Chapter 13

s and p – BLOCK ELEMENTS

After completing this lesson, you will be able to:

- Recognize the demarcation of periodic table into s block, p block, d block and r block.
- Describe how physical properties like atomic radius, ionization energy, electron negativity, electrical conductivity and melting and boiling points of element change within a group and within a period and the Periodic Table.
- Describe reactions of period 3 elements with water, oxygen and chlorine.
- Describe reaction of oxides and chlorides of period 3 element with water.
- Describe reaction of group 1 element with water, oxygen and chlorine.
- Discuss the trend in solubility of the hydroxides, sulphates and carbonates of group 2 elements.
- Discuss the trends in thermal stability of the nitrates and carbonates of group 2 elements.

Period 3 (Na to Ar)

Atomic and Physical Properties of The Period 3 Elements

(This period contains Na, Mg, Al, Si, P, S, Cl and Ar)

This topic describes and explains the trends in atomic and physical properties of the Period 3 elements from sodium to argon. It covers ionization energy, atomic radius, electronegativity, electrical conductivity, melting point and boiling point.

a) Atomic Properties

13.1.1.1 Electronic Structures

In period 3 of the periodic table, the 3s and 3p orbitals are filling with electrons. Just as a reminder, the shortened versions of the electronic structures for the eight elements are:

Na [Ne] $3s^1$

Mg [Ne] $3s^2$

Al [Ne] $3s^2$ $3p_x^1$

Si [Ne] $3s^2$ $3p_x^1$ $3p_y^1$

P [Ne] $3s^2$ $3p_x^1$ $3p_y^1$ $3p_z^1$

S [Ne] $3s^2$ $3p_x^2$ $3p_y^1$ $3p_z^1$

Cl [Ne] $3s^2$ $3p_x^2$ $3p_y^2$ $3p_z^1$

Ar [Ne] $3s^2$ $3p_x^2$ $3p_y^2$ $3p_z^2$

In each case, [Ne] represents the complete electronic structure of a neon atom.

Trends in Atomic radius

We know that the number of shells in all the elements of a given period remains the same but the value of effective nuclear charge, increases from left to right. The increased effective nuclear charge pulls the electron cloud of the atom nearer to the nucleus and thus the size of atoms and ions goes on decreasing from left to right. Thus, in going from left to right in a periodic of s-and p-block elements atomic and iconic radii decrease with increase of atomic number. This fact can be illustrated by considering the atomic (covalent) and ionic radii of the elements as shown below.

Table 13.1 *Ionic radii (in Å) of representative elements (s- and p-block elements). In parentheses are given the oxidation states of the elements.*

Group → / Period ↓	s-block elements		p-block elements				
	I A	II A	III A	IV A	V A	VI A	VII A
1	H 2.08 (-1) 0.29 (+1)						
2	Li 0.60 (+1)	Be 0.31 (+2)	B 0.20 (+3)	C 2.60 (-4) 0.15 (+4)	N 1.71 (-3) 0.11 (+5)	O 1.40 (-2) 0.09 (+6)	F 1.36 (-1) 0.07 (+7)
3	Na 0.95 (+1)	Mg 0.65 (+2)	Al 0.50 (+3)	Si 2.71 (-1) 0.41 (+4)	P 2.12 (-3) 0.34 (+5)	S 1.84 (-2) 0.29 (+6)	Cl 1.81 (-1) 0.26 (+7)
4	K 1.33 (+1)	Ca 0.99 (+2)	Ga 1.13 (+1) 0.62 (+3)	Ge 0.93 (+2) 0.53 (+4)	As 2.22 (-3) 0.47 (+5)	Se 1.98 (-2) 0.42 (+6)	Br 1.95 (-1) 0.39 (+7)
5	Rb 1.48 (+1)	Sr 1.13 (+2)	In 1.32 (+1) 0.81 (+3)	Sn 1.12 (+2) 0.71 (+4)	Sb 0.45 (-3) 0.62 (+5)	Te 2.21 (-2) 0.56 (+6)	I 2.16 (-1) 0.50 (+7)
6	Cs 1.69 (+1)	Ba 1.35 (+2)	Tl 1.40 (+1) 0.95 (+3)	Pb 1.20 (+2) 0.84 (+4)	Bi 1.20 (+3) 0.74 (+5)	Po - -	At - -
7	Fr 1.76 (+1)	Ra 1.40 (+2)					

Q1. Give Trends in Electronegativity in modern periodic table.

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

The Pauling scale is the most commonly used. Fluorine (the most electronegativity element) is assigned a value of 4.0, and values range down to cesium and francium which are the least electronegativity at 0.7.

The Trend

The trend across Period 3 looks like this:

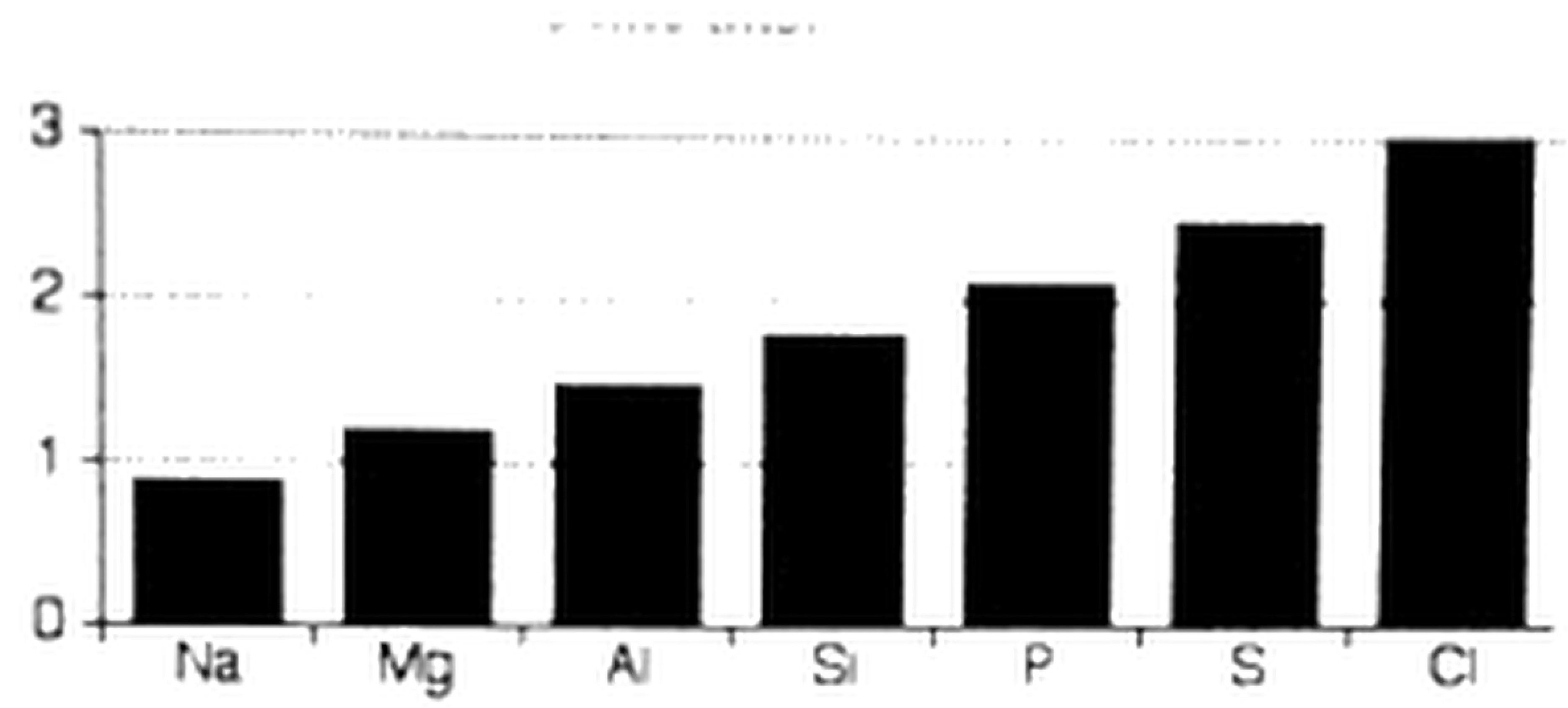


Fig. 13.2 Electronegativities

In going from left to right in a period of s- and p- block elements, the electronegativity value increase. This increase can be explained on the basis of any of the following facts.

i. On moving from left to right in a period, there is a decrease in size of the atoms. Smaller atoms have greater tendency to attract the electrons towards themselves I.e. smaller atoms have higher electronegativity values.

ii. On mobbing from left to right in a period the is an increase of ionization energy and electron affinity of the elements. The atoms of the elements which have higher value of ionization energies and electron affinities also have higher electro negativities.

The variation of electronegativity in a period and a group of reprehensive elements (s- and p- block elements) is show in Fig 13.3

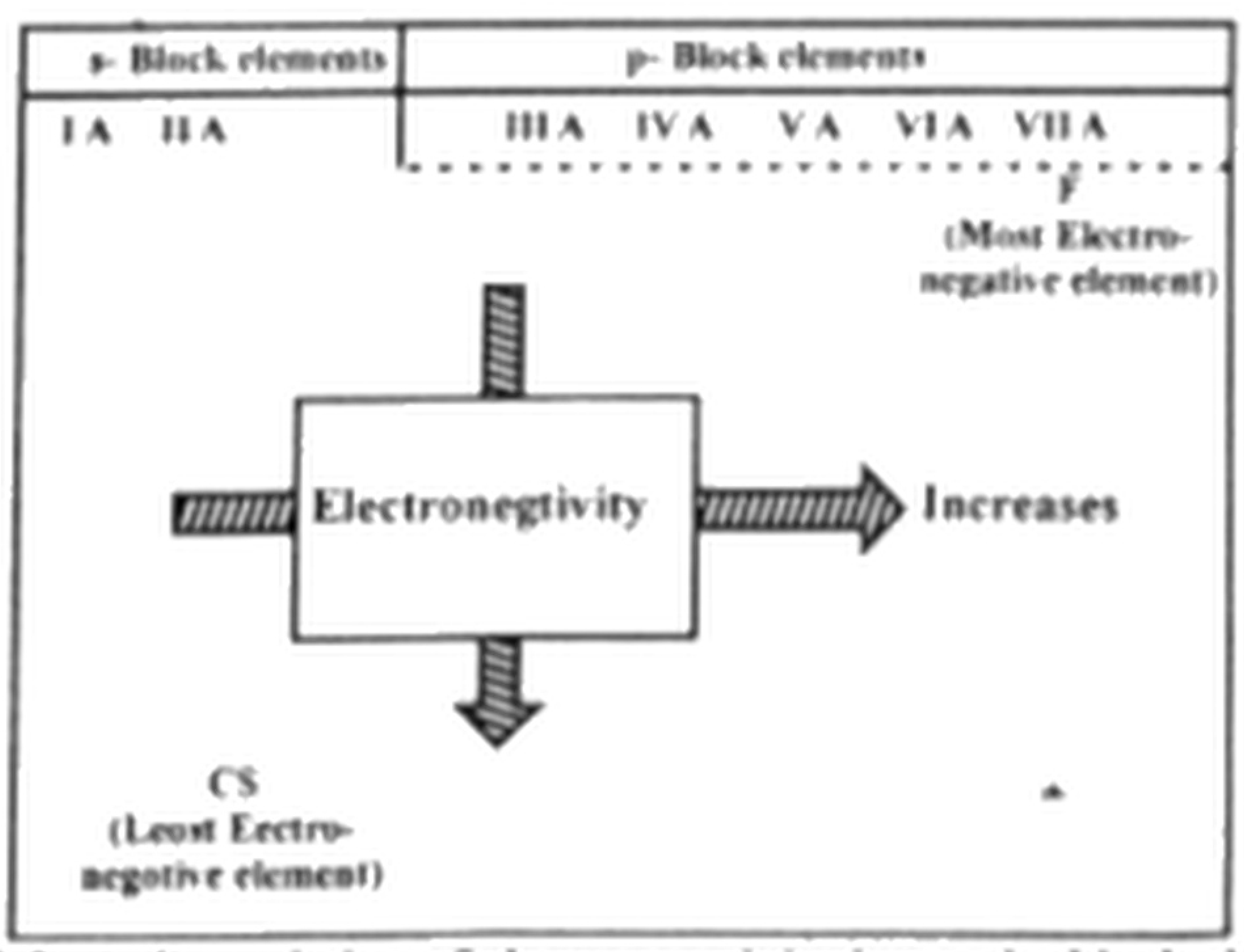


Fig 13.3 Periodic variation of electronegativity in s and p block elements.

Notice that argon is not included. Electronegativity is about the tendency of an atom to attract a *bonding* pair of electrons. Since argon doesn't form covalent bonds, you obviously can't assign it electronegativity.

Explaining the Trend

The trend is explained in exactly the same way as the trend in atomic radii.

As you go across the period, the bonding electrons are always in the same level – the 3- level. They are always being screened by the same inner electrons.

All that differs is the number of protons steadily increases and so attracts the bonding pair more closely.

B) Physical Properties

This section is going to look at the electrical conductivity and the melting and boiling points of the elements. To understand these, you first have to understand the structure of each of the elements.

Structure of the elements

The structure of the elements changes as you go across the period. The first three (i.e. Na, Mg, Al) are metallic, silicon Is giant covalent, and the rest (i.e. P, S, Cl, Ar) are simple molecules.

Three Metallic Structures

Sodium, magnesium and aluminium all have the metallic structures.

In sodium, only one electron per atom is involved in the metallic bond – the single 3s electron. In magnesium, both of its outer electrons are involved, and in aluminium all three.

The other difference you need to be aware of is the way the atoms are packed in the metal crystal.

Sodium is 8-co-ordinated – each sodium atom is touched by only 8 other atoms.

Both magnesium and aluminium are 12-co-oridnted (although in slightly different ways.) This is a more efficient way to pack atoms, leading to less wasted space in the metal structures and to stronger bonding in the metal.

Q2. Draw and discuss structure giant molecules.

Answer

Silicon has a giant covalent structure just like diamond. A tiny part of the structure looks like this:

