercise

State what would be observed and write equations for the reactions that would take place, if any,

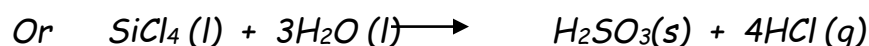
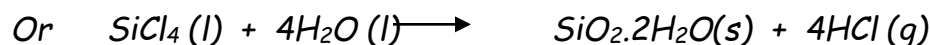
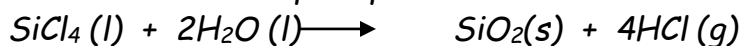
when the following compounds are treated with water.

(i) Carbon tetrachloride

Two separate layers form

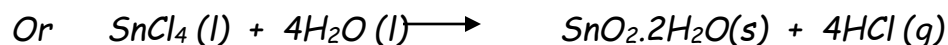
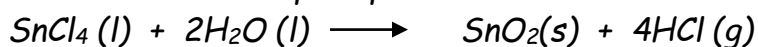
(iii) Silicon tetrachloride

White fumes and a white precipitate



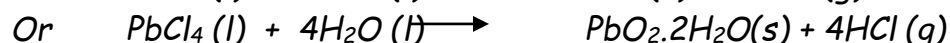
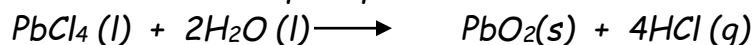
(iii) Tin(IV) chloride

White fumes and a white precipitate



(iv) Lead(IV) chloride

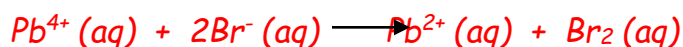
White fumes and a brown precipitate



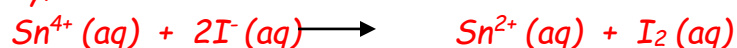
Note:

The tetrabromide and tetraiodides of lead and tin do not exist. They cannot be prepared because of the strong oxidising action of lead(IV) and tin(IV) ions and the strong reducing action of bromide and iodide ions.

Thus when a solution containing lead(IV) ions is mixed with one containing bromide ions, the lead(IV) ions would oxidize the bromide ions to bromine. The bromide ions would reduce the lead(IV) ions to lead(II) ions, so it's impossible to form lead(IV) bromide.



Similarly;



Exercise

Explain why lead(IV) chloride exists but lead(IV) bromide does not.

The bromide ion has a larger radius than the chloride ion, hence the bromide ion is a stronger reducing agent than the chloride ion. So the bromide ion reduces lead(IV) ions to lead(II) ions thus lead(IV) bromide cannot exist. The chloride ion cannot reduce lead(IV) ions hence lead(IV) chloride exists

(b) The dichlorides (MCl_2)

Stable dichlorides are only formed by germanium, tin and lead.

Appearance

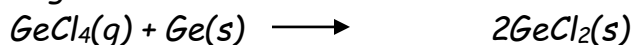
Germanium(II) chloride, GeCl_2 is a pale yellow solid

Tin(II) chloride, SnCl_2 is a white solid

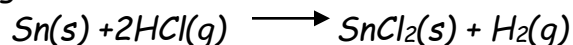
Lead(II) chloride, PbCl_2 is a white solid

Preparation

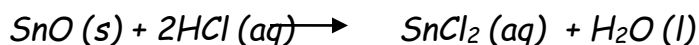
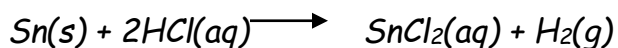
Germanium(II) chloride is made by passing the vapour of germanium(IV) chloride over hot germanium.



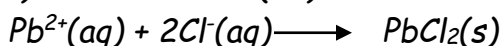
Anhydrous tin (II) chloride is best obtained by heating tin in a current of dry hydrogen chloride.



Hydrated tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ can be obtained by heating tin with concentrated hydrochloric acid or reacting tin(II) oxide and dilute hydrochloric acid followed by crystallization.

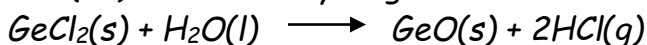


Lead (II) chloride is prepared by precipitation when dilute hydrochloric acid or sodium chloride solution is added to an aqueous solution of a lead(II) salt (eg lead(II) nitrate or lead(II) ethanoate solutions)



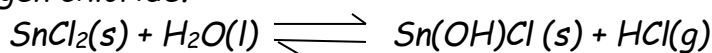
Hydrolysis of the dichlorides

Germanium(II) chloride is covalent and is hydrolysed by water forming germanium(II) oxide and hydrogen chloride.

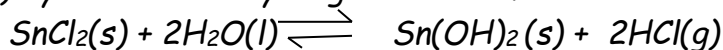


Observation: yellow solid turns to a white solid and white fumes.

Anhydrous tin(II) chloride is predominantly covalent. It reacts with water (is hydrolysed) to form a white suspension of basic tin(II) chloride with liberation of hydrogen chloride.

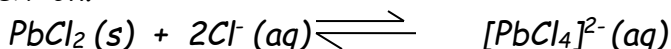


If water is hot and present in a large excess, tin(II) chloride is hydrolysed to form tin(II) hydroxide and hydrogen chloride.



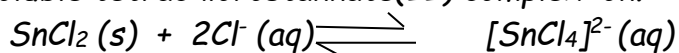
Although lead(II) chloride is ionic, it is insoluble in cold water but soluble in hot water.

It is more soluble in concentrated hydrochloric acid than in water because it reacts with chloride ions in the acid to form a soluble tetrachloroplumbate(II) complex ion.

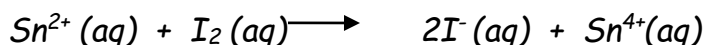
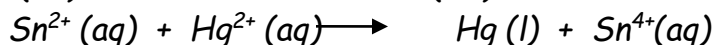


Note:

Tin(II) chloride is also soluble in concentrated hydrochloric acid due to formation of a soluble tetrachlorostannate(II) complex ion.



Tin(II) chloride is a strong reducing agent, reducing mercury(II) ions to mercury; iron(III) ions to iron(II) ions; iodine to iodide ions; acidified dichromate(VI) ions to chromium(III) ions and acidified manganate(VII) ions to manganese(II) ions. The tin(II) ions are oxidized to tin(IV) ions.



Exercise

1. (a) Write the equation and state the conditions for the reactions leading to the formation of

(i) tin(II) chloride

Heat and dry hydrogen chloride gas

(ii) tin(IV) chloride

Heat and dry chlorine gas

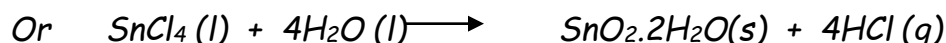
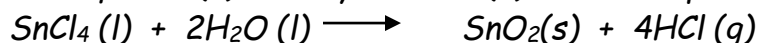
(b) Tin(II) chloride and tin(IV) chloride were separately exposed to air.

(i) State what was observed in each case

With SnCl_2 : No observable change

With SnCl_4 : White (misty) fumes

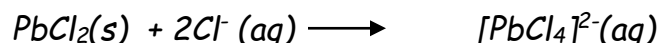
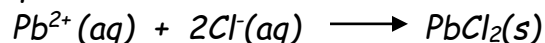
(ii) Write the equation(s) for any reaction(s) that took place



(c) Write the equation for the reaction between tin(II) chloride and iron(III) sulphate solution.

2. Concentrated hydrochloric acid was added drop-wise to lead(II) nitrate solution until it was in excess. State what was observed and write an equation for the reaction

A white precipitate that dissolved in excess forming a colourless solution



THE HYDRIDES .MH₄

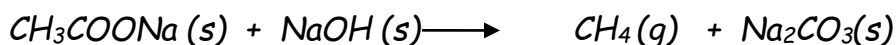
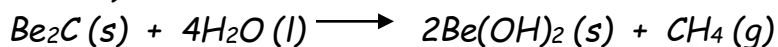
All the elements form tetravalent hydrides - ie methane CH₄, silane SiH₄, germane GeH₄, stannane SnH₄ and plumbane PbH₄.

They are covalent, colourless gases at room temperature, with simple molecular structures.

Their boiling points increase from methane to plumbane because molecular mass increases from methane to plumbane so the van der Waals forces between the molecules also increase in strength in the same direction.