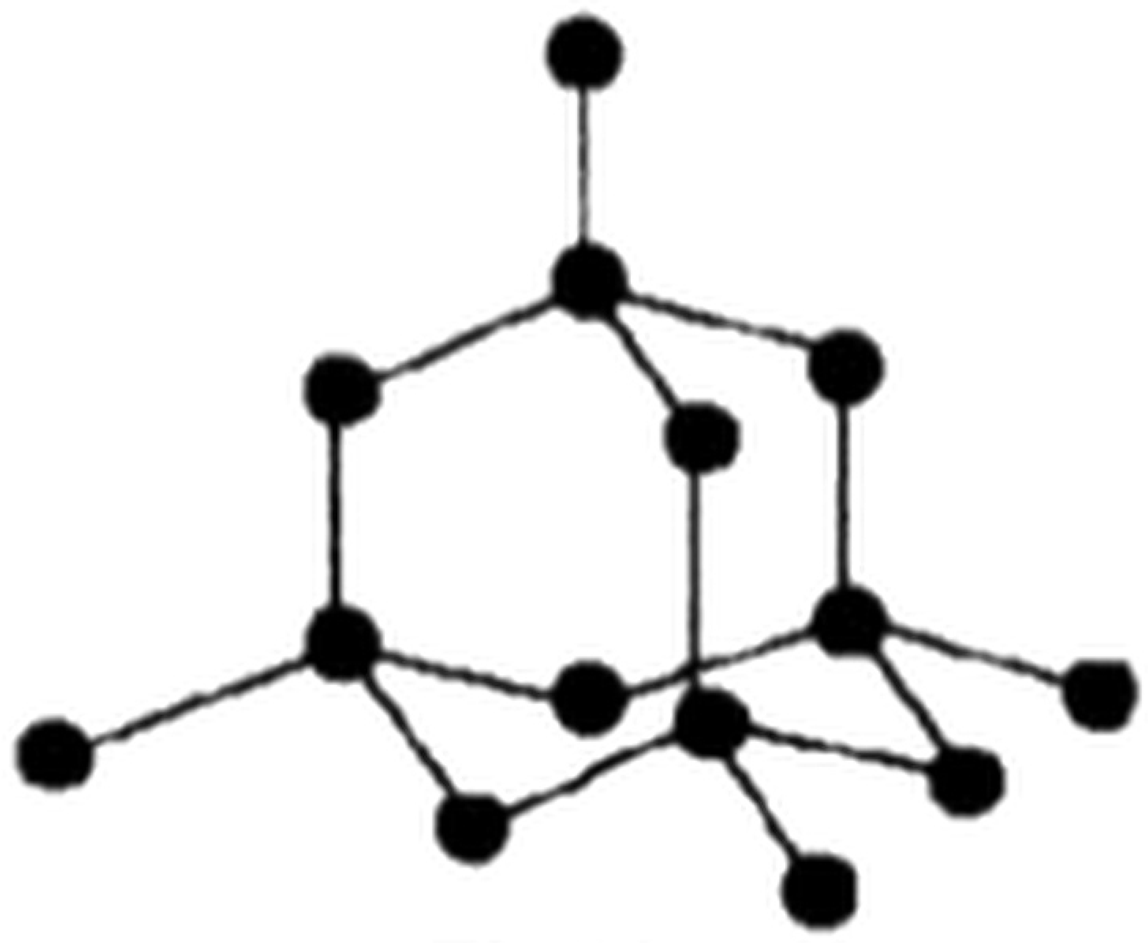
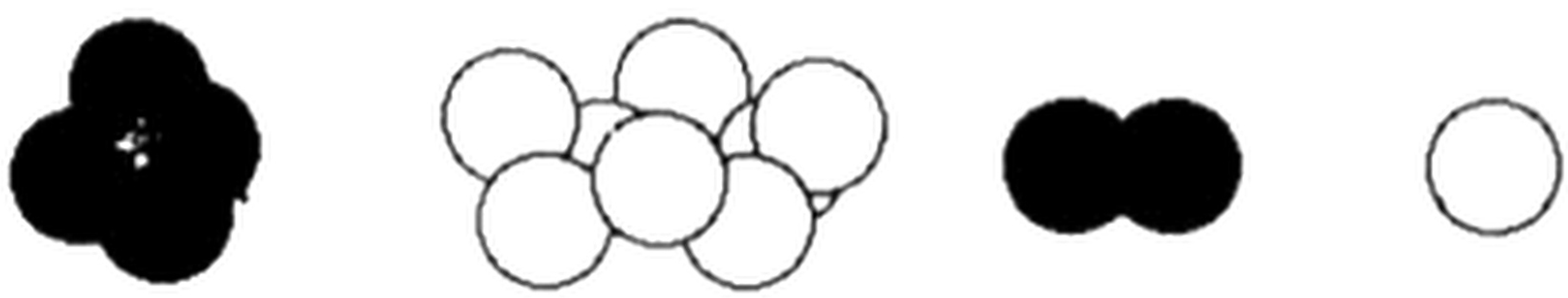


Fig 13.4

The structure is held together by strong covalent bonds in all three dimensions.

Four simple molecular structures

The structures of phosphorus (i.e. white etc.) and Sulphur (i.e. rhombic or monoclinic etc) vary depending on the type of phosphorus or Sulphur you are talking about.



a P_4 molecule an S_8 molecule a Cl_2 molecule an Ar molecule

The atoms in each of these molecules are held together by covalent bonds (apart, of course, from argon).

In the liquid or solid state, the molecules are held close to each other by van der Waals dispersion forces.

Electrical Conductivity

- Sodium, magnesium and aluminium are all good conductors of electricity. Conductivity increases as you go from sodium to magnesium to aluminium as they have free electrons.
- Silicon is a semiconductor.
- None of the rest conduct electricity.

The three metals, of course, conduct electricity because the delocalized electrons (the "sea of electrons") are free to move throughout the solid or the liquid metal.

In the silicon case, explaining how semiconductors conduct electricity is beyond the scope of this level. With a diamond structure, you mightn't expect it to conduct electricity, but it does!

The rest don't conduct electricity because they are simple molecular substances. There are no electrons free to move around.

Q3. Draw and discuss Trends in Melting and Boiling Points of si, p, Cl and Ar.

Answer

The chart shows how the melting and boiling points of the elements change as you go across the period. The figures are plotted in Kelvin rather than °C to avoid having negative values.

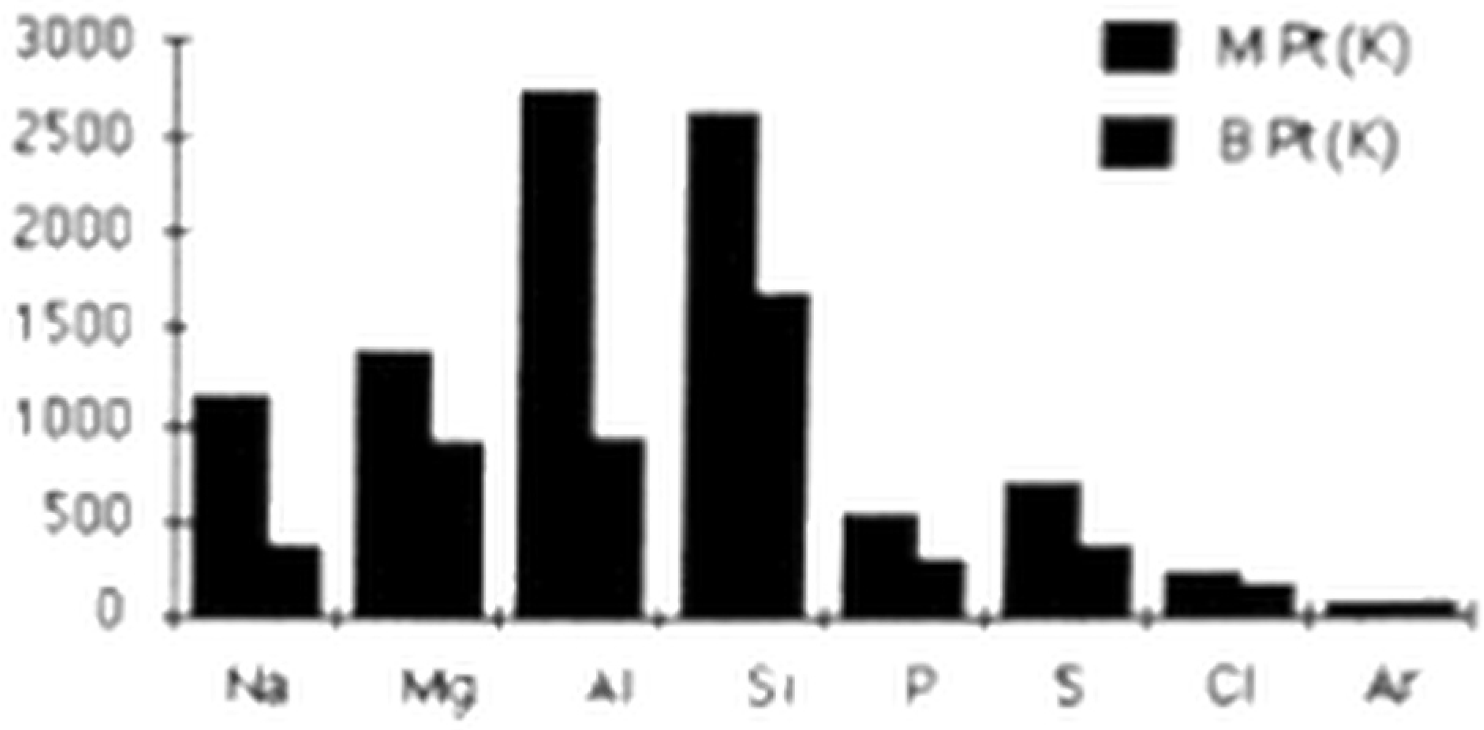


Fig 13.5 Melting and Boiling Point

Silicon

Silicon has high melting and boiling points because it is a giant covalent structure. You have to break strong covalent bonds before it will melt or boil.

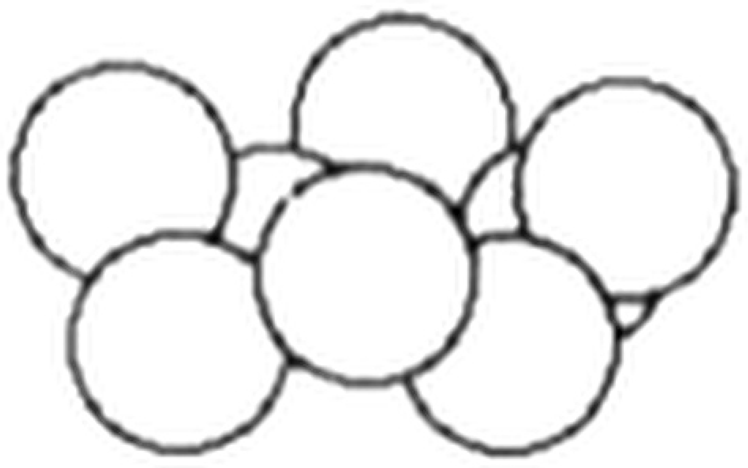
Because you are talking about a different type of bond, it isn't possible to try to directly compare silicon's melting and boiling points with aluminums.

The four molecular elements

Phosphorus, Sulphur, chlorine, and argon are simple molecular substances with only van der Waals attraction between the molecules. Their melting and boiling points will be lower than those of the first four members of the period which have giant structures.

The size of the melting and boiling points is governed entirely by the sizes of the molecule: Remember the structure of the molecules.


a P_4 molecule


an S_8 molecule


a Cl_2 molecule


an Ar molecule

Phosphorus

Phosphorus contains P_4 molecules. To melt phosphorus, you don't have to break any covalent bonds –just the much weaker van der Waals forces between the molecules.

Sulphur

Sulphur consists of S_8 rings of atoms. The molecules are bigger than phosphorus molecules, and so the van der Waals attractions will be stronger, leading to a higher meting and boiling point.

Chlorine

Chlorine, Cl_2, is a such smaller molecule with comparatively weak van der Waals attraction, and so chlorine will have a lower melting and boiling point than Sulphur or phosphorus.

Argon

Argon molecules are just simple argon atoms, Ar. The scope for van der Waals attractions between these is very limited and so the melting and boiling points of argon are lower again.

Q4. Give Chemical Reactions of the Period 3 Elements.

Answer

This section describes the reaction of the Period 3 elements from sodium to argon with water, oxygen and chlorine.

1) Reaction with Water

Sodium

Sodium has a very exothermic reaction with cold water producing hydrogen and a colorless solutions of sodium hydroxide.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

Magnesium

Magnesium has a very slight reaction with cold water, but burns in steam.

A very clean coil of magnesium dropped into cold water eventually gets covered in small bubbles of hydrogen which float it to the surface. Magnesium hydroxide is formed as a very thin layer on the magnesium and this tends to stop the reaction.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

Magnesium burns in steam with its typical white flame to produce white magnesium oxide and hydrogen.

$$Mg + H_2O \longrightarrow MgO + H_2$$

Aluminium

Aluminium powder heated in steam produces hydrogen and aluminium oxide. The reaction is relatively slow because of the strong aluminium oxide layer on the metal, and the build-up of even more oxide during the reaction.

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$

Phosphorus and Sulphur

These have no reaction with water.

Chlorine

Chlorine dissolves in water to some extent to give a green solution. A reversible reaction takes place to produce a mixture of hydrochloric acid and chloric(I) acid (hypochlorous acid).

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

In the presence of sunlight, the chloride(I) acid slowly decomposes to produce more hydrochloric acid, releasing oxygen gas, and you may come across an equation showing the overall change:

$$2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2$$

Argon

There is no reaction between argon and water.

2) Reaction with Oxygen

Sodium

Sodium burns in oxygen with an orange flame to produce a white solid mixture of sodium oxide and sodium peroxide.

For the simple oxide:

$$4Na + O_2 \longrightarrow 2Na_2O$$

For the peroxide:

$$2Na + O_2 \longrightarrow Na_2O_2$$

Magnesium

Magnesium burns in oxygen with an intense white flame to give white solid magnesium oxide.

$$2Mg + O_2 \longrightarrow 2MgO$$

Phosphorus

White phosphorus catches fire spontaneously in air, burning with a white flame and producing clouds of white smoke – a mixture of phosphorus (3) oxide and phosphorus (5) oxide.

The properties of these depend on the amount of oxygen available. In an excess of oxygen, the product will be almost entirely phosphorus (5) oxide.

For the phosphorus (3) oxide:

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

For the phosphorus (5) oxide:

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

Sulphur

Sulphur burns in air or oxygen on gentle heating with a pale blue fame. It produces colorless Sulphur dioxide gas.

$$S + O_2 \longrightarrow SO_2$$

Chlorine and argon

Despite having several oxides, chlorine won't react directly with oxygen. Argon doesn't react either.

Properties of the oxides of elements in period 3

Formula of Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} (P_4O_6)	SO_3 (SO_2)	Cl_2O_7 (Cl_2O)
State of Oxide	solid	solid	solid	solid	solid	liquid	liquid
Conduction of Electricity by Molten or liquid Oxide	good	good	good	v poor	Nil	Nil.	Nil.
Structure of oxide	Giant Structures				Simple molecular structure		
Enthalpy change of Formation of oxide at 298K/kJ mol-1	-416	-602	-1676	-910	-2984	-395	80
Enthalpy change of Formation of oxide at 298K/kJ mol-1 O/kJ	-416	-602	-559	-455	-298	-132	80
Effect of adding oxide to water	reacts to form NaOH (aq) alkaline solution	reacts to form $Mg(OH)_2$	does not react with water but it is amphoteric	does not react with water but it is acidic	P_4O_{10} reacts to form H_3PO_4 acid solution	SO_3 reacts to form H_2SO_4 acid solution	Cl_2O_7 reacts to form $HClO_4$ acid solution
Nature of Oxide	Basic (alkaline)	Basic (weakly alkaline)	Amphoteric	Acidic	Acidic	Acidic	Acidic

3) Reactions with chlorine

Sodium

Sodium burns in chlorine with a bright orange flame. White solid chloride is produces.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

Magnesium

Magnesium burns with its usual intense white flame to give with magnesium chloride.

$$Mg + Cl_2 \longrightarrow MgCl_2$$

Aluminium

Aluminium is often reacted with chlorine by passing dry chlorine over aluminium foil heated in a long tube. The aluminium burns in the stream of chlorine to produce very pale yellow aluminium chloride. This sublimes (turns straight from solid to vapour and back again) and collects further down the tube water it is cooler.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

Silicon

When chlorine is passed over silicon powder heated in a tube, it reacts to produce silicon tetrachloride. This is a colorless liquid which vaporizes and can be condensed further along the apparatus.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

Phosphorus

White phosphorus burns in chlorine to produce a mixture of two chlorides, phosphorus (3) chloride and phosphorus (5) chloride (phosphorus trichloride and phosphorus pentachloride).

Phosphorus (3) chloride is a colorless fuming liquid.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

Phosphorus (5) chloride is an off-white (going towards yellow) solid.

$$P4 + 10Cl_2 \longrightarrow 4PCl_5$$

Sulphur

When a stream of chlorine is passed over some heated Sulphur, it reacts to form an orange, evil-smelling liquid, disulphur dichloride, S_2Cl_2.

$$2S + Cl_2 \longrightarrow S_2Cl_2$$

Chlorine and argon

It obviously doesn't make sense to talk about chlorine reacting with itself, and argon doesn't react with chlorine.

Q5. Give Physical Properties of the Oxides of 3rd period elements.

Answer

This section explains the relationship between the physical properties of the oxides of Period 3 elements (sodium to chlorine) and their structures. Argon is obviously omitted because it doesn't form an oxide.

A quick summary of the trends

The oxides

The oxides we'll be looking at are:

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
				P_4O_6	SO_2	Cl_2O

Those oxides in the top row are known as the *highest oxides* of the various elements. These are the oxides where the Period 3 elements are in their highest oxidation states. In these oxides, all the outer electrons in the period 3 element are being involved in the bonding – from just the one with sodium, to all seven of chlorine's outer electrons.

I. **Structures**

The trend in structure is from the metallic oxides containing giant structures of ions on the left of the period via a giant covalent oxide (silicon dioxide) in the middle to molecular oxides on the right.

II. The metallic oxides (e.g. Sodium, magnesium, aluminium etc.)

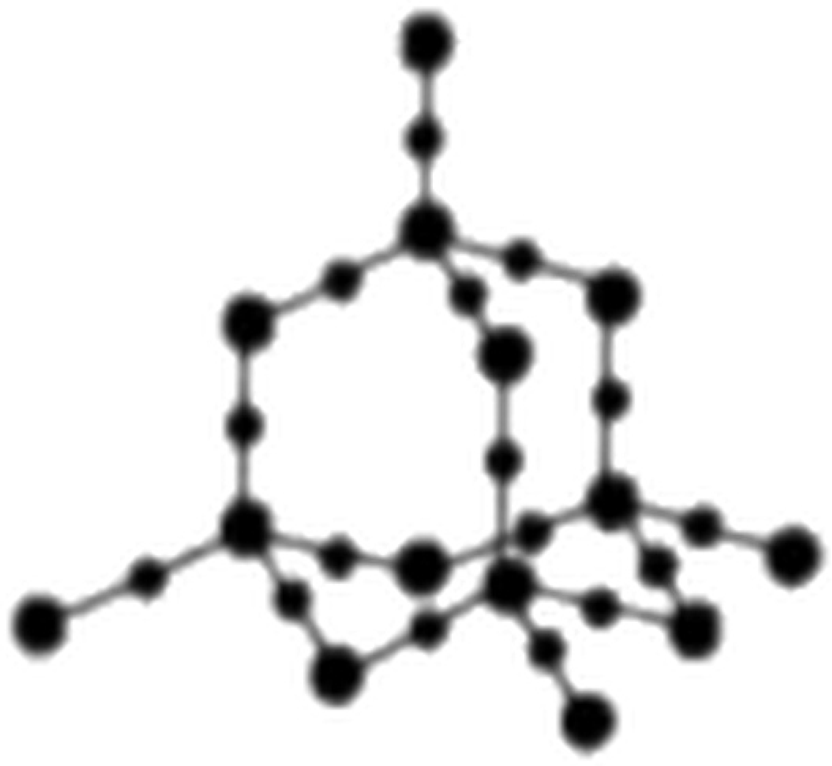
Sodium, magnesium and aluminium oxides structure/diagram is same as sodium chloride which you have read in previous classes.

III. Giant Covalent Oxides (e.g. Silicon dioxide (silicon (4) oxide))

i. **Structure**

Crystalline silicon has the same structure as diamond. To turn it into silicon dioxide, all you need to do is to modify the silicon structure by including some oxygen atoms.

- Notice that each silicon atom is bridged to its neighbors by an oxygen atom.



ii. The molecular oxides (e.g. Phosphorus, Sulphur and chlorine oxides)

A. The phosphorus oxides

Phosphorus has two common oxides, phosphorus (III) oxide, P_4O_6, and phosphorus(V) oxide, P4010.

i. **Phosphorus (111) oxide**

Phosphorus (III) oxide is a white solid, melting at 24°C and boiling at 173°C.

The structure of its molecules best worked out starting from a P4 molecule which is a little tetrahedron

a P_4 molecule

Fig. 13.6

Pull this apart so that you can see the bonds...

[illegible]
Fig. 13 7

and then replace the bonds by new bonds linking the phosphorus atoms via oxygen atoms. These will be in a V-shape (rather like in water).

P400 rndocAc

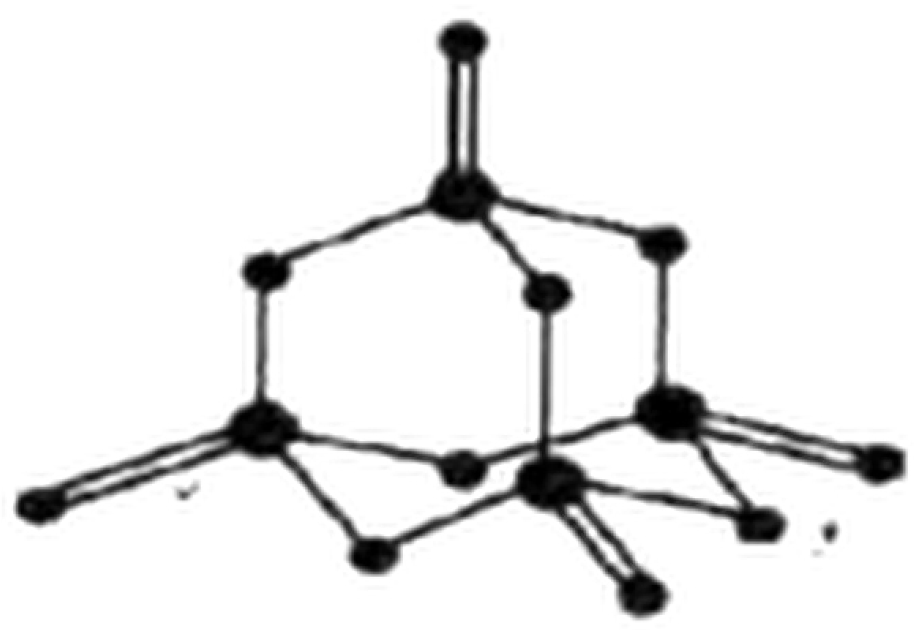
The phosphorus is using only three of its outer electrons (the 3 unpaired p electrons) to form bonds with the oxygens.

ii) Phosphorus(V) oxide

Phosphorus(V) oxide is also a white solid, subliming (turning straight from solid to vapour) at 300°C. In this case, the phosphorus uses all five of its outer electrons in the bonding.

Solid phosphorus(V) oxide exists in several different forms - some of them polymeric. We are going to concentrate on a simple molecular form, and this is also present in the vapour.

This is most easily drawn starting from P_4O_6. The other four oxygens are attached to the four phosphorus atoms via double bonds.



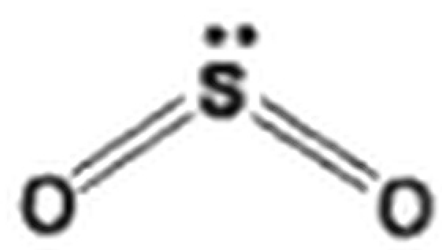
• P40 iA prnatous•

B) The Sulphur oxides

Sulphur has two common oxides, Sulphur dioxide (Sulphur (IV) oxide), SO_2, and Sulphur trioxide (Sulphur (VI) oxide), SO_3.

I) Sulphur dioxide

Sulphur dioxide is a colorless gas at room temperature with an easily recognized choking smell. It consists of simple SO_2 molecules.

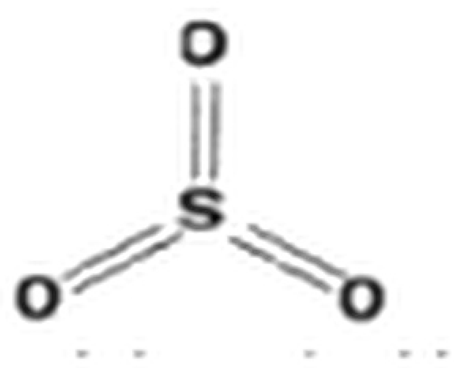


The Sulphur uses 4 of its outer electrons to form the double bonds with the oxygen, leaving the other two as a lone pair on the Sulphur. The bent shape of SO_2 is due to this lone pair.

II) Sulphur trioxide

Pure Sulphur trioxide is a white solid with a low melting and boiling point.

Gaseous Sulphur trioxide consists of simple SO_3 molecules in which all six of the Sulphur's outer electrons are involved in the bonding.



There are various forms of solid Sulphur trioxide. The simplest one is a trimer, S_2O_3, where three SO_3 molecules are joined up and arranged in a ring.

Fig. 13.8

There are also other polymeric forms in which the SO_3 molecules join together in long chains. For example:

Fig. 13.9

The fact that the simple molecules join up in this way to make bigger structures is what makes the Sulphur trioxide a solid rather than a gas.

C) The chlorine oxides

Chlorine forms several oxides. Here we discuss only two which are - chlorine(I) oxide, $C1_20$, and chlorine (VII) oxide, $C1_20_7$.

Chlorine(I) oxide

Chlorine (1) oxide is a yellowish-red gas at room temperature. It consists of simple small molecules.

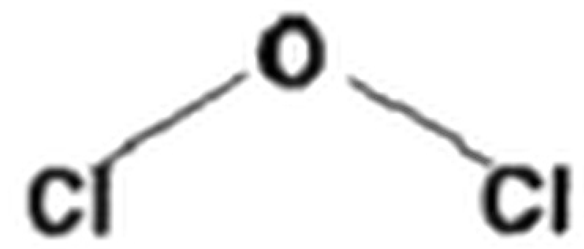


Fig. 13.10

In this structure chlorine uses its one outer electron and bonds with oxygen.

Chlorine (VII) oxide

Chlorine (VII) oxide is a colorless oily liquid at room temperature.

In chlorine (VII) oxide, the chlorine uses all of its seven outer electrons and bonds with oxygen. This produces a much bigger molecule.

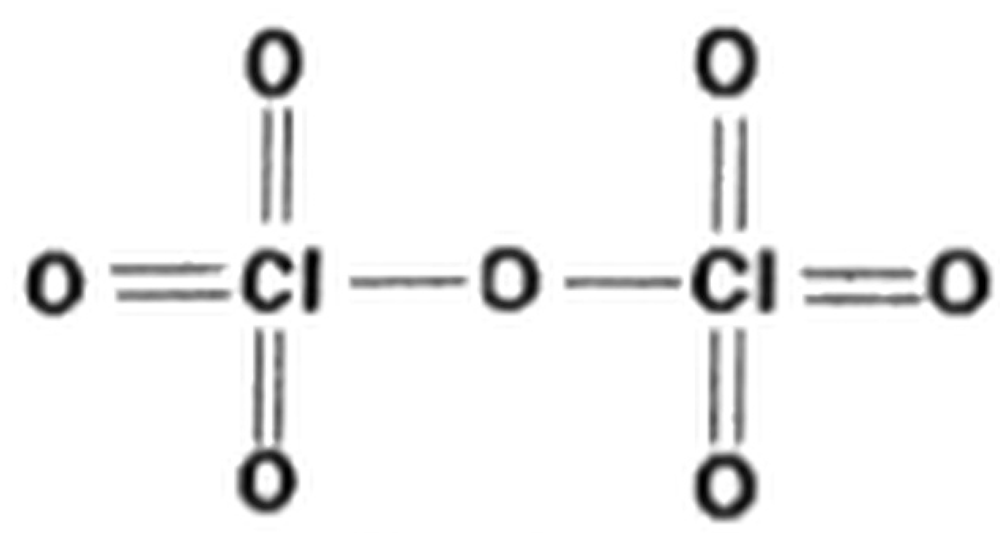


Fig. 13.11

ii) Melting and boiling points

The giant structures (the metal oxides and silicon dioxide) will have high melting and boiling points because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in three dimensions.

The oxides of phosphorus, Sulphur and chlorine consist of individual molecules - some small and simple; others polymeric.

The attractive forces between these molecules will be van der Waals dispersion and dipole-dipole interactions. These vary in size depending on the size, shape and polarity of the various molecules - but will always be much weaker than the ionic or covalent bonds you need to break in a giant structure.

These oxides tend to be gases, liquids or low melting point solids.

Q6. Give Acid-Base Behavior of the Oxides of 3rd period

Answer

This topic looks at the reactions of the oxides of Period 3 elements (sodium to chlorine) with water and with acids or bases where relevant. (Take quick review from table 13.2)

iii) Electrical conductivity

None of these oxides has any free or mobile electrons. That means that none of them will conduct electricity when they are solid.

The ionic oxides can, however, undergo *electrolysis* when they are molten. They can conduct electricity because of the movement of the ions towards the electrodes and the discharge of the ions when they get there.

i. Trend in acid-base behavior

The trend in acid-base behaviour is shown in various reactions, but as a simple summary:

The trend is from strongly basic oxides on the left-hand side to strongly acidic ones on the right, via an amphoteric oxide (aluminium oxide) in the middle. An amphoteric oxide is one which shows both acidic and basic properties.

ii) Reactions of Oxides with water, Acids and Bases

Chemistry of the individual oxides

Sodium oxide (Na_20)

Sodium oxide is a simple strongly basic oxide. it is basic because it contains the oxide ion, 0^{2-}, which is a very strong base with a high tendency to combine with hydrogen ions.

Reaction with water

Sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution. Depending on its concentration, this will have a pH around 14.

$$Na_20 + H_2O \longrightarrow 2NaOH$$

Reaction with acids

As a strong base, sodium oxide also reacts with acids. For example, it would react with dilute hydrochloric acid to produce sodium chloride solution.

$$Na_20 + 2HCl \longrightarrow 2NaCl + H_2O$$

Magnesium oxide (MgO)

Magnesium oxide is again a simple basic oxide, because it also contains oxide ions. However, it isn't as strongly basic as sodium oxide because the oxide ions aren't so free.

In the sodium oxide case, the solid is held together by attractions between l+ and lions. In the magnesium oxide case, the attractions are between 2+ and 2-. It takes more energy to break these.

Reaction with water

If you shake some white magnesium oxide powder with water, nothing seems to happen (it doesn't look as if it reacts). However, if you test the pH of the liquid, you find that it is somewhere around pH 9 (showing that it is slightly alkaline).

There must have been some slight reaction with the water to produce hydroxide ions in solution. Some magnesium hydroxide is formed in the reaction, but this is almost insoluble - and so not many hydroxide ions actually get into solution.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

Reaction with acids

Magnesium oxide reacts with acids as you would expect any simple metal oxide to react. For example, it reacts with warm dilute hydrochloric acid to give magnesium chloride solution.

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$

Aluminium oxide (Al_20_3)

As it is amphoteric oxide. It has reactions as both a base and an acid.

Reaction with water

Aluminium oxide doesn't react in a simple way with water and doesn't dissolve in it. Although it still contains oxide ions, they are held too strongly in the solid lattice to, react with the water.

Reaction with acids

Aluminium oxide will react with hot dilute hydrochloric acid to give aluminium chloride solution.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

Reaction with bases

Aluminium oxide has also got an acidic side to its nature, and it shows this by reacting with bases such as sodium hydroxide solution.

Various aluminates are formed, compounds where the aluminium is found in the negative ion. This is possible because aluminium has the ability to form covalent bonds with oxygen.

With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colorless solution of sodium tetra-hydroxoaluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$$

Phosphorus(V) oxide (P_40_{10})

Reaction with Water

Phosphorus(V) oxide reacts violently with water to give a solution containing a mixture of acids, the nature of which depends on conditions. We usually just consider one of these, phosphoric(V) acid, H_3PO_4 (also known just as phosphoric acid or as orthophosphoric acid).

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

O

||

HO — P — OH

|

OH

Reaction with Base:

As it is acidic so it reacts with NaOH as follows:

$$NaOH + H_3PO_4 \longrightarrow NaOh_2PO_4 + H_2O$$

$$2NaOH + H_3PO_4 \longrightarrow NaOh_2PO_4 + 2H_2O$$

$$3NaOH + H_3PO_4 \longrightarrow NaOh_2PO_4 + 3H_2O$$

Again, if you were to react phosphorus(V) oxide directly with sodium hydroxide solution rather than making the acid first, you would end up with the same possible salts.

This is getting ridiculous, and so I will only give one example out of the possible equations:

$$12NaOH + P_4O_{10} \longrightarrow 4Na_3PO_4 + 6H_2O$$

The sulphur Oxides (SO_x)

We are going to be looking at sulphur dioxide, SO_2, and sulphur trioxide, SO_3.

Sulphur Dioxide

Reaction with Water:

Sulphur dioxide is fairly solution in water, reacting with it to give a solution of sulphurous acid, H_2SO_3.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Reaction with Base:

As it is acidic so it reacts with NaOH and CaO as follows:

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

$$CaO + SO_2 \longrightarrow CaSO_3$$

Sulphur trioxide

Sulphur trioxide reacts violently with water to produce a fog of concentrated sulphuric acid droplets.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Reaction with Base:

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

In principle, you can also get sodium hydrogen sulphate solution by using half as much sodium hydroxide and just reacting with one of the two acidic hydrogens in the acid. In practice, I personally have never ever done it.

Sulphur trioxide itself will also react directly with bases to form sulphates. For example, it will react with calcium oxide to form calcium sulphate. This is just like the reaction with sulphur dioxide described above.

$$CaO + SO_3 \longrightarrow CaSO_4$$

The chlorine oxides ($C1_20_x$)

Chlorine forms several oxides, but the only two are chlorine (VII) oxide, 01_20_7, and chlorine(I)oxide, $C1_20$. Chlorine (VII) oxide is also known as Dichlorine heptoxide, and chlorine(I) oxide as Dichlorine monoxide.

Chlorine(V11) oxide

Chlorine (VII) oxide is the highest oxide of chlorine - the chlorine is in its maximum oxidation state of +7. It continues the trend of the highest oxides of the Period 3 elements towards being stronger acids.