Preparation

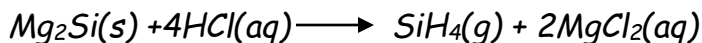
Methane is prepared by hydrolysis of beryllium carbide or aluminium carbide or heating sodium ethanoate with soda lime (solid mixture of sodium hydroxide and calcium oxide)



The hydrides of the Si, Ge Sn and Pb can be made by reduction of their tetrachlorides with lithium aluminium hydride at 0°C in the presence of ether.



Silane, SiH₄, can also be prepared by reacting magnesium silicide with dilute hydrochloric acid



Thermal stability of the hydrides

When heated, they all decompose to form the element and hydrogen gas with increasing ease down the group due to decrease in decomposition temperatures shown in the table below

Hydride	Decomposition temperature (°C)
CH ₄	800°C
SiH ₄	450°C
GeH ₄	285°C
SnH ₄	150°C
PbH ₄	0°C

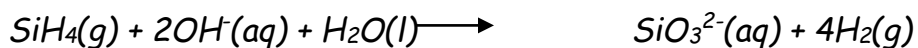
Therefore thermal stability of the hydrides decreases down the group. This is because atomic radius increases down the group, so the covalent bond formed between atoms of group (IV) elements and hydrogen becomes longer, hence weaker, resulting into decrease in the decomposition temperature hence decrease in thermal stability.

As their thermal stability decreases, their ease of decomposition into the element and hydrogen increases and hence they become stronger reducing agents. Thus PbH₄ is the strongest reducing agent where as CH₄ is the weakest reducing agent.

Hydrolysis of hydrides

Methane does not react with water (ie is not hydrolysed) because the carbon atom lacks empty 2d-orbitals so it cannot accept the lone pairs of electrons from the water molecules.

Silane, SiH₄ is hydrolysed by water slowly and more rapidly in the presence of an alkali to form a silicate and hydrogen gas. This because the silicon atom has empty (vacant) 3d-orbitals which can accomodate lone pairs of electrons on oxygen atoms of water molecules.



Germane, stannane and plumbane are surprisingly resistant to hydrolysis.

Exercise

(a) The decomposition temperatures of hydrides of group IV elements of the Periodic Table are given in the table below

Formula of the hydride	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
Decomposition temperature ($^{\circ}\text{C}$)	800	450	285	150	0

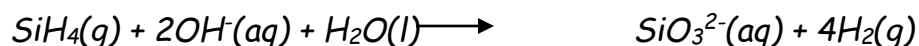
(i) State the relationship between the decomposition temperatures and thermal stability of the hydrides

Both the decomposition temperature and thermal stability of the hydrides decrease from methane to plumbane

(ii) Explain your answer in (a) (i)

This is because atomic radius of the elements increases from carbon to lead. Thus the group IV atom-hydrogen bond (M-H) strength decreases resulting into decrease in amount of energy required to break the covalent bond.

(b) Write the equation for the reaction of silicon tetrahydride with sodium hydroxide solution.



Reasons why the chemistry of carbon differs from that of other group IV elements in the Periodic Table

Carbon has the smallest atomic radius in the group. This gives rise to

- Very high electronegativity/ very low electropositivity hence carbon is unable to form stable cations
- Strong covalent bonds between carbon and other non-metal atoms
- multiple bond formation between its own atoms and atoms of some other non-metals.

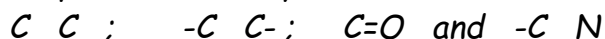
Carbon atom lack vacant 2d-orbitals. This explains why most compounds of carbon are resistant to hydrolysis; and why carbon does not form complexes.

Differences between the chemistry of carbon and the rest of the elements in group IV of the Periodic Table

1. Carbon has a unique property of catenation. Catenation is the ability of an element to form covalent bonds between its own atoms resulting into formation of long chains or rings. Thus carbon atoms bond together in extremely long chains and rings.

The ability of carbon to catenate is due to its very small atomic radius. Thus the carbon-carbon covalent bonds are short and very strong. Down the group, atomic radius increases thus the element-element bond becomes longer and weaker, hence tendency to catenate decreases.

2. Carbon unlike other members in the group can form multiple bonds with itself and with other non-metallic elements. Eg in alkenes, alkynes, carbonyl compounds, carboxylic acids and nitriles



3. Carbon shows a maximum covalency of four because it lacks empty 2d orbitals. Other elements have a maximum covalency of 6 (hence coordination number of 6) because their atoms have empty d-orbitals of the right energy, so they can expand their octets.
4. Carbon does not form complex ions, because it has no lone pairs of electrons and lacks empty 2d-orbitals so it cannot accept lone pairs of electrons from the ligands. The other members in the group form complex ions like e.g. $[SiF_6]^{2-}$; $[GeCl_6]^{2-}$; $[SnCl_6]^{2-}$; $[PbCl_6]^{2-}$, etc., because their atoms have vacant d-orbitals of the right energy to accept lone pairs of electrons from the ligands.
5. Carbon forms gaseous oxides while other members in the group form solid oxides.
6. Carbon compounds are relatively inert (unreactive) whereas compounds of other members in the group are highly reactive.
7. Carbon does not show inert pair effect.

GROUP VII ELEMENTS (The Halogens)

Introduction

The elements of group (VII) are fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and radioactive astatine (At). They are all non-metallic elements. Their name "halogens" means "salt formers" in Greek, because they readily react with metals to form salts.

Group (VII) elements have a general outer electronic configuration (structure) ns^2np^5 - ie halogen atoms have seven electrons in their outer shells (energy levels).

Halogens exist as diatomic molecules ie F_2 , Cl_2 , Br_2 and I_2 . The bonds in these molecules are single covalent bonds.

Table showing some of the properties of group(VII) elements

Element	Fluorine, F	Chlorine, Cl	Bromine, Br	Iodine, I
Atomic number	9	17	35	53
Outer shell electronic configuration	$2s^2 2p^5$	$3s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$
Atomic radius(nm)	0.072	0.099	0.114	0.133
Ionic radius(nm)	0.133	0.18	0.195	0.215
Melting point($^{\circ}C$)	-220	-101	-7	114
Boiling point ($^{\circ}C$)	-188	-35	59	183
Electron affinity($KJmol^{-1}$)	-333	-348	-328	-295
Bond dissociation energy($KJmol^{-1}$)	158	242	193	151
Oxidation states	-1	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7
Solubility (g/100g of water) at $20^{\circ}C$	Nil	0.59	3.6	0.018

Appearance

Fluorine is a pale yellow gas. Chlorine is a yellowish-green gas, bromine is a dark red liquid (its vapour is brown) and iodine is black shiny solid (sublimes on heating to form a purple/violet vapour).

Bond type and oxidation states

They combine chemically by gaining one electron to form a univalent halide ion X^- (present in ionic compounds) or by sharing electron(s) to form one or more covalent bonds (in molecular compounds) like Cl-Cl, Br-Br, H-F, H-Cl, etc.

Because atoms of chlorine, bromine and iodine have easily accessible vacant d-orbitals, they are able to form covalent compounds in which the octet of electrons is expanded. This enables these elements to show higher valencies of 3, 5 and 7 with oxidation states of +3, +5 and +7 in some of their compounds. Eg in the inter halogen compounds ICl , ICl_3 , ICl_5 , ICl_7 , iodine has oxidation states of +1, +3, +5 and +7 respectively.

These higher valency states are covalent and arise by promoting electrons from filled p- and s-orbitals in the outermost energy level to empty d-orbitals still in outermost energy level.

Fluorine cannot expand its octet because of lack of 2d-orbitals in its outer most energy level. This prevents fluorine from forming more than one covalent bond, which is why fluorine does not exhibit higher valencies /oxidation states. Fluorine is always univalent (exhibits a covalency of one only) and because it is the most electronegative element, it always has the oxidation state of -1 in its compounds with other elements.

Melting and boiling points

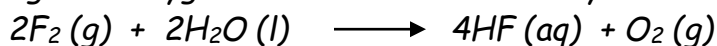
The melting points of halogens increase down the group (from fluorine to chlorine). This is because halogens are non-polar diatomic molecules with van der Waals forces of attraction between the molecules. The strength of these forces increases with increase in molecular mass (or size of the molecules) and since molecular mass (or molecular size) of the halogens increases down the group ie from fluorine to iodine, the strength of the van der Waals forces also increases hence increase in melting point down the group.

Note that in iodine the van der Waals forces are sufficiently strong to bind the iodine molecules so close to each other, hence iodine is a solid.