Reaction with Water:

Chlorine (VII) oxide reacts with water to give the very strong acid, chloric (VII) acid - also known as perchloric acid. The pH of typical solutions will, like sulphuric acid, be around 0.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

Reaction with Base:

Chloric (VII) acid reacts with sodium hydroxide solution to form a solution of sodium chlorate (VII).

$$NaOH + HClO_4 \longrightarrow NaClO_4 + H_2O$$

Chlorine(VII) oxide itself also reacts with sodium hydroxide solution to give the same product.

$$2NaOH + Cl_2O_7 \longrightarrow 2NaClO_4 + H_2O$$

Chlorine(I) oxide

Reaction with Base:

Chlorine(I) oxide is far less acidic thin chlorine (VII) oxide. It reacts with water to some extent to give chloric(I) acid, HOCl - also known as hypochlorous acid.

$$Cl_2O + H_2O \longrightarrow 2HOC$$

Reaction with Base:

Chloric(I) acid reacts with sodium hydroxide solution to give a solution of sodium chlorate (1) (sodium hypochlorite).

$$NaOH + HOCl \longrightarrow NaOCl + H_2O$$

Chlorine(I) oxide also reacts directly with sodium hydroxide to give the same product.

$$2NaOH + Cl_2O \longrightarrow 2NaOCl + H_2O$$

Q7. Discuss Chlorides of the Period 3 Elements.

Answer

This topic looks at the structures of the chlorides of the Period 3 elements (sodium to sulphur), their physical properties and their reactions with water.

1) The structures

Sodium chloride and magnesium chloride are ionic and consist of giant ionic lattices at room temperature

Aluminium chloride and phosphorus(V) chloride are tricky! They change their structure from ionic to covalent when the solid turns to a liquid or vapour. The others are simple covalent molecules.

2) Melting and boiling points

Sodium and magnesium chlorides are solids with high melting and boiling points because of the large amount of heat which is needed to break the strong ionic attractions.

The rest are liquids or low melting point solids. Leaving aside the aluminium chloride and phosphorus(V) chloride cases where the situation is quite complicated, the attractions in the others will be much weaker intermolecular forces such as van der Waals dispersion forces. These vary depending on the size and shape of the molecule, but will always be far weaker than ionic bonds.

3) Electrical conductivity

Sodium and magnesium chlorides are ionic and so will undergo *electrolysis* when they are molten. Electricity is carried by the movement of the ions and their discharge at the electrodes.

In the aluminium chloride and phosphorus(V) chloride cases, the solid doesn't conduct electricity because the ions aren't free to move. In the liquid (where it exists - both of these sublimes at ordinary pressures), they have converted into a covalent form, and so don't conduct either.

The rest of the chlorides don't conduct electricity either solid or molten because they don't have any ions or any mobile electrons.

4) Reactions with water

Sodium and magnesium chloride just dissolve in water

The other chlorides all react with water in a variety of ways described below for each individual chloride. The reaction with water is known as *hydrolysis*.

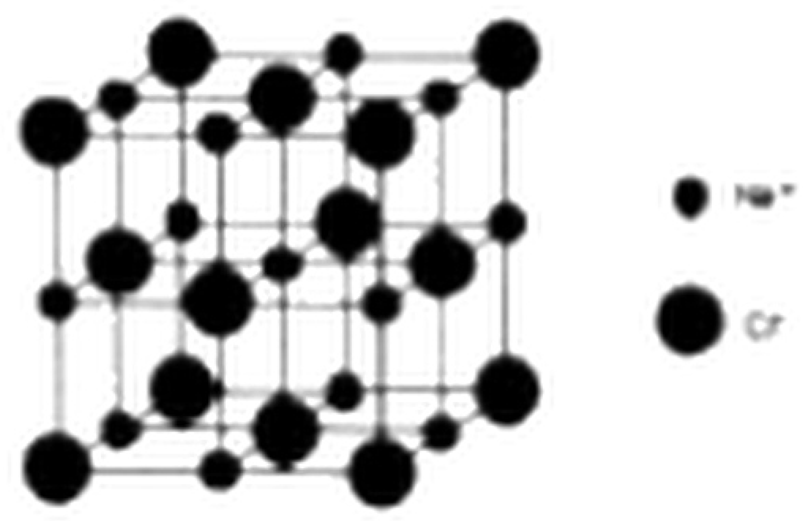
The individual chlorides

Sodium chloride, NaCl

Sodium chloride is a simple ionic compound consisting of a giant array of sodium and chloride ions.

A small representative bit of a sodium chloride lattice looks like this:

This is normally drawn in an exploded form as:



The strong attractions between the positive and negative ions need a lot of heat energy to break, and so sodium chloride has high melting and boiling points.

It doesn't conduct electricity in the solid state because it hasn't any mobile electrons and the ions aren't free to move. However, when it melts it undergoes electrolysis.

Sodium chloride simply dissolves in water to give a neutral solution.

Magnesium chloride, $MgCl_2$

Magnesium chloride is also ionic, but with a more complicated arrangement of the ions to allow for having twice as many chloride ions as magnesium ions.

Again, lots of heat energy is needed to overcome the attractions between the ions, and so the melting and boiling points are again high.

Solid magnesium chloride is a non-conductor of electricity because the ions aren't free to move. However, it undergoes electrolysis when the ions become free on melting.

Magnesium chloride dissolves in water to give a faintly acidic solution (pH = approximately 6).

When magnesium ions are broken off the solid lattice and go into solution, there is enough attraction between the 2+ ions and the water molecules to get co-ordinate (dative covalent) bonds formed between the magnesium ions and lone pairs on surrounding water molecules.

Hexaaquamagnesium ions are formed, $[Mg(H20)6]^{2+}$.

$$MgC12_{(3)} + 6H2O(1) \longrightarrow Mg\,(H\,2^{0})63^{2+}(e4) + 2Crlac1$$

Ions of this sort are acidic.

Aluminium chloride, $AlC1_3$

$$Al_2Cl \longrightarrow 2AlCl_3$$

Solid aluminium chloride doesn't conduct electricity at room, temperature because the ions aren't free to move. Molten aluminium chloride (only possible at increased pressures) doesn't conduct electricity because there aren't any ions any more.

The reaction of aluminium chloride with water is surprising. If you drop water onto solid aluminium chloride, you get a violent reaction producing clouds of steamy fumes of hydrogen chloride gas.

The aluminium chloride reacts with the water rather than just dissolving in it. In the first instance, hexaaquaaluminium ions are formed together with chloride ions.

$$AlCl_{3(s)} + 6H_2O_{(l)} \longrightarrow [Al(H_2O)_6]^{3+}{}_{(aq)} + 3Cl^-{}_{(aq)}$$

You will see that this is very similar to the magnesium chloride equation given above - the only real difference is the charge on the ion.

Silicon tetrachloride, $SiCl_4$

Silicon tetrachloride is a simple covalent chloride. There isn't enough electronegativity difference between the silicon and the chlorine for the two to form ionic bonds.

Do you know?

Silicon tetrachloride is a colorless liquid at room temperature which fumes in moist air. The only attractions between the molecules are van der Waals dispersion forces.

It doesn't conduct electricity because of the lack of ions or mobile electrons.

It fumes in moist air because it reacts with water in the air to produce hydrogen chloride. If you add water to silicon tetrachloride, there is a violent reaction to produce silicon dioxide and fumes of hydrogen chloride. In a large excess of water, the hydrogen chloride will, of course, dissolve to give a strongly acidic solution containing hydrochloric acid.

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

The phosphorus chlorides

There are two phosphorus chlorides - phosphorus (III) chloride, PCl_3, and phosphorus(V) chloride, PCl_5.

Phosphorus (III) chloride (phosphorus trichloride), PCl_3

This is another simple covalent chloride - again a fuming liquid at room temperature.

Do you know:

Phosphorus (III) chloride reacts violently with water. You get phosphorous acid, H_3P03, and fumes of hydrogen chloride (or a solution containing hydrochloric acid if lots of water is used).

$$PCl_3 + 3H_20 \longrightarrow H_3P0_3 + 3HCl$$

Phosphorus(V) chloride (phosphorus pentachloride), PCl_5

Unfortunately, phosphorus(V) chloride is structurally more complicated.

Phosphorus(V) chloride is a white solid which sublime at 163°C. The higher the temperature goes above that, the more the phosphorus(V) chloride dissociate (splits up reversibly) to give phosphorus (111) chloride and chlorine.

$$PCl_5 \longleftrightarrow PCl_3 + Cl_2$$

Phosphorus(V) chloride has a violent reaction with water producing fumes of hydrogen chloride. As with the other covalent chlorides, if there is enough water present, these will dissolve to give a solution containing hydrochloric acid.

The reaction happens in two stages. In the first, with cold water, phosphorus oxychloride, $POC1_3$, is produced along with HC1.

$$PCl_5 + H_20 \longrightarrow POCl_3 + 2HCl$$

If the water is boiling, the phosphorus(V) chloride reacts further to give phosphoric(V) acid and more HC1. Phosphoric(V) acid is also known' just as phosphoric acid or as orthophosphoric acid.

$$P0013 + 3H20 \longrightarrow H3PO4 + 3HCl$$

The overall equation in boiling water is just a combination of these:

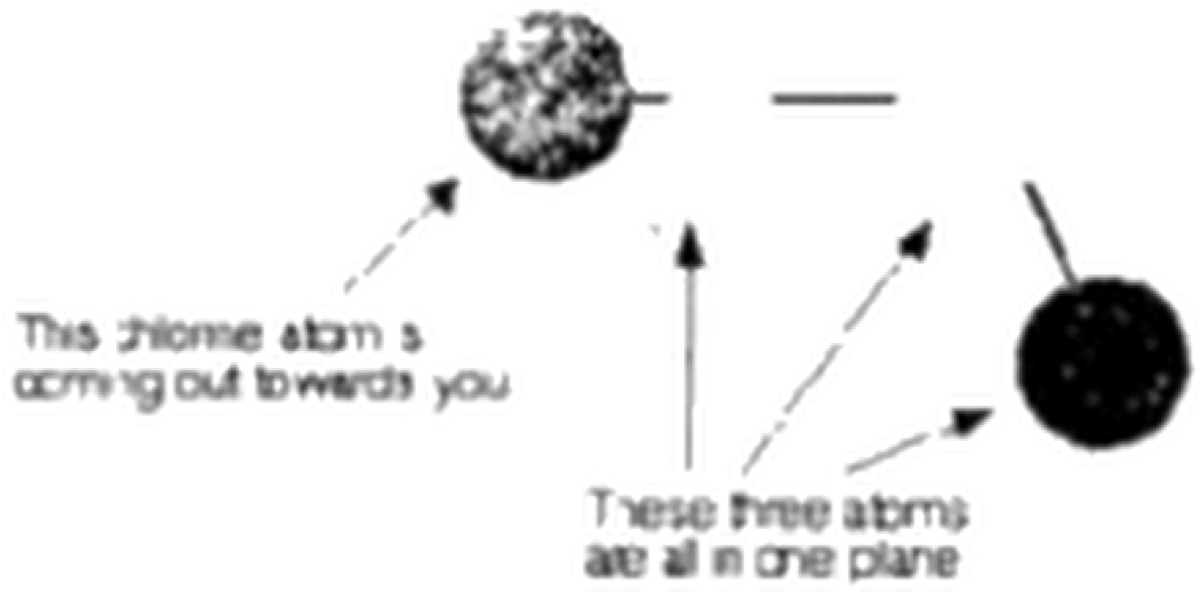
$$PCl_5 + 4H_20 \longrightarrow H_3PO_4 + 5HC1$$

Disulphur dichloride, S_2Cl_2

Disulphur dichloride is formed when chlorine reacts with hot sulphur.

Disulphur dichloride is a simple covalent liquid (orange and smelly).

The shape is difficult to draw convincingly. The atoms are all joined up in a line but twisted:



The reason for drawing the shape is to give a hint about what sort of intermolecular attractions are possible. There is no plane of symmetry in the molecule and that means that it will have an overall permanent dipole.

> Do you know?
>
> Disulphur Dichloride has Van der Waals dispersion forces and dipole-dipole attractions.

Disulphur dichloride reacts slowly with water to produce a complex mixture of things including hydrochloric acid, sulphur, hydrogen sulphide and various Sulphur containing acids and anions (negative ions).

Q8. Discuss Hydroxides of The Period 3 Elements.

Answer

This topic looks briefly at how the chemistry of the "hydroxides" of the Period 3 elements from sodium to chlorine varies as you cross the period.

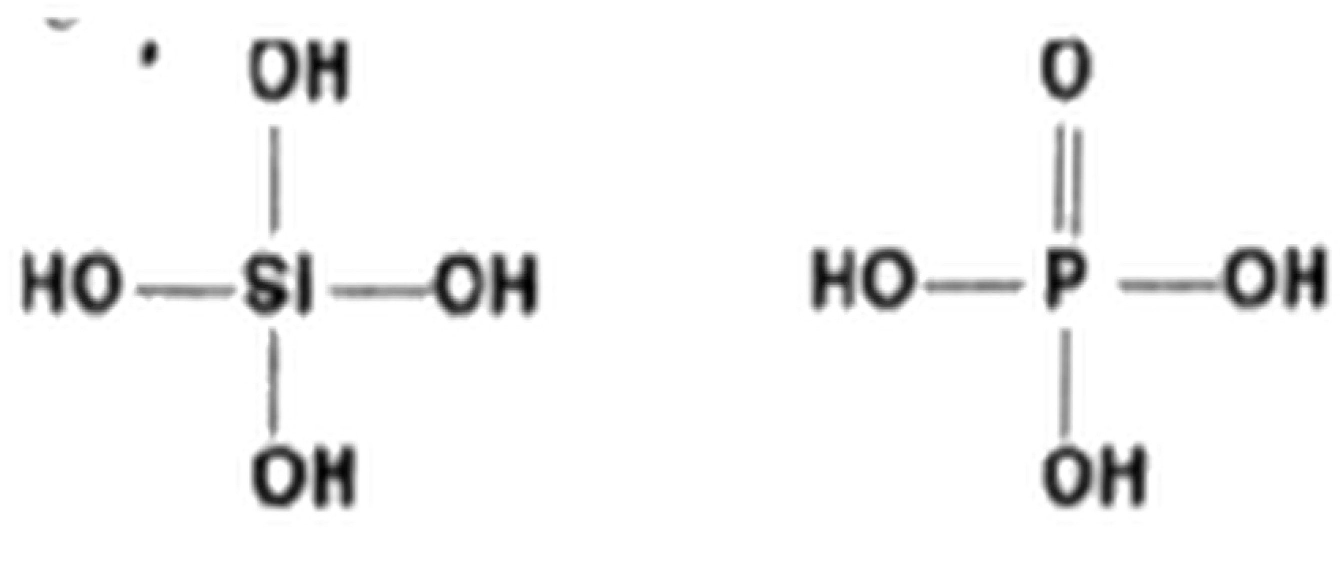
> A quick summary of the trends.
>
> Sodium and magnesium hydroxides.

Aluminium hydroxide, like aluminium oxide, is amphoteric - it has both basic and acidic properties.

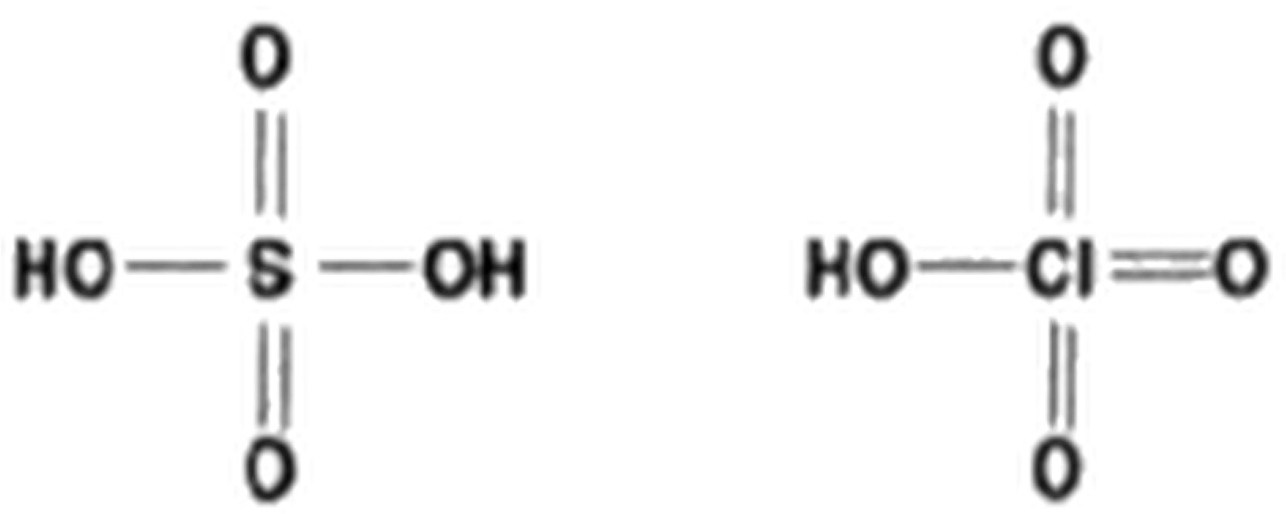
The other "hydroxides"

In all of these –OH groups covalently bound to the atom from period 3. These compounds are all acidic – ranging from the very weakly acidic silicic acids (one of which is shown below) to the very strong sulphuric or chloric acids.

There are other acids (also containing –OH groups) formed by these elements, but these are the ones where the period 3 elements is in its highest oxidation state.



orthosilicic acid phosphoric(V) acid



1) Sodium and magnesium hydroxides

These are both basic because they contain hydroxide ions - a strong base.

Both react with acids to form salts. For example, with dilute hydrochloric acid, you get colorless solutions of sodium chloride or magnesium chloride.

$$NaoH + HCl \longrightarrow NaCl + H_2O$$

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

2) Aluminium hydroxide

Aluminium hydroxide is amphoteric.

Like sodium or magnesium hydroxides, it will react with acids. This is showing the basic side of its nature.

With dilute hydrochloric acid, a colorless solution of aluminium chloride is formed.

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

But aluminium hydroxide also has an acidic side to its nature. It will react with sodium hydroxide solution to give a colorless solution of sodium tetrahydroxoaluminate.

$$Al(OH)_3 + NaCH \longrightarrow NaAl(OH)_4$$

3) The other "hydroxides"

1) Orthosilicic acid is very weak.

2) Phosphoric(V) acid is a weak acid - although somewhat stronger than simple organic acids like ethanoic acid.

3) Sulphuric acid and chloric (VII) acids are both very strong acids.

The main ·factor in determining the strength of the acid is how stable the anion (the negative ion) is once the hydrogen has been removed. This in turn depends on how much the negative charge can be spread around the rest of the ion.

If the negative charge stays entirely on the oxygen atom left behind from the -OH group, it will be very attractive to hydrogen ions. The lost hydrogen ion will be easily recaptured and the acid will be weak.

On the other hand, if the charge can be spread out (delocalized) over the whole of the ion, it will be so "dilute" that it won't attract the hydrogen back very easily. The acid will then be strong.

Q9. Discuss Group 1 Elements.

Answer

1) Atomic and Physical Properties of the Group 1 Elements

This section explores the trends in some atomic and physical properties of the Group 1 elements - lithium, sodium, potassium, rubidium and cesium. You will find separate sections below covering thy trends in atomic radius, first ionization energy, electronegativity, melting and boiling points, and density.

2) Trends in Atomic Radius

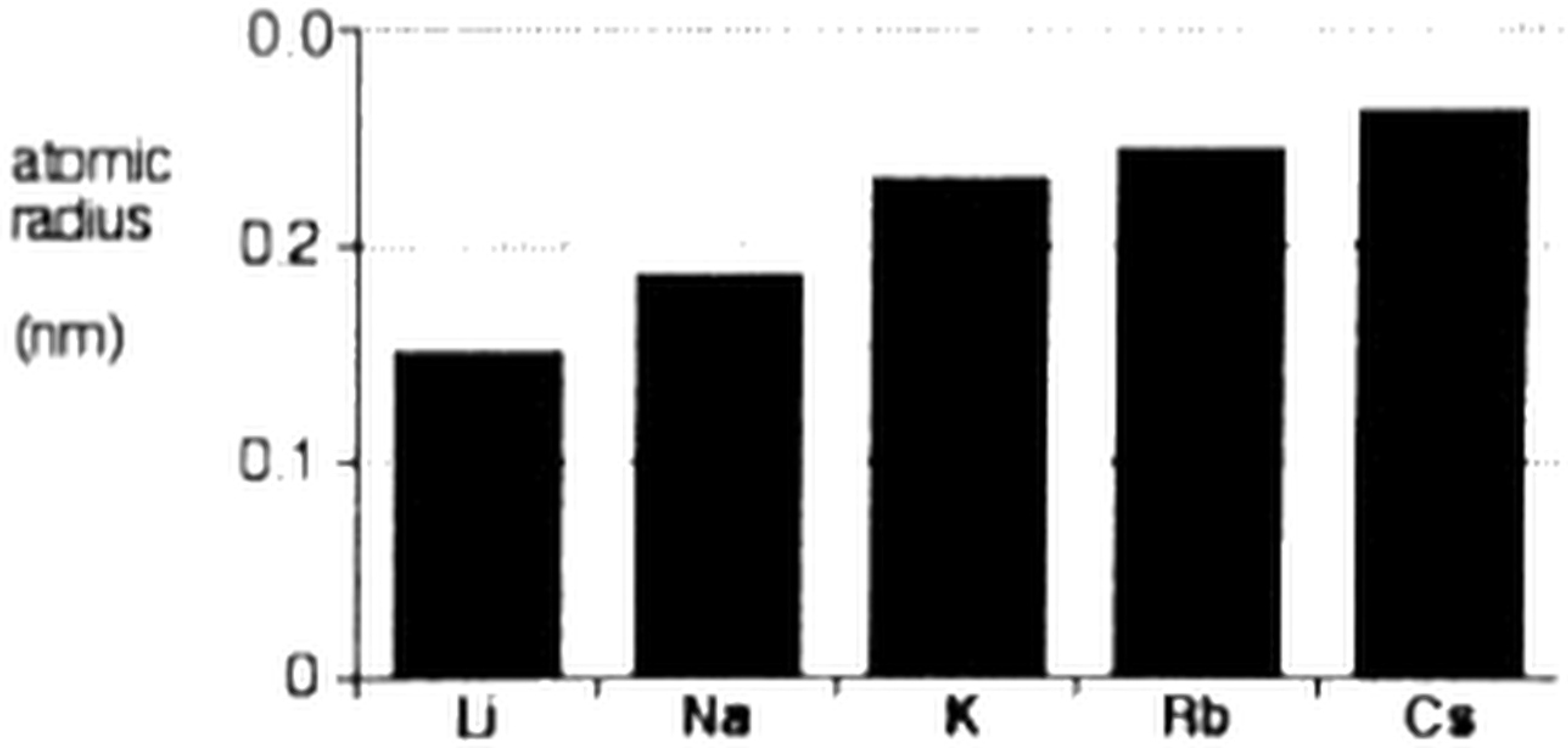


Fig. 13.12 Atomic Radii of the Group 1 elements

As we move from lithium to cesium, an extra shell of electrons is added to each element. The addition of an extra shell increases the atomic volume. We find therefore, that there in an increase of atomic and ionic radii (of M+ ions) as we move from lithium to cesium.

Some Physical Properties of alkali metals					
Property	Li	Na	K	Rb	Cs
Atomic weight	6.94	22.99	39.1	25.47	132.91
Atomic volume	12.97	23.63	45.36	55.8	69.95
Atomic (i.e. metallic radius for coordination number 12)	1.55	1.9	2.35	2.46	2.6
Covalent radius	1.23	1.54	2.03	2.16	2.36
Ionic radius M+ ions	0.6	0.95	1.33	1.48	1.69

Boiling Point	1330	892	760	688	670
Ionizations energy (kj/mol) (I1)	520.3	495.8	418.9	403.0	375.7
	7298.1	4562.4	3051.4	2633.0	2230.0
Standard oxidation potential	3.04	2.71	2.99	2.99	2.99
Sublimation energy(ev/ion)	1.7472	1.2432	1.032	0.984	0.9024
Hydration Energy(eV/ion)	5.904	3.792	3.6955	3.36	0.624
Electronegativity	1	0.9	0.8	0.8	0.7
Colour of the flame	Crimson Red	Golden Yellow	Violet	Violet	Violet
Heat of atomization at 25c (cV/atm)	1.7472	1.2432	1.032	0.984	0.9024
Ionic conduction of M+ ion	33.5	43.5	64.6	67.5	63

3) Trends in First Ionization Energy

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions - in other words, for I mole of this process:

$$X_{(g)} \longrightarrow X^{+}_{(g)} + e^{-}$$

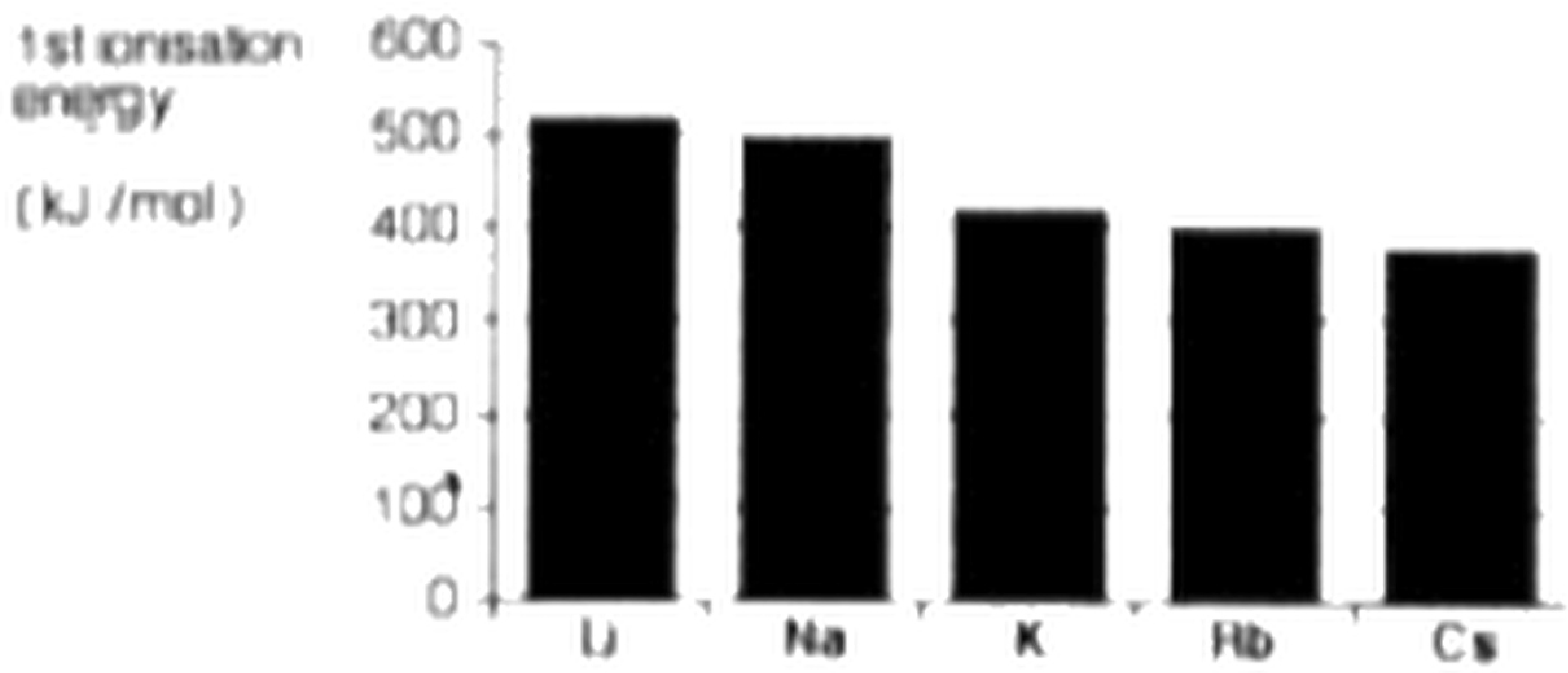


Fig. 13.13 First-Ionization Energy of the Group 1 elements

Notice that first ionization energy falls as you go down the group.

We know that alkali metal has only one electron in their outermost shell (nsl electron). This nsl electron is so weakly held with the nucleus that it can be removed very easily. Alkali metals therefore have low ionization energies.

As the distance of ns I electron from the nucleus increases on moving from Li to Cs its

removal becomes more and more easy as we proceed from Li to Cs i.e. the amount of energy (ionization energy) used in the removal of nsl electron is maximum in case of energies of alkali metals go on decreasing from Li to Cs as shown in table 13.3.

The second ionization energies are fairly high, since the loss of the second electron from M+ cation which has a noble gas configuration is quite difficult.

4) Trends in Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.

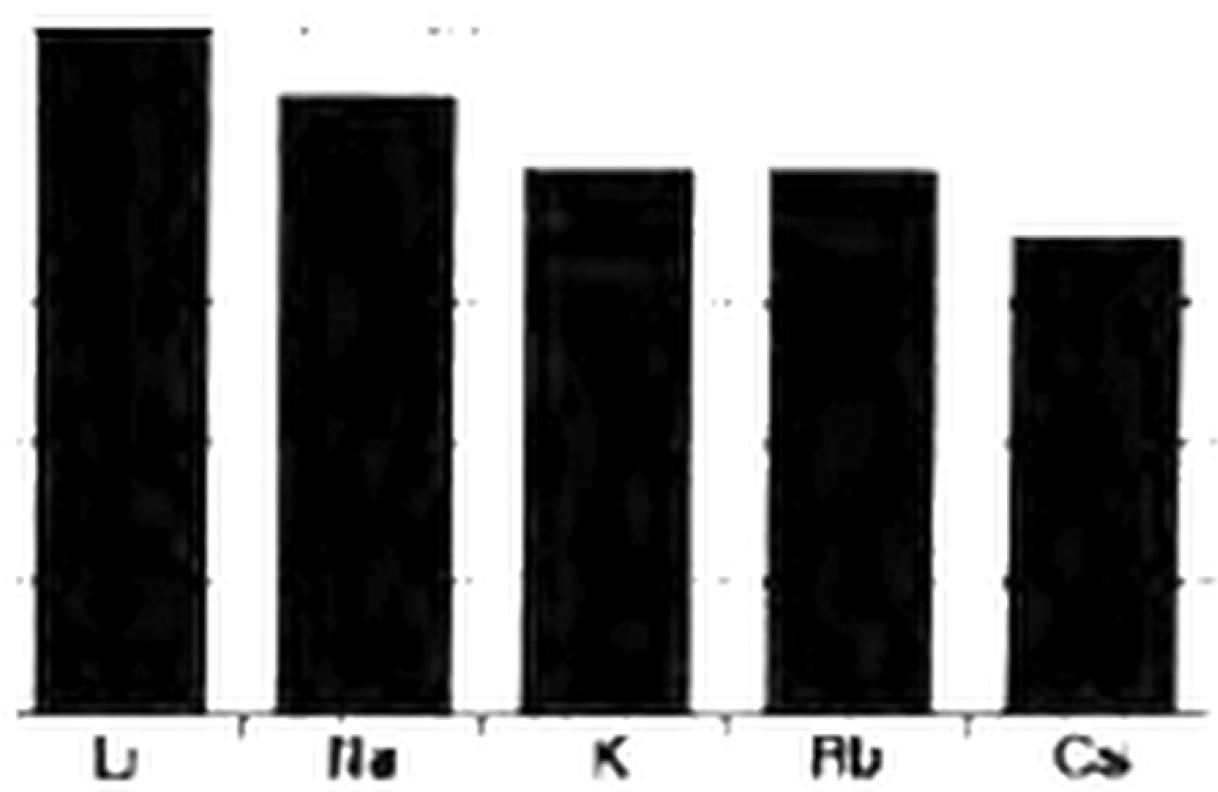


Fig 13.14 Electronegativities of the Group 1 elements

We have seen that the outer electron (i.e. ns I electron) of the atom of alkali metals is loosely held with the nucleus and hence it can be easily excited to the higher energy levels even by a small amount of heat energy (e.g. by heating the metals or their salts into Bunsen burner). During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic. Since the amount of energy absorbed during the excitation process is different in different atoms, different colors are imparted by the atoms to the flame. The property of alkali metals to give coloration in the burner flame has been used to detect their presence in salts by a test, known as flame test.