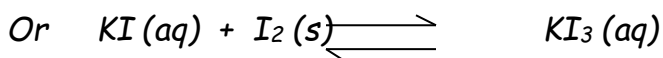
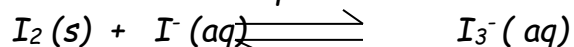
Solubility

Generally, the solubilities of halogens (Cl_2 , Br_2 and I_2) in water (a polar solvent) are low - ie they sparingly soluble in water, because the van der Waals forces of attraction holding diatomic molecules of halogens are different from the hydrogen bonds that hold water molecules together. As such water molecule tend to cohere so that mixing with halogen molecules is largely prevented leading to low solubility.

Fluorine does not dissolve in water at all; instead it reacts vigorously with water, oxidizing it to oxygen and itself reduced to hydrofluoric acid.



Though iodine is sparingly soluble in water it very soluble in aqueous potassium iodide (giving a brown solution) because iodine combines with the iodide ion to form a stable and soluble complex ion called the triiodide ion.



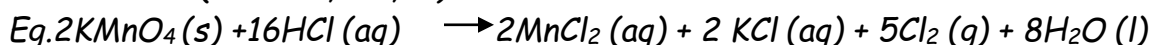
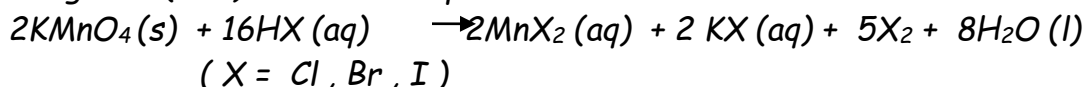
Solutions of chlorine in polar solvents like water are pale green. Solutions of bromine and iodine in polar solvents (eg water) are brown in colour.

However, halogens are more soluble in non-polar organic solvents like benzene, tetra chloromethane, cyclo hexane, etc, because the forces that hold molecules of the non-polar organic solvent and the halogens are similar - these are the van der Waals forces.

Solutions of chlorine, bromine and iodine in non-polar organic solvents (eg CCl_4 , benzene, etc) are yellow, red and purple/violet respectively.

LABORATORY PREPARATION OF HALOGENS (Cl_2 , Br_2 AND I_2)

1. Action of concentrated solution of hydrohalic acid on potassium manganate(VII) at room temperature.



In the above reaction the manganate(VII) ions oxidize the halide ion in the hydrohalic acid solution to the halogen molecules. The manganate (VII) ion is then reduced to manganese(II) ions.

2. Heating concentrated solution of a hydrohalic acid with manganese(IV) oxide or lead(IV) oxide. Both manganese(IV) oxide or lead(IV) oxide oxidize the halide ions in acid to the halogen. In this case the halogens bromine and iodine are formed as vapours.

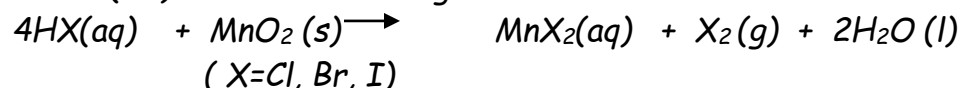


3. Heating a mixture of concentrated sulphuric acid, alkali metal halide and manganese(IV) oxide or lead(IV) oxide. In this case the hydrohalic acid is produced in situ.

The reaction takes place in two stages. First, the reaction between the acid and the alkali metal halide to form the hydrohalic acid



The second reaction involves oxidation of the halide ions by manganese(IV) oxide or lead(IV) oxide to the halogen.



Note that in all the above preparations, the halogens X_2 are obtained by oxidation of the halide ions X^- in $\text{HX}(\text{aq})$ by suitably strong oxidizing agents like potassium manganate(VII), lead(IV) oxide or manganese(IV) oxide.

However, fluorine cannot be obtained from the fluoride ion by chemical oxidation because this would require a more powerful oxidant than fluorine which does not exist since fluorine is the strongest oxidizing agent known.

The only possible way of preparing fluorine is by electrolysis of a mixture of hydrogen fluoride and molten potassium fluoride (the electrolyte) using carbon graphite and steel as anode and cathode respectively. The electrolyte must be free from any traces of water with which fluorine would react rapidly.

CHEMICAL REACTIVITY

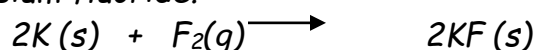
Reactivity of the halogens decreases from fluorine to iodine because atomic radius increases down the group, therefore nuclear attraction for electrons decreases.

Fluorine is exceptionally very reactive due to the abnormally low bond dissociation of the F-F bond. This is because fluorine has a very small atomic radius. Therefore the F-F bond is short, resulting into strong repulsion between the non-bonding(lone) electron pairs on both combined atoms which greatly weakens the F-F bond, hence little energy is required to break it. This effect becomes negligible in other halogens because of increase in atomic radius, hence increase in bond length.

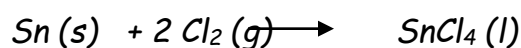
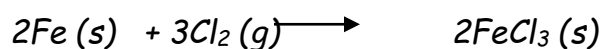
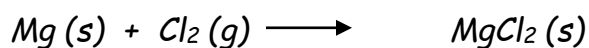
Reactions of halogens with metals:

The halogens react readily with metals but the vigour of the reaction depends on the position of the metal in the reactivity series and the particular halogen which is reacting - ie reactivity of the halogens with a particular metal decreases down the group.

Fluorine combines readily and directly with all metals to form a metal fluoride. For instance potassium ignites spontaneously in fluorine to form a white solid of potassium fluoride.



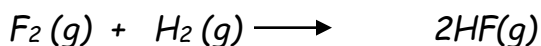
With chlorine the metal is heated in dry chlorine to form a metal chloride. Metals with more than one oxidation state (eg iron and tin) will form a higher chloride in combination with chlorine.



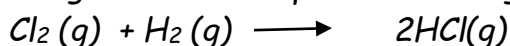
Reaction with non- metals

Reaction with hydrogen:

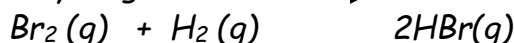
Fluorine reacts explosively with hydrogen even in the dark to form hydrogen fluoride.



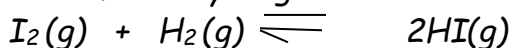
Chlorine reacts with hydrogen to form hydrogen chloride. The reaction is slow in diffused light but it is explosive in sunlight.



Bromine reacts with hydrogen at 200 °C in the presence of a catalyst of platinum to form hydrogen bromide.



Iodine reacts reversibly with hydrogen at 400 °C in the presence of a catalyst of platinum to form hydrogen iodide.

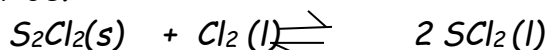


Reaction with sulphur:

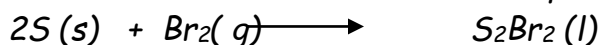
When chlorine gas is passed into molten sulphur, disulphur dichloride, S_2Cl_2 is obtained as a red repulsive-smelling liquid.



If chlorine gas is passed through disulphur dichloride at 0°C, sulphur dichloride, SCl_2 is obtained as a red liquid. It readily dissociates into chlorine and disulphur dichloride.



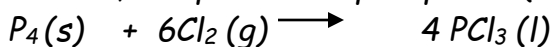
Disulphur dibromide is obtained as a red liquid when sulphur reacts with bromine



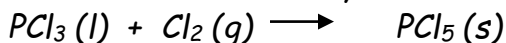
Iodine does not with sulphur

Reaction with phosphorus:

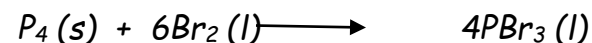
White phosphorus burns spontaneously (with a pale green flame) at room temperature in chlorine whereas red phosphorus reacts with chlorine when heated. In both cases, the product is phosphorus(III) chloride, a colourless liquid



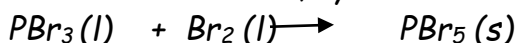
If excess chlorine is used, a yellow solid of phosphorus(V) chloride is formed.



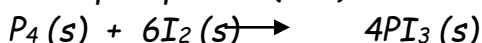
White phosphorus reacts with bromine in carbon disulphide to form phosphorus(III) bromide.



If excess bromine is used, a yellow solid of phosphorus(V) bromide is formed.



With iodine phosphorus(III) iodide is formed. It is a red solid.



PI_5 does not exist.