5) Trends in Melting and Boiling Points

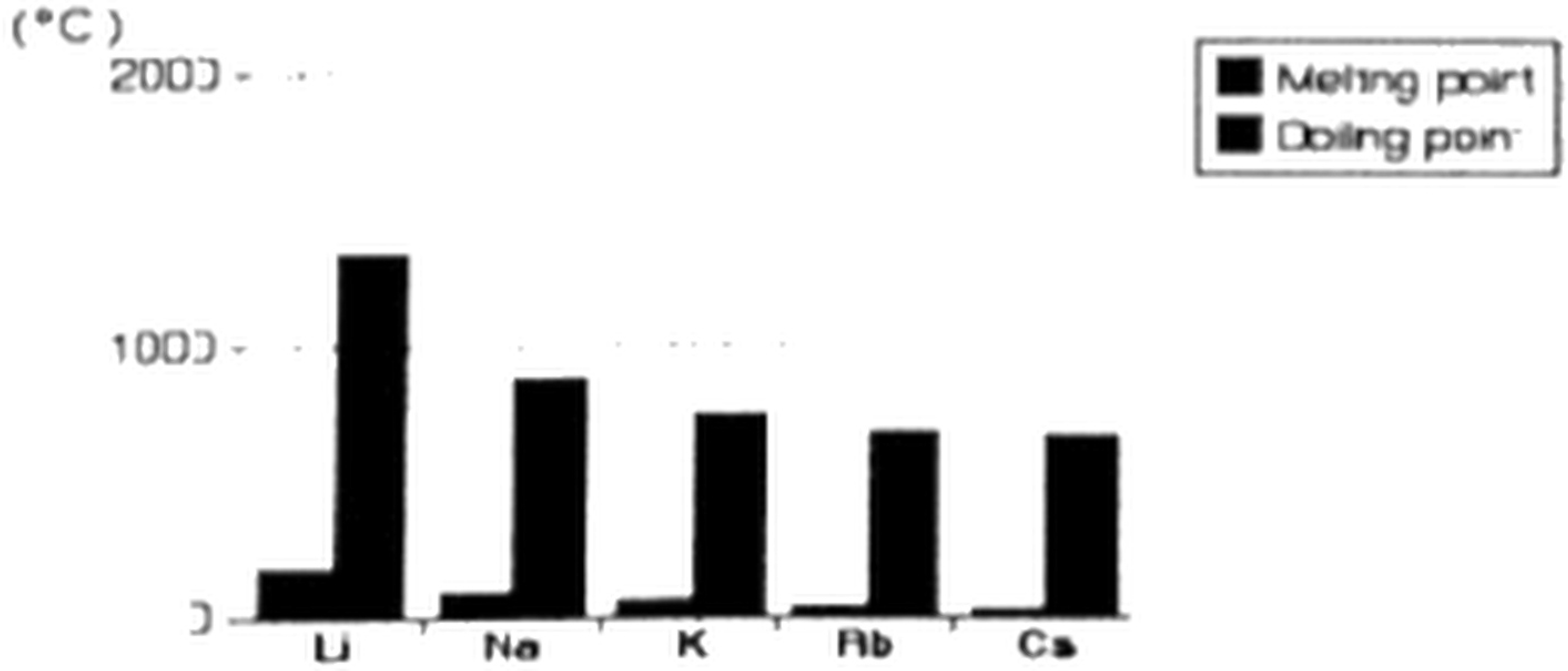


Fig 13.15 Melting and Boiling Points of the Group 1 elements

You will see that both the melting points and boiling points fall as you go down the Group.

The melting and boiling points are very low because of the presence of weak inner atomic bonds in the solid state of the alkali metals. These bonds are due to their atomic radii and mainly due to their electronic configuration having a single valence electron as compared to large number of available vacant orbital. As the size of the metal atoms increases, the repulsion of the non-bonding electrons also increases. This increase in the repulsion of non-bonding electron decreases the melting and boiling points of alkali metals when we move from Li to Cs (as shown in table 13.3).

Trends in Density

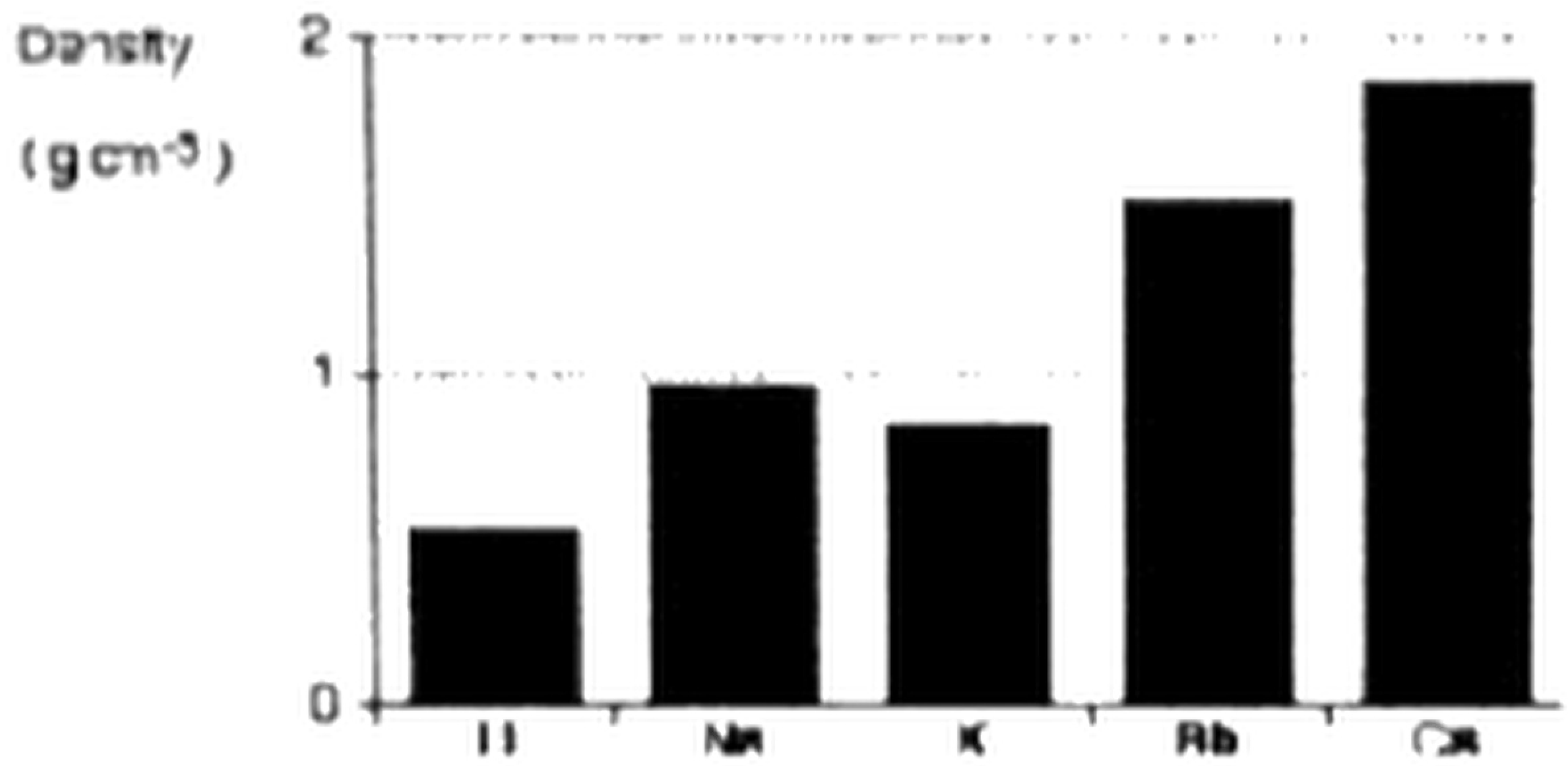


Fig. 13.16 Densities of the Group 1 elements

The densities of alkali metals are quite low due to the large atomic volumes. Li, Na and K are lighter than water. The densities increase with the increase in atomic from Li to Cs indicating that greater atomic with more than compensates for the bigger size of the atoms. K is however, lighter than Na which is due to an unusual increase in atomic size of K.

Elements	Li	Na	K	Rb	Cs
Densities at 0°C (g/c.c)	0.534	0.972	0.859	1.525	1.903

6) Trends in Reactivity with Water

In this topic, we discuss the reactions of the Group 1 elements - lithium, sodium, potassium, rubidium and cesium with water. It uses these reactions to explore the trend in reactivity in Group 1.

With the exception of Li, the alkali metals are extremely soft and readily fused. They are highly malleable (i.e. can be pressed out into sheets) and ductile (i.e. can be drawn into wires). When freshly cut, they have a bright luster which quickly tarnished as soon as metal comes in contact with atmosphere.

Summary of the trend in reactivity

The Group 1 metals become more reactive towards water as you go down the Group.

Explaining the trend in reactivity

Looking at the enthalpy changes for the reactions

The overall enthalpy changes

As you go down the Group, the amount of heat given off increases as you go from lithium to cesium. Not so!

The table gives estimates of the enthalpy change for each of the elements undergoing the reaction:

$$X_{(s)} + H_2O_{(l)} \longrightarrow HOH_{(aq)} + \tfrac{1}{2}H_{2(g)}$$

	enthalpy change (Kj/mol)
Li	-222
Na	-184
K	-196
Rb	-195
Cs	-203

You will see that there is no pattern all in these values. They are all fairly similar and, surprisingly, lithium is the metal which releases the most heat during the reaction!

When these reactions happen, the differences between them lie entirely in what is happening to the metal atoms present. In each case, you start with metal atoms in a solid and end up with metal ions in solution.

Overall, what happens to the metal is this:

$$X_{(s)} \longrightarrow X^{+}_{(aq)} + e$$

Reactions with Oxygen

This topic mainly looks at the reactions of the Group 1 elements (lithium, sodium, potassium, rubidium and cesium) with oxygen including the simple reactions of the various kinds of oxides formed.

A) The Reactions with Air or Oxygen

Alkali metals react with 0_2 or air rapidly and thus get tarnished due to the formation of their oxide on the surface of *the metals*. It is for this reason that alkali *metals* are stored in kerosene or paraffin oil.

Li when burnt in 0_2 gives mainly lithium monoxide, (normal oxide) Li_20.

$$4Li + O_2 \longrightarrow 2Li_2O$$

Na when burnt in 0_2 forms sodium peroxide, Na_20_2

$$2Na + O_2 \longrightarrow Na_2O_2$$

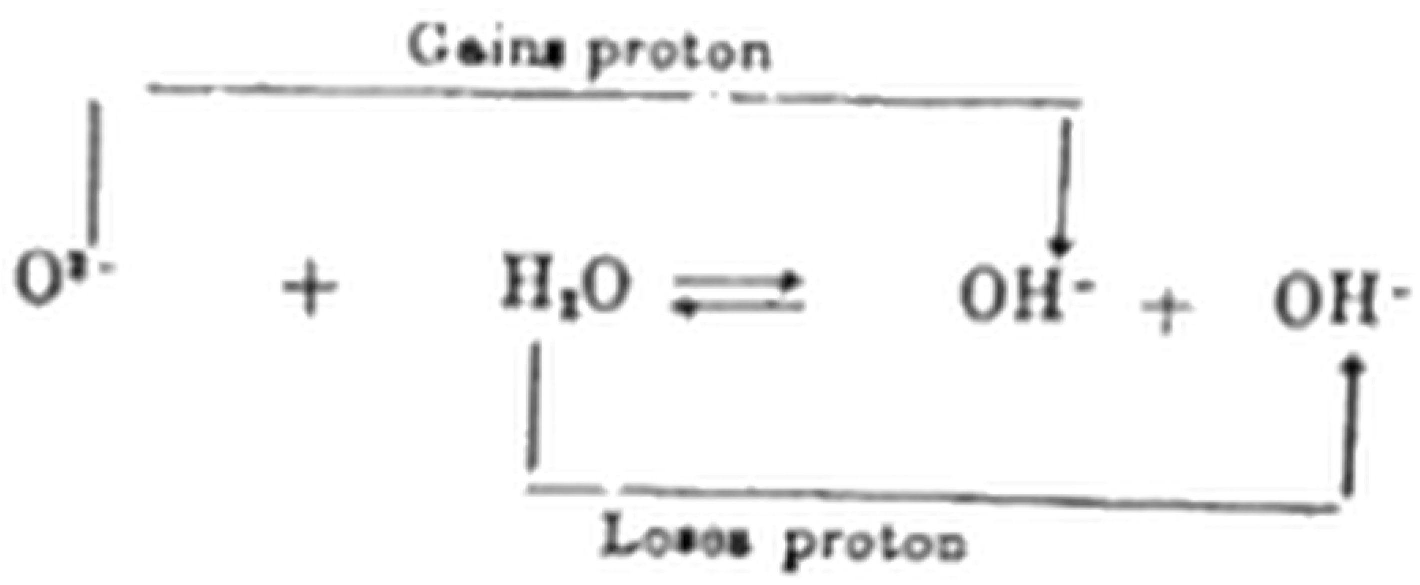
Other alkali metals react with 02 to form super oxide of MO2 type.

$$M + O_2 \longrightarrow MO_2$$

Since the normal oxides of alkali metals other than that of Li ($L1_20$) are not formed by the direct reaction between the metals and 0_2 they are formed by indirect methods, e.g. by reducing peroxides, nitrite and nitrates with the metals itself.

$$2Na_20_2 + 4Na \longrightarrow 4Na_20$$
$$2NaNO_2 + 6Na \longrightarrow 4Na_20 + N_2$$
$$2NaNO_2 + 10Na \longrightarrow 6Na_20 + N_2$$

Properties. Normal oxides (0^{2-}) react with H_2O to form hydroxides by proton exchange.



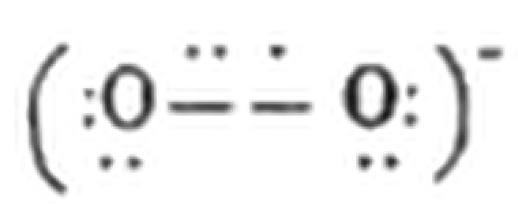
The peroxides (0_2^{2-}) and superoxide (0^{2-}) are strong oxidizing agents and react with H_2O to give H_2O_2 and O_2.

$$0_2^{2-} + 2H_2O + H_2O_2$$

$$2[O\text{-}O] + 2H_2O \longrightarrow H_2O_2 + O_2$$

Normal oxides have anti-fluorite structure and are ionic in nature since they contain monoxide in, 0^{2-} Peroxides contain peroxide ion, 02^{2-} or $[-O-O]^{2-}$.

The super oxide ion has a three-electron bond as shown below.



The presence of one unpaired electron in it makes this in paramagnetic and colored.

B) Reactions of the Oxides with Water and Dilute Acids

1. The simple oxides, X_20

Reaction with water

These are simple basic oxides, reacting with water to give the metal hydroxide.

For example, lithium oxide reacts with water to give a colorless Solution of lithium hydroxide.

$$X_2O + H_2O \longrightarrow 2XOH$$

Reaction with dilute acids

These simple oxides all react with an acid to give a salt and water. For example, sodium oxide will react with dilute hydrochloric acid to give colorless sodium chloride solution and water.

$$X_20 + 2HCl \longrightarrow 2XCl + H_2O$$

2. The peroxides, X_20_2

Reaction with water

If the reaction is done ice cold (and the temperature controlled so that it doesn't rise even though these reactions are strongly exothermic), a solution of the metal hydroxide and hydrogen peroxide is formed.

$$X_2O_2 + 2H_2O \longrightarrow 2XOH + H_2O_2$$

If the temperature increases (as it inevitably will unless the peroxide is added to water very slowly), the hydrogen peroxide produced decomposes into water and oxygen. The reaction can be very violent overall.

Reaction with dilute acids

These reactions are even more exothermic than the ones with water. A solution containing a salt and hydrogen peroxide is formed. The hydrogen peroxide will decompose to give water and oxygen if the temperature rises again, it is almost impossible to avoid this. Another potentially violent reaction!

$$X_2O_2 + 2HCl \longrightarrow 2XCl + H_2O_2$$

3. The superoxides, XO_2

Reaction with water

This time, a solution of the metal hydroxide and hydrogen peroxide is formed, but oxygen gas is given off as well. Once again, these are strongly exothermic reactions and the heat produced will inevitably decompose the hydrogen peroxide to water and more oxygen. Again violent!

$$2XO_2 + 2H_2O \longrightarrow 2XOH + H_2O_2 + o_2$$

Reaction with dilute acids

Again, these reactions are even more exothermic than the ones with water. A solution containing a salt and hydrogen peroxide is formed together with oxygen gas. The hydrogen peroxide will again decompose to give water and oxygen as the temperature rises. Violent!

$$2XO_2 + 2HCl \longrightarrow 2XCl + H_2O_2 + O_2$$

C) Reactions of the elements with Chlorine

Sodium burns with an intense orange flame in chlorine is exactly the same way that it does in pure oxygen. The rest also behave the same in both gases.