Note that halogens do not react (combine) with oxygen, nitrogen or carbon directly. However, fluorine combines directly with carbon to form carbon tetrafluoride, CF_4

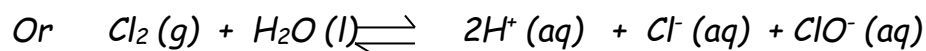
Reaction with water

Fluorine reacts vigorously with water, oxidizing it to oxygen and is itself reduced to hydrofluoric acid.



The above reaction is exothermic and the resultant solution is colourless and contains no dissolved fluorine gas as it all reacts.

Chlorine reacts slowly and reversibly with water in a disproportionation reaction (chlorine is oxidized and reduced in the same reaction) to form hydrochloric acid and hypochlorous acid (chloric(I) acid).

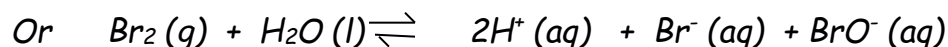


The resultant solution is faintly green in colour because it contains some dissolved chlorine.

When the solution is exposed to sun light, the hypochlorous acid decomposes with liberation of oxygen gas.



Bromine reacts very slowly (much slower than chlorine) and reversibly with water in a disproportionation reaction (bromine is oxidized and reduced in the same reaction) to form hydrobromic acid and hypobromous acid (bromic(I) acid). The resultant solution is brown due to some dissolved bromine.



The bromate(I) ion formed disproportionates to form a bromide and bromate(V) ion.



Iodine, however, is just sparingly soluble in water and does not react with water.

Reaction with alkalis

Reaction with cold dilute alkalis (sodium hydroxide or potassium hydroxide solution)

Fluorine reacts with cold dilute alkalis to give oxygen difluoride, a fluoride and water. The resulting solution is colourless.



Or (If alkali is sodium hydroxide solution)



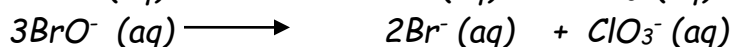
Chlorine and bromine react with cold dilute alkalis disproportionation reactions to form pale yellow solutions containing the corresponding halide and halate(I) salts.



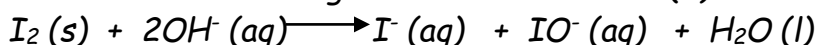
Or (If alkalis is sodium hydroxide solution)



On heating, the pale yellow solutions turn colourless because the halate(I) ion responsible for the yellow colour disproportionates to give the halide and halate(V) ion which are colourless.



Iodine reacts with cold dilute alkalis in a disproportionation reaction to form a colourless solution containing the iodide and iodate(I) salts.



Or (If alkalis is sodium hydroxide solution)



Reaction with hot concentrated alkalis

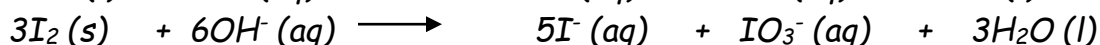
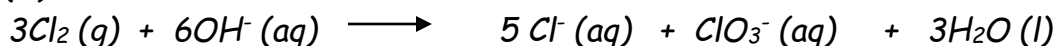
Fluorine vigorously oxidizes hot concentrated alkalis to oxygen and water and is itself reduced to a fluoride.



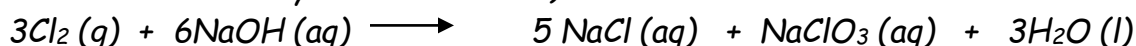
Or (If alkali is sodium hydroxide solution)



All the other halogens (chlorine, bromine and iodine) react with hot concentrated alkalis to form colourless solutions containing the corresponding halides and halate(V) salts.



Or (If alkalis is sodium hydroxide solution)



Note:

The reactions of halogens (Cl_2 , Br_2 and I_2) with alkalis are commercially in the manufacture of the halate(I) and halate(V) salts such as:

- sodium chlorate (I), NaOCl - used as an antiseptic
- sodium chlorate(V), NaClO_3 - used as a weed killer (herbicide)
- potassium chlorate (V), KClO_3 -used to make safety matches ,explosives and disinfectants

Laboratory preparation of potassium chlorate(V) KClO_3

Procedure:

Chlorine gas is passed through a hot concentrated solution of potassium hydroxide until the solution becomes pale yellow, which means that chlorine has gone into excess and so all the potassium hydroxide has reacted. Potassium chloride and potassium chlorate(V) are formed during the reaction.

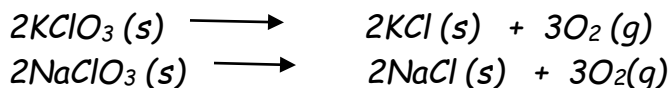


The solution is then carefully heated to evaporate much of the water and on cooling the hot solution, much of the potassium chlorate(V) crystallizes out as white solid because the salt has a lower solubility at lower temperatures than the potassium chloride much of which remains in solution.

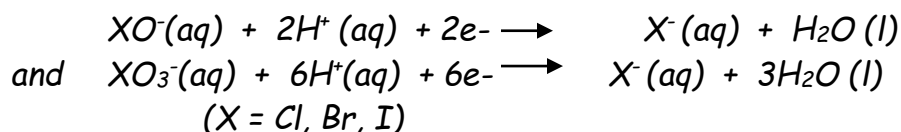
The potassium chlorate(V) is filtered off, washed and purified by recrystallizing it to get rid of any accompanying potassium chloride impurity.

Note: For the sodium salts, the chloride crystallizes out first followed by the chlorate(V) salt.

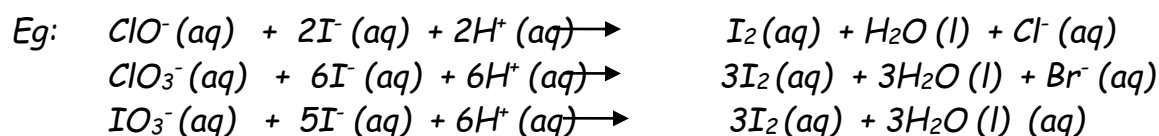
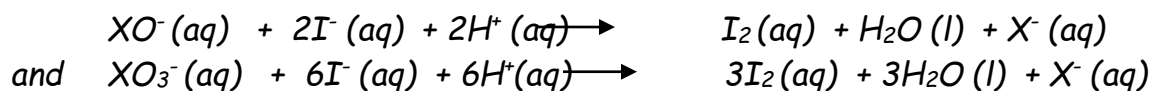
The chlorate(V) of sodium and potassium decompose on heating to liberate oxygen gas



The halate (I) XO^- and halate (V) ions, XO_3^- ions are oxidants especially in acidic solution with the essential reaction:

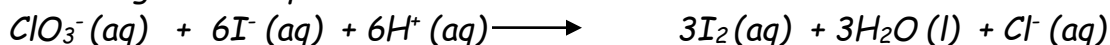


These ions will for example oxidize iodide ions (say in potassium iodide solution) to iodine.



Revision question:

- 2.0 g of a mixture of potassium chloride and potassium chlorate (V) were dissolved in water and the solution made up to 250cm^3 . 10.0 cm^3 of the solution was mixed with excess acidified potassium iodide solution. The iodine liberated required 8.0cm^3 of a 0.2M sodiumthiosulphate solution for complete reaction. Potassium chlorate(V) and potassium iodide react according to the equation.



Iodine reacts with thiosulphate ions according to the equation



Calculate the percentage of potassium chlorate(V) in the mixture.

- Explain why chlorine is more soluble in dilute sodium hydroxide than in water.

Solution:

Chlorine reacts with sodium hydroxide irreversibly (completely) to form sodium chloride and sodium chlorate(I) both of which are soluble in water hence it dissolves in the alkali.



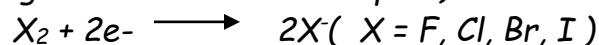
Chlorine is moderately soluble in water because of two reasons. First, the van der Waals forces of attraction between molecules of chlorine are different from the hydrogen bonding through which water molecules associate and so mixing of the two does not readily occur.

Secondly some chlorine reacts with water reversibly to form hydrochloric acid and hypochlorous acid which is a weak acid

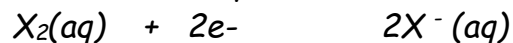


Oxidising reactions of halogens

Halogens have high electronegativities and high electron affinities. Therefore they readily accept electrons to form halide ions and so act as oxidizing agents. (Recall - an oxidizing agent is an electron acceptor)



The oxidizing power of the halogens is measured by the value of the standard electrode potential for the process

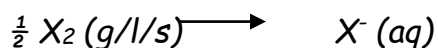


Element	F	Cl	Br	I
Electrode potential/V	+2.87	+1.36	+1.07	+0.54

The electrode potential values for the halogens become less positive from fluorine to iodine reflecting the decreasing oxidizing power down the group.

The value of the electrode potential (hence oxidation potential) of the halogen depends on the energy change that occurs when one mole of hydrated halide ions are formed from the halogen (element) in its standard state.

Therefore the oxidizing strength of halogens depends on several energy terms involved during the transformation of halogen in its standard state to its hydrated ions ie



This is best represented by the energy cycle below.

Despite the electron affinity of chlorine being the largest, fluorine is the strongest oxidizing agent since it has the most negative energy change for the transformation of the element in standard state to hydrated halide ions (ie $\frac{1}{2} X_2$ (standard state) $\longrightarrow X^-$ (hydrated)) when all the energy terms in the cycle are summed as summarized in the table below.

Halogen	$\frac{1}{2}$ enthalpy of fusion	$\frac{1}{2}$ enthalpy of vaporisation	$\frac{1}{2}$ enthalpy of bond dissociation	Electron affinity	Enthalpy of hydration	Energy change H
F	-	-	+158/2	-333	-524	-778
Cl	-	-	+242/2	-348	-378	-605
Br	-	+30/2	+193/2	-328	-348	-564.5
I	+15/2	+42/2	+152/2	-295	-308	-499

Fluorine is a stronger oxidizing agent than chlorine (and other halogens) because of two reasons:

First, fluorine has very low bond dissociation energy (hence low atomization energy) due to the weakness of the F-F bond.

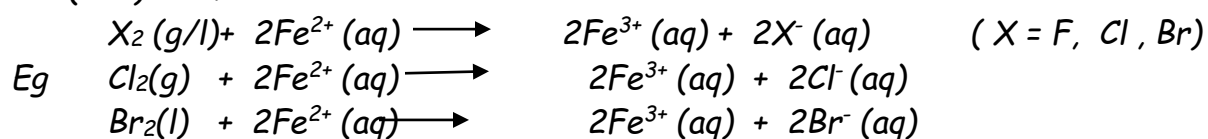
Secondly, the fluoride ion has very high hydration energy because it is very small in size, thus it strongly attracts water molecules which leads to liberation of a large amount of energy during its hydration.

Both effects make fluorine to have largest negative enthalpy change for formation of one mole of hydrated fluoride ions from the element in its standard state, hence fluorine is the strongest oxidizing agent of all halogens.

The fall (or decrease) in oxidizing ability of halogen down the group is due to increase radius of the halide ions resulting into a decrease in hydration energies of the halide ions hence making the enthalpy change of formation of hydrated halide ions from the elements in their standard states less negative down the group.

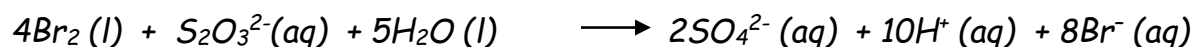
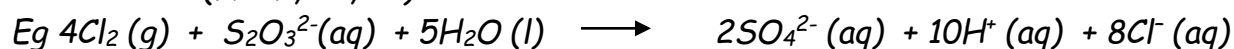
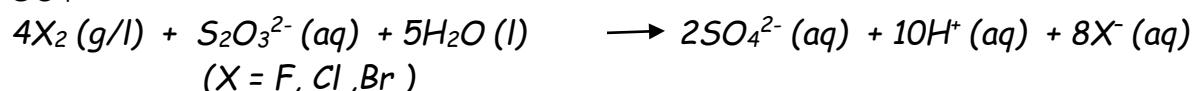
Fluorine is the strongest oxidizing agent known. Therefore it enables /makes the elements with which it combines to bring out their highest positive oxidation states unlike other halogens. For example AgF_2 , SF_6 , IF_7 , SiF_6

Fluorine , chlorine and bromine all oxidize iron(II) ions to iron(III) ions during which green colour of aqueous iron(II) ions turns to yellow/brown colour of iron(III) ions.



Iodine is, however, such a weak oxidizing agent that it cannot remove electrons from iron(II) ions- ie it can not oxidise iron(II) ions to iron(III) ions.

Fluorine , chlorine and bromine can all oxidize thio sulphate ions , $\text{S}_2\text{O}_3^{2-}$ to sulphate ions SO_4^{2-} , increasing the oxidation state of sulphur from +2 in $\text{S}_2\text{O}_3^{2-}$ to +6 in SO_4^{2-}

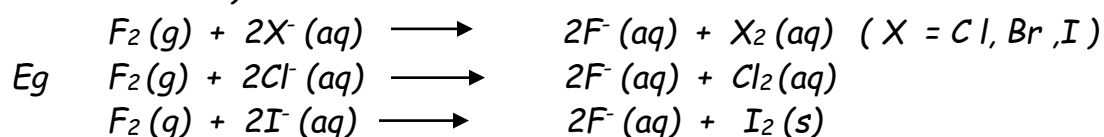


Iodine , however , is too weak an oxidant that it will oxidize the thiosulphate ion to the tetrathionate ion , $\text{S}_4\text{O}_6^{2-}$ increasing the oxidation state of sulphur from +2 in $\text{S}_2\text{O}_3^{2-}$ to +2 $\frac{1}{2}$ in $\text{S}_4\text{O}_6^{2-}$

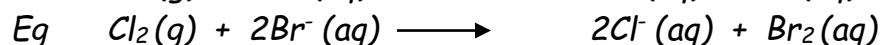
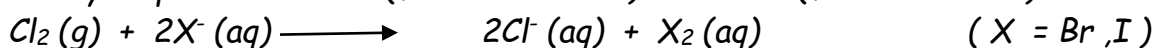


Displacement reactions

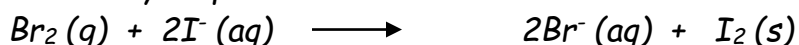
These illustrate the relative oxidizing powers of halogens. In general, any halogen higher in the group will oxidize halide ions of halogen lower in the group to halogen molecules. Thus fluorine displaces chlorine, bromine and iodine from the corresponding halide salts in solution (through oxidation of the chloride, bromide and iodide ions)



Chlorine only displaces bromine (from a bromide) and iodine (from an iodide).



Bromine will only displace iodine from iodides.



Iodine will not oxidize any halide ions as it is a weak oxidizing agent.

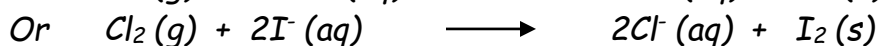
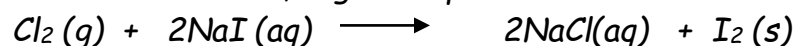
Questions:

1. State and explain what is observed when chlorine gas is bubbled through aqueous sodium iodide solution

Solution

The colourless solution turns brown and a black precipitate is formed/deposited.

This is so because chlorine oxidizes the iodide ions in colourless solution of sodium iodide to iodine some of which dissolves to form a brown solution but as more iodine is formed, it gets deposited as a black solid



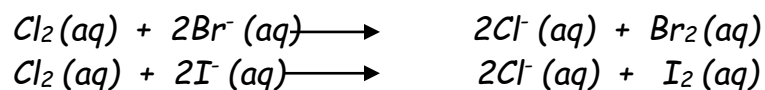
2. Given the following: Chlorine water, aqueous solutions containing a bromide and iodide ions in separate test tubes and tetra chloromethane. Describe briefly how you would distinguish between the iodide and bromide ions. Explain your answer.

solution

To an aqueous solution containing bromide ions is added chlorine water followed by carbon tetrachloride and the mixture shaken for some time and allowed to stand. A red coloration appears in the organic layer.

To an aqueous solution containing iodide ions is added chlorine water followed by carbon tetrachloride and the mixture shaken for some time and allowed to stand. A violet coloration appears in the organic layer.

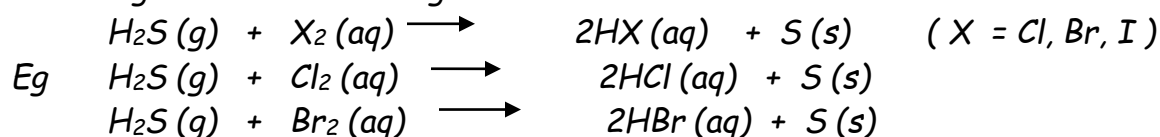
This is because chlorine water contains dissolved chlorine which oxidizes the bromide and iodide ions in the aqueous solutions to bromine and iodine respectively.