In each case, there is a white solid residue which is the simple chloride, XCl. There is nothing in any way complicated about these reactions!

$$2X + Cl_2 \longrightarrow 2XCl$$

D) Effect of heat on Nitrates, Carbonates and Hydrogen-Carbonates

i) The facts

Group 1 compounds are more stable to heat than the corresponding compounds in Group 2. You will often find that the lithium compounds behave similarly to Group 2 compounds, but the rest of Group 1 are in some way different.

Nature of Carbonates, bicarbonates and nitrates

The carbonates ($M2C0_3$) and bicarbonates ($MHCO_3$) are highly stable to heat. With increase of electropositive character from Li to Cs, the stability of these salts increases their nitrates decompose on strong heating to the corresponding nitrite and 02, (Exception is $LiNO_3$).

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

ii) Explaining the trend in terms of the polarizing ability of the positive ion

When alkali metal cations approach near an anion attracts the outer most electrons of the anion and repels the nucleus. Thus, the distortion or polarization of the anion takes place. This distortion results in the sharing of electrons between two oppositely charged ions, i.e. the bond between the cation and anion becomes partly covalent in character. In general, the smaller cations polarize the anions more effectively than bigger one. Therefore, the lithium salts are slightly covalent while other alkali metal salts are ionic.

E) Flame Tests

This topic describes how to do a flame test for a range of metal ions and briefly describes how the flame colour arises.

Flame tests are used to identify the presence of a relatively small number of metal ions in a compound. Not all metal ions give flame colors.

For Group 1 compounds, flame tests are usually by far the easiest way of identifying which metal you have got. For other metals, there are usually other easy methods which are more reliable - but the flame test can give a useful hint as to where to look.

Q10. Give Flame Tests of Group I-A elements.

Answer

Practical details

Clean a platinum or nichrome (a nickel-chromium alloy) wire by dipping it into concentrated hydrochloric acid and then holding it in a hot Bunsen flame. Repeat this until the wire doesn't produce any colour in the flame.

When the wire is clean, moisten it again with some of the acid and then dip it into a small amount of the solid you are testing so that some sticks to the wire. Place the wire back in the flame again.

If the flame colour is weak, it is often worthwhile to dip the wire back in the acid again and put it back into the flame as if you were cleaning it. You often get a very short but intense flash of colour by doing that.

The colors

Different colors shown by different elements are given below.

	Flame Colour
Li	Red
Na	Golden Yellow
K	Lilac(pink)
Rb	Red (reddish-violet)
Cs	Blue

Ca	Orange-red
Sr	Red
Ba	Pale green
Cu	Blue-green (often with white flashes)
Pb	Greyish-white

Note:

What do you do if you have a red flame colour for an unknown compound and don't know which of the various reds it is?

Get samples of known lithium, strontium (etc) compounds and repeat the flame test, comparing the colors produced by one of the known compounds and the unknown compound side by side until you have a good match.

The origin of flame colour

We have seen that the outer electron (i.e. ns' electron) of atom of alkali metals is loosely held with the nucleus and hence it can be easily excited to the higher energy levels even by a small amount of heat energy (e.g. by heating the metals or their slats into Bunsen burner). During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic spectrum and hence the colour is imparted by the atoms to the flame. Sine the amount of energy absorbed during the excitation process is different in different atoms, different colour are imparted by the atoms to the flame. The property of alkali metals to give coloration in the Bunsen flame has been used to detect their presence in salts by a test known as flame test.

Group 2 Elements

Q11. Give Trends of Properties of II-A elements Atomic and Physical Properties.

Answer

This section explores the trends in some atomic and physical properties of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium. You will find separate sections below covering the trends in atomic radius, first ionization energy, electronegativity and physical properties.

1) Trends in Atomic Radius

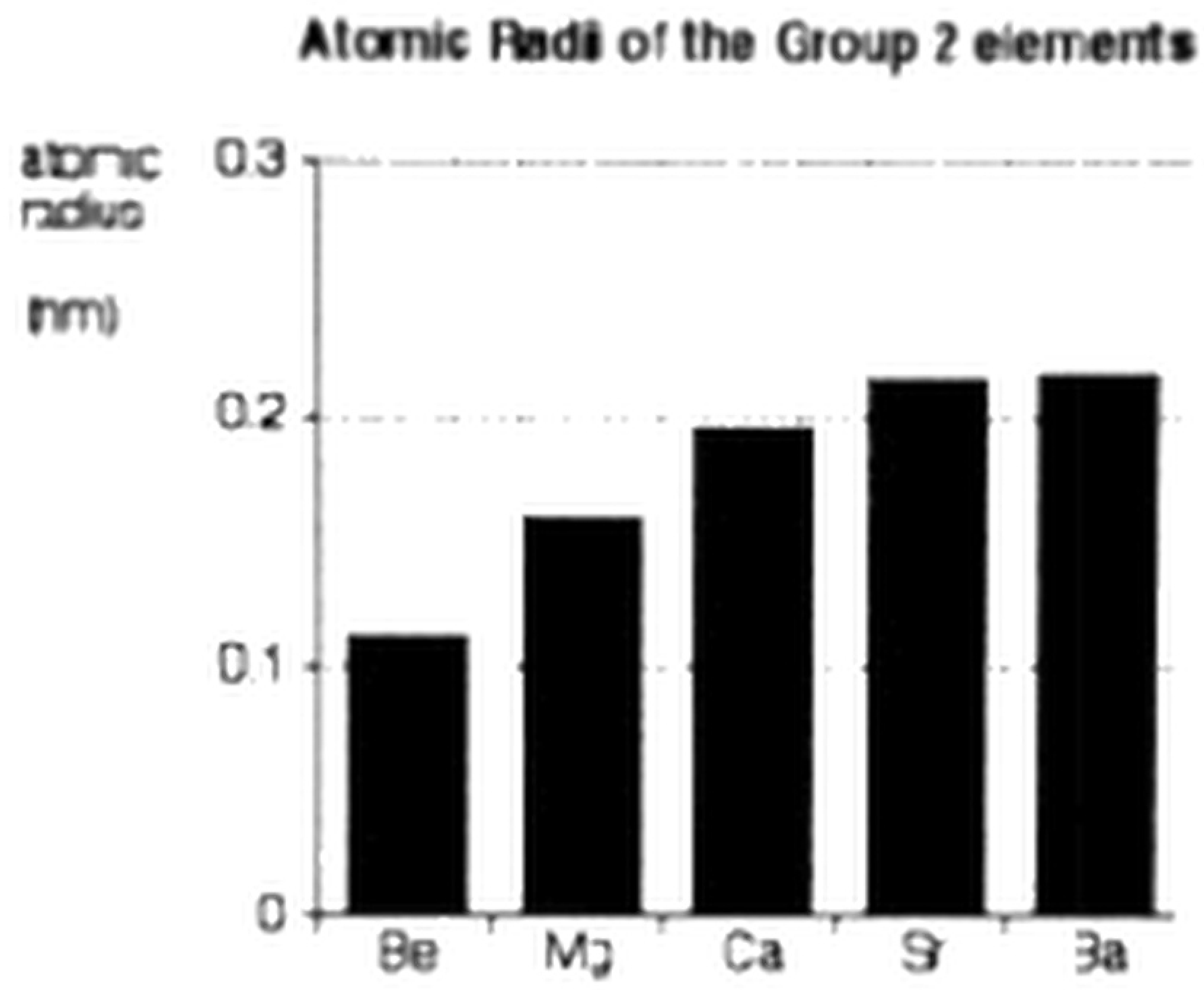


Fig. 13.17 Atomic Radii of the Group 2 elements

You can see that the atomic radius increases as you go down the Group. Notice that beryllium has a particularly small atom compared with the rest of the Group.

Explaining the increase in atomic radius

Atomic volume, atomic and ionic radii

Because of the addition of an extra shell of electrons to each element from Be to Ra, the atomic volume increases from Be to Ra. With the increases of atomic volume, the atomic and ionic radii (of M^2 ions) also increase from Be to Ra. The atomic radii of these elements are however, smaller than those of alkali metals in the same period. This is due to the fact that the alkaline earth metals in the same period. This is due to the fact that the alkaline earth metals have higher nuclear charge which tends to draw the orbit electrons towards the nucleus. The smaller values of atomic radii result in that the alkaline earth metals are harder, have higher densities and higher melting points than alkali metals.

Some physical properties of alkaline earth metals

Property	*Be*	*Mg*	*Ca*	*Sr*	*Ba*	*Ra*
Atomic weight	9.01	24.31	40.08	87.62	137.34	226
Abundance (% of earth's crust)	6.4 x 10.4	2.0	3.45	0.915	0.040	1.3x10.10
Density (gm/c.c.)	1.84	1.74	1.55	2.54	3.75	6.00
Melting point (°C)	1277	650	838	763	714	700
Boiling point (°C)	2770	1107	1440	1380	1610	–
Atomic volume (c.c.)	4.90	13.97	25.9	34.54	36.7	38.0
Atomic (i.e., metallic) radius for co-ordination number 12 (A°)	1.12	1.60	1.97	2.15	2.22	–
Covalent radiue (A°)	0.90	1.36	1.74	1.91	1.98	–
Tonic (crystal radius of M^{2+} ion for co-ordination number + (A°)	0.31	0.65	0.99	1.13	1.35	140
Ionisation energies (KJ/mole)						
I_1	899.5	737.7	829.8	547.5	502.9	509.4
I_2	1757.1	1450.7	1145.4	1064.3	965.2	979.06
$I_1 + I_2$	2656.6	2188.4	1735.2	1613.8	1468.1	1488.46
Oxidation state	+2	+2	+2	+2	+2	+2
Electronegativity	1.5	1.2	1.0	0.9	0.9	0.9
Flame colouration	None	None	Brick red	Crimson	Apple green	Red
Oxidation potentials (volts) for $M(s) \longrightarrow M^{2+}(aq) + 2e$	1.70 1.70	1.37	2.87	2.89	2.90	2.92
Heat of automisation at 25°C and 1 atm pressure (KJ/mole)	327.26	146.89	181.21	163.21	175.77	–
Heat of hydration (KJ/mole)	2385.45	1925.1	1653.07	1458.67	1276.42	–
Ionic potential of M2 + ion (i.e., charge/radius ratio).	6.66	3.08	2.12	1.82	1.55	1.33

2) Trends in First ionization Energy

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions • in other words, for 1 mole of this process:

$$X_{(g)} \longrightarrow X^{+}_{(g)} + \ldots$$

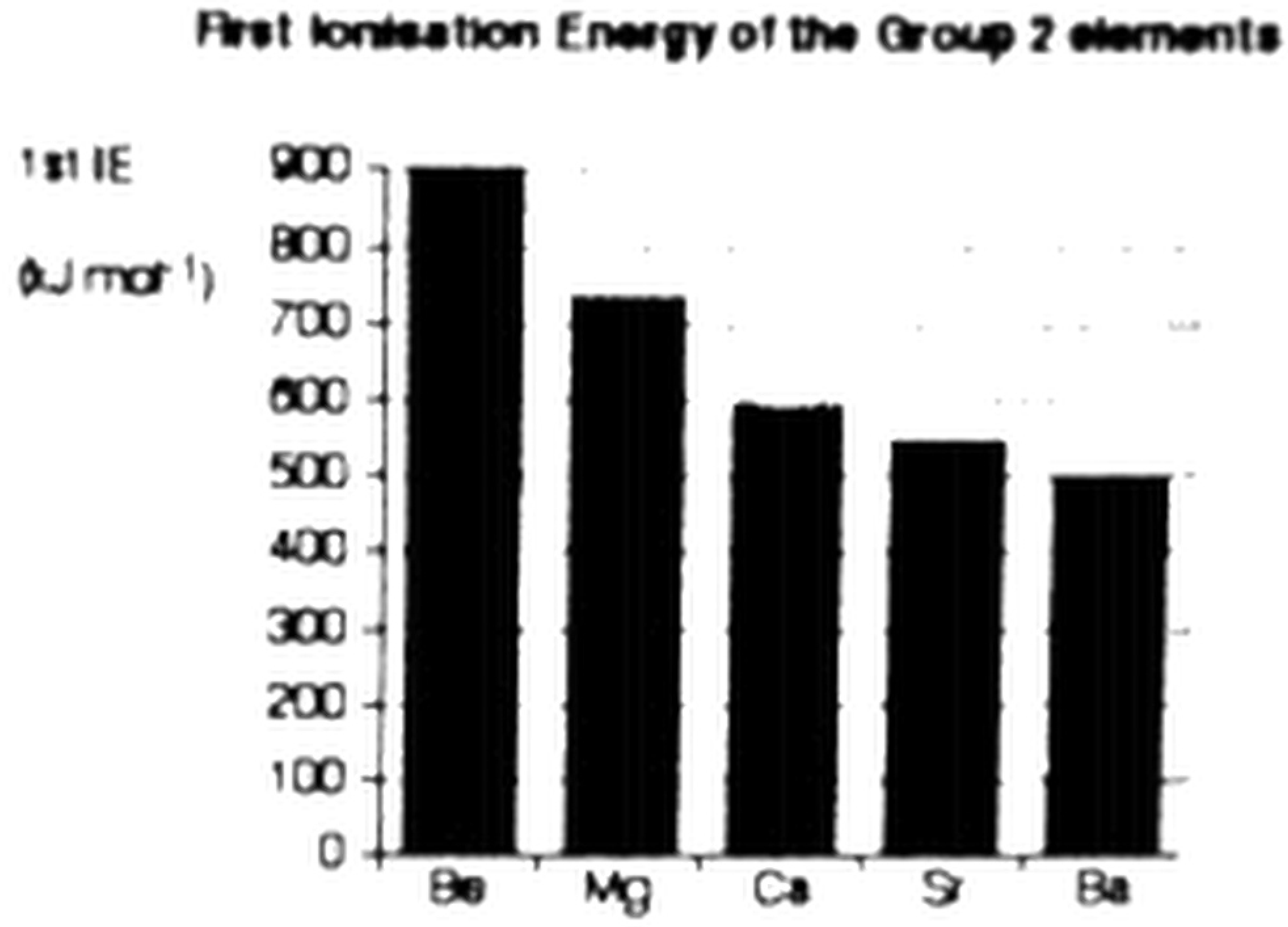


Fig. 13.18 First Ionisation energy of the Group 2 elements

Notice that first ionization energy falls as you go down the group.

Explaining the decrease in first ionization energy

The first and second ionization energies of these elements decrease with the increase of atomic radii from Be to Ba. However, both these values for Ra are slightly higher than those of Ba (for values see table no 13.4)

3) Trends in Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.