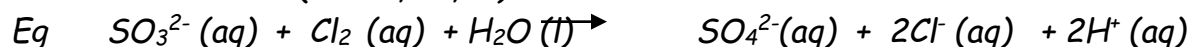
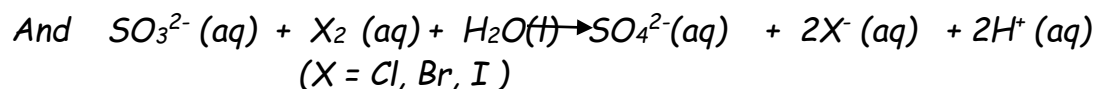
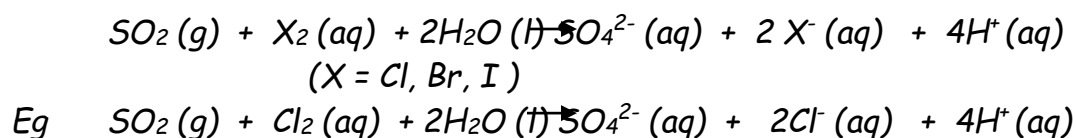
Carbon tetrachloride is, however immiscible with water (ie the two liquids form separate layers when mixed) and the halogens formed (bromine and iodine) distribute themselves between the two solvents (water and carbontetrachloride). However, the halogens are more soluble in carbon terachloride (the organic solvent) and so the red colour (due to dissolved bromine) and violet colour (due to dissolved iodine) are observed in the carbon tetrachloride layer.

Other oxidizing reactions of halogens

The halogens chlorine, bromine and iodine will oxidize hydrogen sulphide gas in presence of water to sulphur which forms as a yellow precipitate. The colours of the halogen are also discharged and the brown iodine solution turns colourless.



Sulphur dioxide, sulphurous acid and any soluble sulphite are all oxidized in aqueous solution by chlorine, bromine and iodine to the sulphate. The colour of the halogen is discharged - ie, the greenish- yellow chlorine turns colourless, brown (reddish-brown) bromine turns colourless, the brown iodine turns colourless.



Halide ions as reducing agents (reductants)

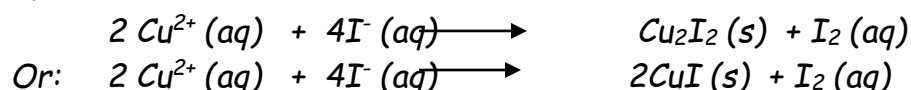
Halide ions become stronger reductants from fluoride F^- to iodide, I^- . In other words the strength of the halide ions as reductants (electron donors) increases in the order



Explanation:

The radius of the halide ions increases down the group. Hence the nuclear attraction for the outermost electrons in the ions decreases so tendency for them to be lost increases, hence increase in reducing ability of the ions.

The iodide ion is a common reductant in acidic solution. It will reduce blue copper(II) ions in solution copper (I) iodide which appears as a white precipitate. The colourless iodide ions are oxidized to iodine responsible for the brown colour of the resultant solution.



The copper(I) iodide is stained brown by the iodine, but this could be removed by adding sodium thiosulphate which reduces the iodine to iodide ions and is itself oxidized to tetrathionate ions, hence revealing the white colour of the precipitated copper(I) iodide.

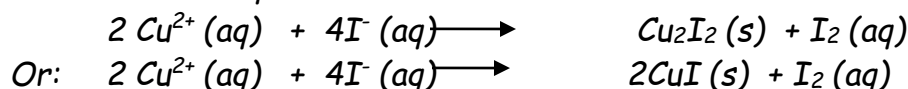


Revision question:

1.(a) State what is observed when potassium iodide solution is added to copper(II) sulphate solution

The bluecopper(II) sulphate solution turns brown and a whiteprecipitate is formed

(b) Write an ionic equation for the reaction that occurs



2. 6.4 g of a copper(II) salt were dissolved in water and the solution made to 250 cm³. To 25.0cm³ of this solution was added excess potassium iodide solution and the iodine liberated required 23.50 cm³ of 0.1M sodium thiosulphate solution for complete reaction. Calculate the percentage of copper in the salt. [ans = 23.28%]

3. UNEB q.b [Qn. 4 paper 1 -1996(April)]

Manufacture(Industrial preparation) of chlorine and sodium hydroxide

Chlorine is made on a large scale by the electrolysis of brine (concentrated sodium chloride solution) using either;

- (i) a flowing mercury cathode cell or
- (ii) a diaphragm cell.

Other useful products of electrolysis of brine are sodium hydroxide and hydrogen gas -ie sodium hydroxide and hydrogen are also manufactured on a large scale by electrolysis of brine using any of the above cell.

Manufacture of chlorine by electrolysis of brine using a flowing mercury cathode cell

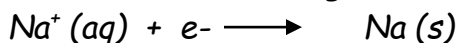
Brine (saturated solution of sodium chloride) is electrolysed between graphite (or titanium) anodes and a cathode of mercury that flows slowly across the bottom of the cell from one end to another. The brine flows in the same direction as the mercury.

Chloride ions are discharged at anode to form chlorine gas.

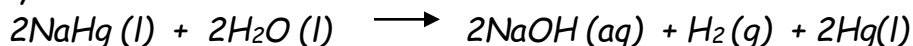


The chlorine is lead off from the cell, dried and stored in gas containers with tight covers.

The sodium ions are discharged at the cathode to form sodium.



The sodium dissolves in mercury to form an amalgam (sodium amalgam). The sodium amalgam is then dissolved in water to form sodium hydroxide and hydrogen gas and mercury.



The sodium hydroxide can be used as a solution or evaporated to give the solid pellets.

Note:

The chloride ions are discharged at anode in preference to the hydroxide ions as because the chloride ions are present in a much higher concentration than the hydroxide ions.

Sodium ions are discharged at cathode in preference to hydrogen ions because of a high over voltage of hydrogen at a mercury surface which raises its negative potential required for the discharge of hydrogen ions.

Advantages of this method (mercury cathode cell method)

- produces pure chlorine (with almost no oxygen content)*
- sodium hydroxide obtained is more concentrated*

Disadvantages:

- Higher voltages required hence higher electricity consumption*
- Mercury pollution due to leakages*
- Higher costs of mercury contamination avoidance measures*
- High costs of brine purification.*

Manufacture of chlorine using the diaphragm cell:

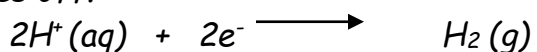
Brine is electrolysed between a titanium anode and a steel cathode in separate compartments separated by a porous (permeable) asbestos diaphragm.

The chloride ions are discharged at anode to form chlorine gas which bubbles off .



Since most of the chloride ions are discharged (removed) at anode, then most of the ions passing through the diaphragm into the cathode compartment are sodium, hydrogen and hydroxide ions.

Hydrogen ions are preferentially discharged at steel cathode and hydrogen gas bubbles off.



The remaining solution in the cathode compartment contains sodium and hydroxide ions (which is essentially sodium hydroxide), but with some chloride ions that shift together with the sodium ions via the diaphragm membrane. On concentration by evaporation, sodium chloride crystallizes out first since it has a low solubility at high temperatures and a concentrated solution of fairly pure sodium hydroxide remains.

Advantages of this method (diaphragm cell method)

- It utilizes brines of lower purity
- It uses lower voltage, hence less electricity consumption than does the mercury cathode cell

Disadvantages:

- The chlorine produced contains oxygen hence need for purification
- The sodium hydroxide is dilute and contaminated with chloride ions requiring evaporative concentration
- Asbestos emission which is a health hazard.
- High cost of asbestos emission avoidance.

Uses of Chlorine

1. It is used as a bleaching agent for cotton, rayon and wood pulp.
2. It is used to sterilize (disinfect) water supplies for domestic and industrial use and for swimming baths
3. It is used to make organic solvents such as trichloro methane and trichloro ethane which serve as solvents for grease and oil removal
4. It is used to make chloroethene (vinyl chloride), the monomer used in the production of plastic called poly vinyl chloride (PVC)
5. Used to make sodium chlorate(V) used as a powerful weed killer and in making DDT (dichloro diphenyl trichloroethane) which is an insecticide.

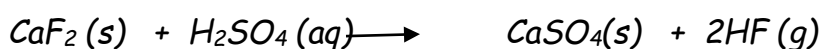
Compounds of halogens

(a) The hydrogen halides (HX) where X = F, Cl, Br, I

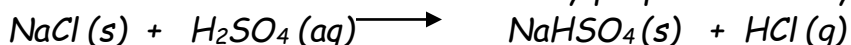
These are hydrogen fluoride HF, hydrogen chloride HCl, hydrogen bromide HBr, and hydrogen iodide, HI. They are all colourless gases at 25°C.

Preparation

Hydrogen iodide is made by heating calcium fluoride with concentrated sulphuric acid.



A similar displacement reaction between sodium chloride and hot concentrated sulphuric acid can be used for the laboratory preparation of hydrogen chloride.



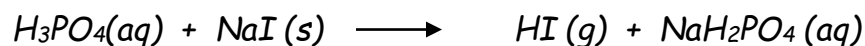
However, hydrogen bromide and hydrogen iodide cannot be prepared satisfactorily by the reaction between a metallic bromide or iodide and concentrated sulphuric acid because the concentrated sulphuric acid oxidizes them to the halogens. The acid is reduced to sulphur dioxide and water.



Therefore, hydrogen bromide and hydrogen iodide are prepared by:

(a) The action of concentrated phosphoric(V) acid (a non-oxidizing acid) on a metallic bromide or iodide.





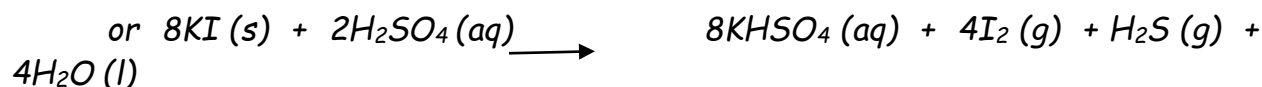
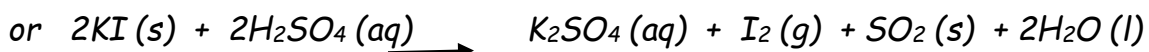
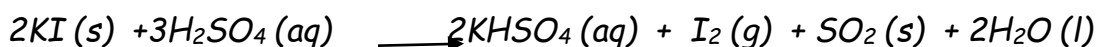
(b) Hydrolysis of phosphorus(III) bromide or phosphorus(III) iodide



Question:

1. State what would be observed and write the equation for the reaction that would take place when solid potassium iodide is heated with concentrated sulphuric acid:

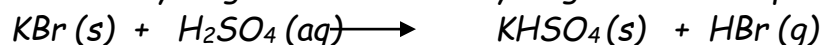
Answer: A violet (or purple) vapour and a black sublimate.



2. Concentrated sulphuric acid reacts with potassium bromide to liberate a sharp smelling gas. With potassium iodide, a gas with a rotten egg smell is evolved. Explain.

Answer:

Concentrated sulphuric acid reacts with potassium bromide and potassium iodide to form hydrogen bromide and hydrogen iodide respectively.



These are strong reducing agents which are easily oxidized by the concentrated sulphuric acid to the halogens bromine and iodine. The acid is reduced by hydrogen bromide to sulphur dioxide which is the sharp smelling gas. Hydrogen iodide reduces the acid to hydrogen sulphide which has a rotten egg smell.



Properties of hydrogen halides:

<i>Hydrogen halide</i>	<i>Boiling point (°C)</i>	<i>Length of H - X bond (nm)</i>	<i>Bond dissociation energy(KJmol⁻¹)</i>	<i>Acid dissociation constant, K_a (mol dm⁻³)</i>
<i>HF</i>	<i>19.9</i>	<i>0.092</i>	<i>562</i>	<i>5.6 × 10⁻⁴</i>
<i>HCl</i>	<i>-85.0</i>	<i>0.127</i>	<i>431</i>	<i>1 × 10⁷</i>
<i>HBr</i>	<i>-66.7</i>	<i>0.141</i>	<i>366</i>	<i>1 × 10⁹</i>
<i>HI</i>	<i>-35.4</i>	<i>0.161</i>	<i>299</i>	<i>1 × 10¹¹</i>

Boiling point

The boiling points of the hydrogen halides increase with increasing relative molecular mass except for hydrogen fluoride which has an abnormally high boiling point.

Fluorine has a very small atomic radius and is highly electronegative, so the hydrogen-fluorine bond very polar, hence the hydrogen fluoride molecules associate via much stronger hydrogen bonds and that is why hydrogen fluoride has an abnormally high boiling point.

Molecules of other hydrogen halides associate through van der Waals forces whose strength

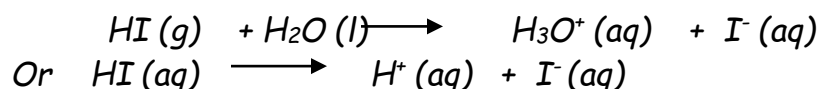
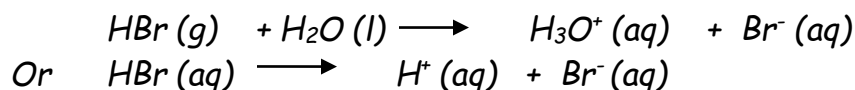
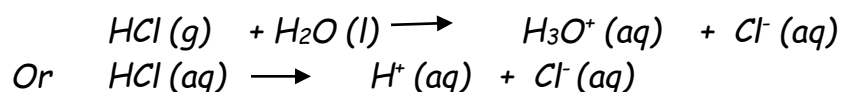
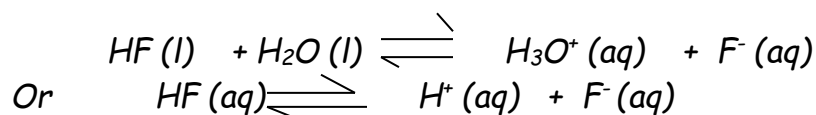
Increases with increasing molecular mass, and that's why the boiling points increase in passing from hydrogen chloride to hydrogen iodide.

Thermal stability:

This is measured by the bond dissociation energy of the H -X bond. The thermal stability of hydrogen halides decreases with increase in atomic radius the halogen. This is because as the atomic radius of halogen atom increases, the length of the length of hydrogen-halogen bond increases and so the bond becomes weaker hence the energy put in to break the bond (ie bond dissociation energy) decreases. Thus HI is the least thermally stable (has the lowest decomposition temperature) and hydrogen fluoride is the most stable to heat (has the highest decomposition temperature).

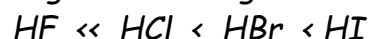
Acidic strength

The pure hydrogen halides are not acidic, but when dissolved in water they undergo ionization to form hydrogen ions (hydroxonium ions) and halide ions:



With the exception of hydrogen fluoride, the other hydrogen halides are strong acids (as reflected by the K_a values).

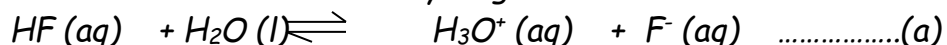
The acid strength increasing down the group - ie, it increases in the order:



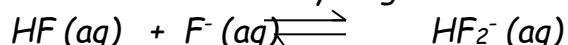
Explanation:

The atomic radius of halogens increases down the group and so the hydrogen - halogen bond length increases, resulting into decrease in strength of the bond so tendency for it to break to release hydrogen ions in solution increases leading to increase in acid strength down the group.

However, hydrogen fluoride is a stronger acid in concentrated solutions than in dilute solution. In dilute solution hydrogen fluoride ionizes as follows



In concentrated solution, the unionized molecules of hydrogen fluoride react with the fluoride ions to form hydrogen difluoride ions, HF_2^-

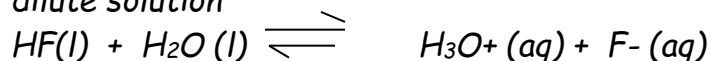


This reaction shifts the equilibrium of the reaction (a) to the right causing more hydrogen fluoride molecules to ionize thus increasing the hydrogen ion concentration in the solution.

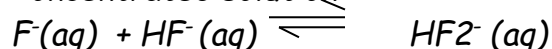
Question:

(a) Write the equation for the ionization of aqueous hydrogen fluoride in

(i) dilute solution



(ii) Concentrated solution



(b) In which of the two solutions(a) above would you expect hydrofluoric acid to be relatively more acidic? Explain your answer.

It is more acidic in a concentrated solution, because the fluoride ions react with hydrogen fluoride molecules to form hydrogen difluoride ions. This displaces the equilibrium in (i) above to the right causing more hydrogen fluoride ions to ionize hence increasing the hydrogen ion concentration in the solution.

Reducing properties of the hydrides

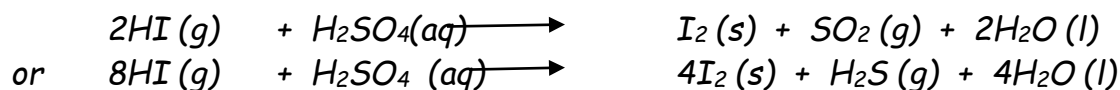
The reducing strength of hydrides increases in the order $\text{HF} \ll \text{HCl} < \text{HBr} < \text{HI}$. ie hydrogen fluoride is the weakest reducing agent while hydrogen iodide is the strongest reducing agent.

Therefore, hydrogen fluoride and hydrochloric acid do not react concentrated sulphuric acid, because they are weak reducing agents so they can not reduce the concentrated acid, a strong oxidizing agent.

Hydrogen bromide reacts moderately with concentrated sulphuric acid, reducing it to Sulphur dioxide and water. The hydrogen bromide is oxidized to bromine.



Hydrogen iodide vigorously reacts with concentrated sulphuric acid, reducing it to sulphur dioxide or hydrogen sulphide and water. The hydrogen iodide is oxidized to iodine.



Oxo (oxy) acids of chlorine

Fluorine forms no stable oxo acids but the other halogens form the following in which the halogen atom are in positive oxidation states as summarized in the table below

<i>Oxidation state of halogen in oxo acid</i>	<i>Oxo acids of chlorine</i>	<i>Oxo acids of bromine</i>	<i>Oxo acids of iodine</i>
<i>+1</i>	<i>HOCl , hypochlorous acid / chloric (I) acid</i>	<i>HOBr , hypobromous acid / bromic (I) acid</i>	<i>HOI , hypoiodous acid / iodic (I) acid</i>
<i>+3</i>	<i>HClO₂ , chlorous acid/ Chloric(III) acid</i>		
<i>+5</i>	<i>HClO₃ , chloric acid / chloric (V) acid</i>	<i>HBrO₃ , bromic acid / bromic (V) acid</i>	<i>HIO₃ , iodic acid / iodic (V) acid</i>
<i>+7</i>	<i>HClO₄ , Perchloric acid / Chloric(VII) acid.</i>	<i>HBrO₄ , Perbromic acid / bromic(VII) acid.</i>	<i>HIO₄ , Periodic acid / iodic(VII) acid.</i>

Acid strength of oxo acids

The strength of oxo acids increases with increases in number of oxygen atoms separately attached to the halogen atom. For instance, the acid strength of oxo acids of chlorine increases in the order $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$

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Explanation: *Oxygen is more electronegative than chlorine and so it strongly attracts the bonding electrons in the chlorine - oxygen bond towards itself. This effect is transmitted through the chlorine atom to the oxygen - hydrogen bond in each of the acid molecule. As the number of oxygen atoms separately bonded to the chlorine atom increases, the electron withdrawing tendency increases, so the*

partial positive charge on the chlorine atom increases leading to increased weakening of the oxygen - hydrogen bond in the molecule, hence increased tendency for it to break to release protons into solution.

Reasons why the chemistry of fluorine is different from that of other halogens

The anomalous behavior of fluorine is due to the following reasons

- (i) Fluorine has the smallest atomic radius and smallest ionic radius among all halogens. This gives rise to:
 - very high electronegativity of fluorine
 - very low bond dissociation energy of the F - F bond due to the strong repulsions between the lone pairs of electrons on each fluorine atom
 - formation of very strong bonds in compounds of fluorine with other elements
 - high lattice energies of ionic fluorides.
 - high hydration energy of the fluoride ion.
 - high positive electrode potential of the fluoride ion.
- (ii) Fluorine atom lacks vacant 2d-orbitals and so forms compound in only one oxidation state (-1 oxidation state)

Differences between the chemistry of fluorine and the rest of the elements in group VII of the Periodic Table

The following are the ways in which properties of fluorine differ from those of other halogens.

- (i) Fluorine is exceptionally more reactive than the other halogens. This is because of the very low bond dissociation enthalpy of the F-F bond in fluorine molecules.
- (ii) Fluorine has only one oxidation state while other halogens have more than one oxidation states. This is because fluorine does not have 2d-orbitals in the second energy level and so cannot expand its octate.
- (iii) Other elements show their highest oxidation states when combined with fluorine than when combined with other halogens. This is because fluorine is the strongest oxidising agent known.

- (iv) *Fluorine combines directly with carbon while other halogens do not.*
- (v) *Fluorine reacts differently from other halogens with compounds that contain oxygen like water and alkalis ie- fluorine does not form oxo ions unlike other halogens*
This is so because of two reasons.
- First, fluorine lacks 2d - orbitals and so cannot expand its octet to show higher valencies (oxidation states) that are required of halogens in the oxo ions*
- Secondly, being the most electronegative element, fluorine never shows a positive oxidation state which other halogen exhibit in their oxo ions.*
- (vi) *Fluorine compounds are more stable than other halogen compounds. This is because of two reasons:*
- First, the very small radius of the fluorine atom enables it to form short covalent bonds which are stronger than those of other halogens.*
- Secondly, the very small radius of the fluoride ion gives ionic fluorides higher lattice energy than corresponding compounds of other halogens.*
- (vii) *Metallic fluorides usually have greater ionic character than other metal halides. This is because the fluoride ion has the smallest radius of all halide ions. Therefore the fluoride ion has the least polarisability ie it is the most weakly polarised halide ion by metal cations.*
- (viii) *The boiling point and melting point of hydrogen fluoride are abnormally high compared to those of other hydrogen halide. This is because fluorine is the most electronegative element, therefore, the H-F bond is more polar than any other hydrogen-halogen bonds and so hydrogen fluoride molecules can associate through strong intermolecular hydrogen bonds unlike other hydrogen halides.*
- (ix) *The solubility of fluorides in water markedly differs from that of other halides of the corresponding metal. For instance, calcium fluoride is insoluble in water while other calcium halides are soluble. On the*

contrary, silver fluoride is soluble in water while other silver halides are insoluble.

Exercise

The properties of fluorine resemble those of oxygen more closely than they do for chlorine. State three properties in which fluorine resembles oxygen but differs from chlorine.

Solution

- (i) Both oxygen and fluorine combine directly with carbon while chlorine does not.
- (ii) The hydrides of oxygen and fluorine (water and hydrogen fluoride) have much higher boiling and melting points because they associate through strong intermolecular hydrogen bonding where as hydrogen chloride molecules associate through weak van der Waals forces.
- (iii) The solubility, melting and boiling points of the fluorides are closer in magnitude to those of the corresponding oxides than they are to the chlorides

Detection (test/identification) of halide ions Cl^- ; Br^- and I^-

Reagent(s)	Test	Observation		
		Cl^-	Br^-	I^-
Silver nitrate solution, dilute nitric acid, ammonia solution	Add silver nitrate solution, followed by dil. nitric acid then ammonia solution.	<p>A white ppt (of AgCl) insoluble in acid but dissolves in excess ammonia to form a colourless solution</p> $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ $\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq})$	<p>A pale yellow (cream) ppt (of AgBr) insoluble in acid and sparingly soluble in excess ammonia solution.</p> $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$	<p>A yellow ppt (of AgI) insoluble in both acid and excess ammonia solution.</p> $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

Solid manganese(IV) oxide, conc.sulphuric acid.	Add solid MnO_2 and conc. H_2SO_4 and heat	Pale green/ greenish-yellow gas (chlorine gas). Refer to notes for equations.	brown (reddish-brown) fumes of bromine. Refer to notes for equations.	Violet vapour of iodine. Refer to notes for equations.
Chlorine water and carbon tetrachloride	Add chlorine water followed by CCl_4 , shake and allow to stand	No observable change	Red colouration in CCl_4 layer. $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$	Violet/purple colouration in CCl_4 layer. $Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$
Lead(II) nitrate solution or lead(II) ethanoate solution	Add a few drops of lead(II) nitrate solution or lead(II) ethanoate solution and warm	White precipitate ,dissolves on warming to form a colorless solution, but reprecipitates on cooling. $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$	Pale yellow precipitate ,dissolves on warming to form a colorless solution. $Pb^{2+}(aq) + 2Br^-(aq) \rightarrow PbBr_2(s)$	A thick yellow precipitate insoluble on warming. $Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$