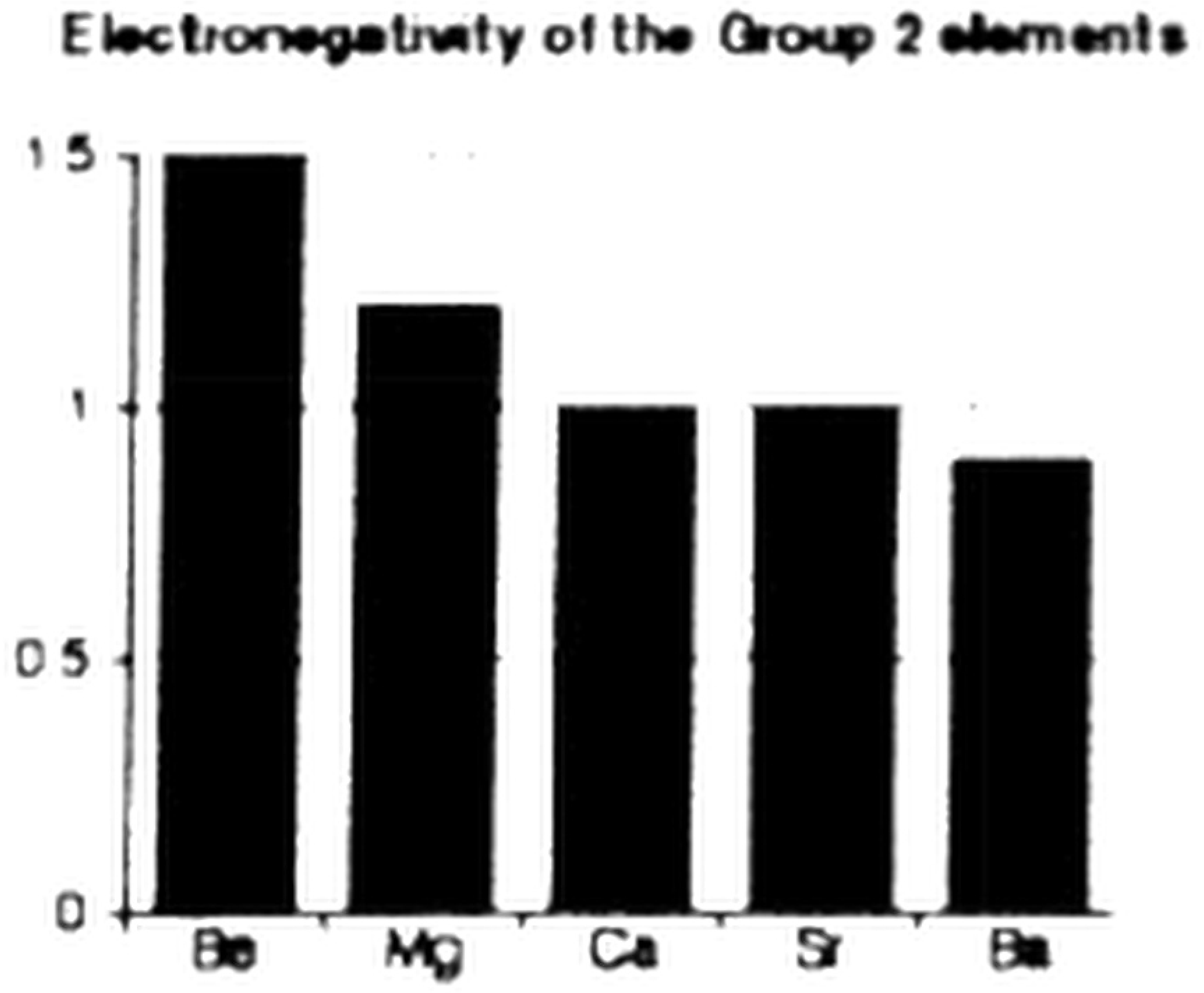


Fig. 13.19 Electronegativity of the Group 2 elements

Summarizing the trend down the Group

As the metal atoms get bigger, any bonding pair gets further and further away from the metal nucleus, and so is less strongly attracted towards it. In other words, as you go down the Group, the elements become less electronegative.

As you go down the Group, the bonds formed between these elements and other things such as chlorine become more and more ionic. The bonding pair is increasingly attracted away from the Group 2 element towards the chlorine (or whatever).

Notice that electronegativity values fall as you go down the group (for values see table)

4) Trends in Melting Point and Boiling Point

A) Melting points

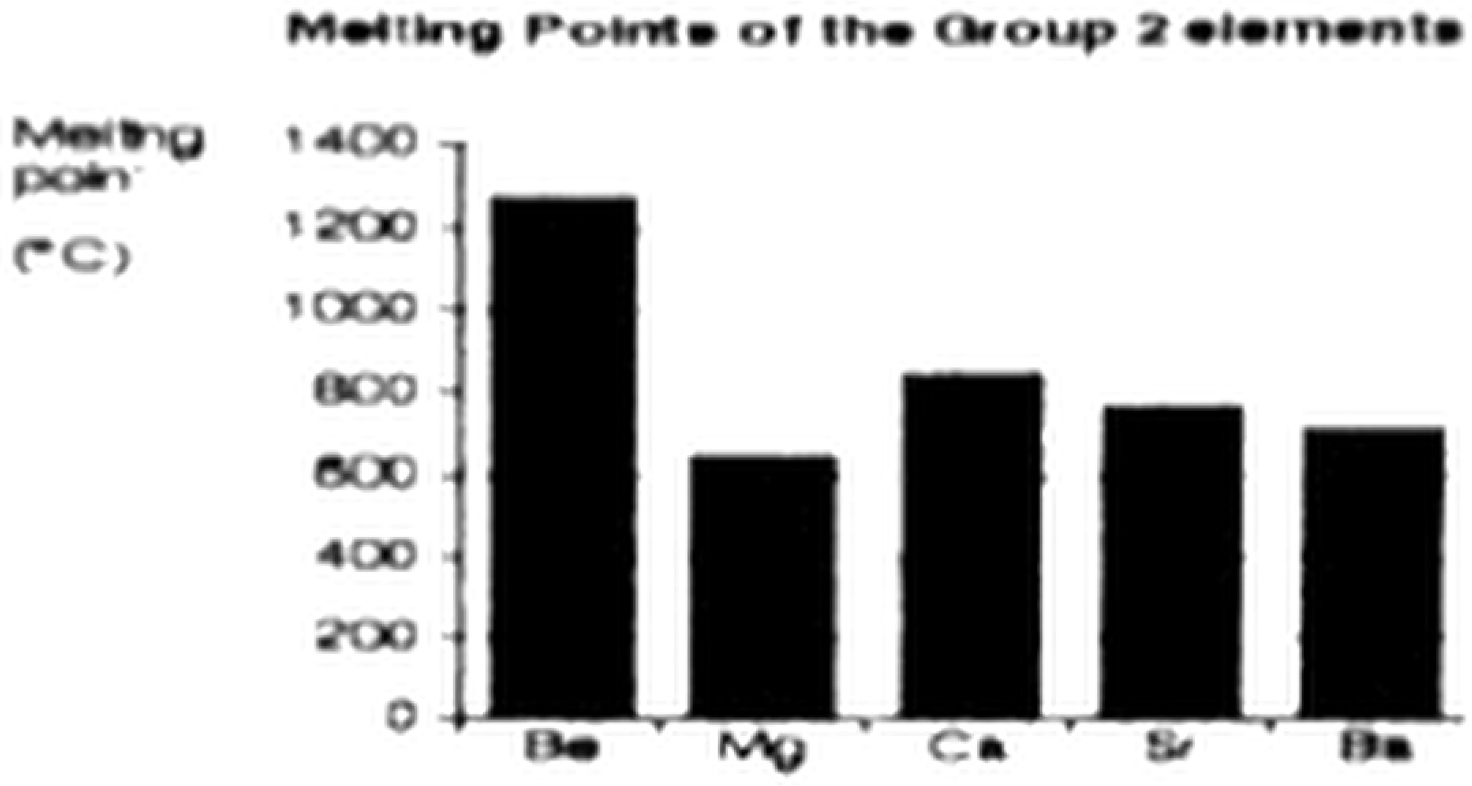


Fig. 13.20 You will see that (apart from where the smooth trend is broken by magnesium) the melting point falls as you go down the Group.

B) Boiling Points

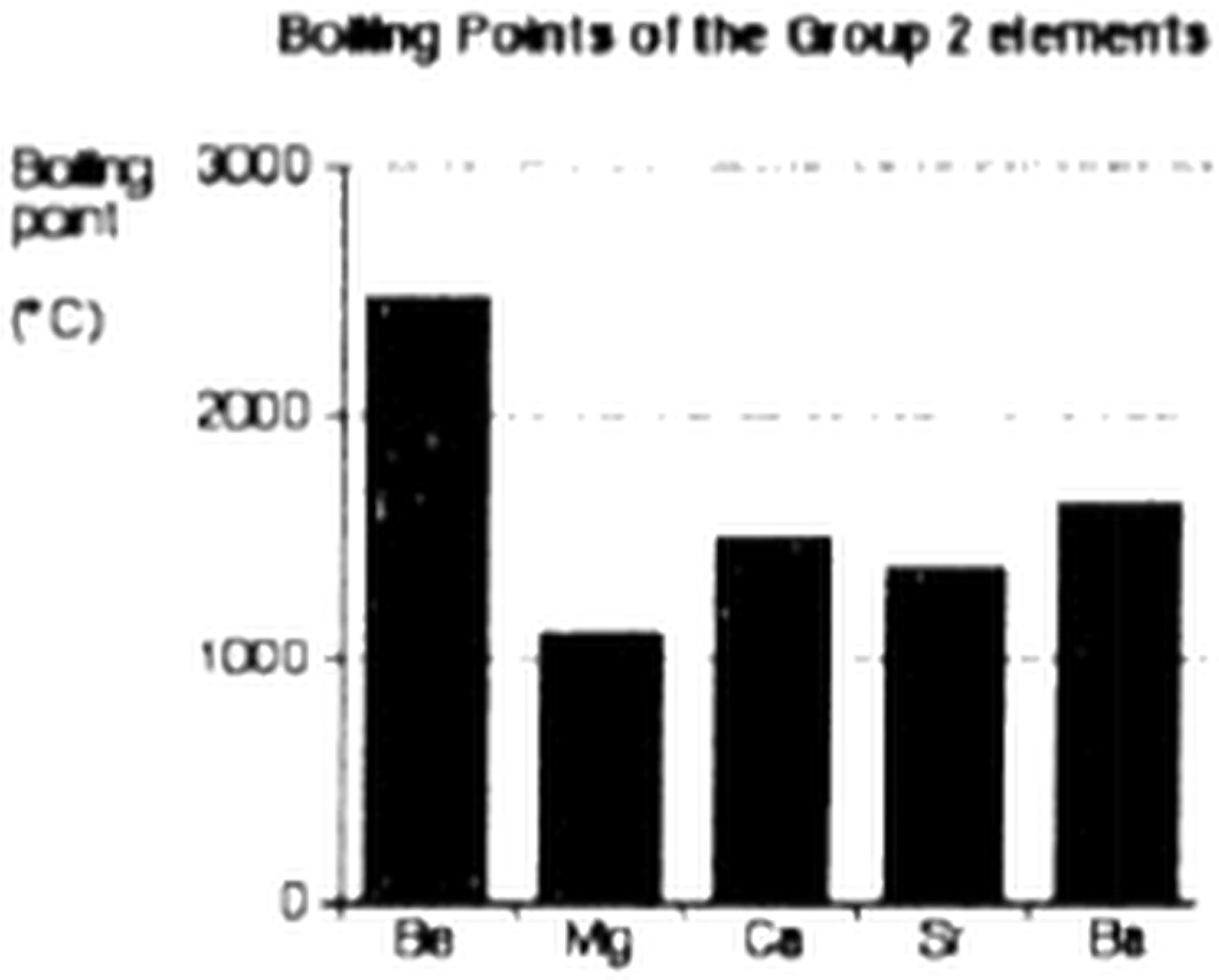


Fig. 13.21 You will see that there is no obvious pattern in boiling points.

It would be quite wrong to suggest that there is any trend here whatsoever.

If we look at figure, the ionization energies of carbon at the top of the group that there is no possibility of it forming simple positive ions, while Sn and Pb have low energies so form positive ion easily.

5) Trends in Reactivity with Water

This section looks at the reactions of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium - with water (or steam). It uses these reactions to explore the trend

The Facts

Beryllium

Beryllium has no reaction with water or steam even at red heat.

Magnesium

Magnesium burns in steam to produce white magnesium oxide and hydrogen gas.

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

Very clean magnesium ribbon has a very slight reaction with cold water. After several minutes, some bubbles of hydrogen form on its surface, and the coil of magnesium ribbon usually floats to the surface. However, the reaction soon stops because the magnesium hydroxide formed is almost insoluble in water and forms a barrier on the magnesium preventing further reaction.

$$Mg_{(s)} + 2H_2O_{(g)} \longrightarrow MgOH_{2(s)} + H_{2(g)}$$

Calcium, strontium and barium

These all react with cold water with increasing vigor to give the metal hydroxide and hydrogen. Strontium and barium have reactivities similar to lithium in Group 1 of the Periodic Table.

Calcium, for _example, reacts fairly vigorously with cold water in an exothermic reaction. Bubbles of hydrogen gas are given off, and a white precipitate (of calcium hydroxide) is formed, together with an alkaline solution (also of calcium hydroxide -calcium hydroxide is slightly soluble).

The equation for the reactions of any of these metals would be:

$$X_{(s)} + 2H_2O_{(l)} \longrightarrow X(OH)_{2(aq\ or\ s)} + H_{2(g)}$$

The hydroxides aren't very soluble, but they get more soluble as you go down the Group. The calcium hydroxide formed shows up mainly as a white precipitate (although some does dissolve). You get less precipitate as you go down the Group because more of the hydroxide dissolves in the water.

Summary of the trend in reactivity

The Group 2 metals become more reactive towards water as you go down the Group.

Explaining the trend in reactivity

$Be(OH)_2$ is not at all basic; in fact it is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates.

$$Be(OH)_2 + 2HCl \longrightarrow BaCl_2 + 2H_20$$
$$Be(OH)_2 + 2NaOH \longrightarrow Ba_2BeO_2 + 2H_20$$

The hydroxides or other metals are basic in character. Their basic character increases on moving down the group. Thus Mg(OH)2 is weakly basic while $Be(OH)_2$ is the strongest base. The increase in basic character of the hydroxides on moving down the group is due to the fact that with the increase in size of M^{2+} cation both the polarity of M-OH bond and the internuclear distance between oxygen of OH- ion and the metals atom increase. As a result of this, there is greater ionization of $M(OH)_2$ and hence basic character increases.

Due to high polarizing power of small Be^{2+} in, $Be(OH)_2$ is covalent while other hydroxides are ionic.

Be(OH)2 and Mg(OH)2 are almost insoluble in H_2O while the hydroxides of other metals are slightly soluble. Their solubility increases on moving down the group as shown by the increasing value of the solubility products of these hydroxides.

$Be(OH)_2 = 1.6 \times 10^{-26}$; $Mg(OH)_2 = 8.9 \times 10^{-12}$; $Ca(OH)_2 = 1.3 \times 10^{4}$;

$Sr(OH)_2 = 3.2 \times 10^{-4}$; $Ba(OH)_2 = 5.4 \times 10^{-2}$

6) Reactions with Oxygen and Nitrogen

i) Reactions of The Group 2 Elements with Air or Oxygen

This topic looks at the reactions of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium - with air or oxygen.

A) Formation of simple oxides

Preparation: The alkaline earth metals form the normal oxides of MO type which are obtained by heating the metal in 0_2 or by heating their carbonates at high temperature e.g.

$$2Ca + 0_2 \longrightarrow 2Ca0$$

Properties:

i) these oxides are extremely stable white crystal line solids due to their high crystal lattice energy obtained by packing doubly charged in sin a sodium chloride type of lattice.

ii) Be0 and Mg0 are quite insoluble in H2O while H2O CaO, SrO qand BaO react with H2O to give soluble hydroxides, $M(OH)^2$ which are strong bases

iii) Be0 is not at all basic in nature; in fact, it is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates.

$$Be(OH)_2 + 2HC1 \longrightarrow BaC1_2 + 2H_20$$

$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_20$$

The oxides of other metals are basic in character. Their basic character increases on moving down the group.

iv) Due to small size Be^{2+} ion, Be0 is covalent which other oxide are ionic. Although Be0 is covalent yet is has a higher melting point and is harder than the oxides of other metals as it is polymeric. Each Be atom is tetrahedrally coordinated by four oxygen atoms.

b) Peroxides Preparation.

The peroxides of heavier metals (Ca, Sr, Ba etc.) can be obtained on heating the normal oxides with 0_2 at high temperature.

$$2Ba0 + 0_2 \longrightarrow 2BaO_2$$

Properties.

The peroxides are white, ionic solids having peroxide anion, $[0\text{-}0]^{2'}$. They react with acids to produce H_20_2.

B) Formation of Nitrides on Heating in Air

All the elements burn in nitrogen to form nitrides, M_2N_2 e.g.

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

These react with H_2O to liberate NH_3 e.g.

Be_3N_2 is volatile while other nitrides are not so.

Q12. Give Trends in Solubility of the Hydroxides, Sulphates and Carbonates.

Answer

This topic looks at the solubility in water of the hydroxides, sulphates and carbonates of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium.

ii) Solubility of the hydroxides

• The hydroxides become more soluble as you go down the Group.

This is a trend which holds for the whole Group, and applies whichever set of data you choose.

Some examples may help you to remember the trend:

Magnesium hydroxide appears to be insoluble in water. However, if you shake it with water, filter it and test the pH of the solution, you find that it is slightly alkaline. This shows that there are more hydroxide ions in the solution than there were in the original water. Some magnesium hydroxide must have dissolved.

Calcium hydroxide solution is used as "lime water". 1 litre of pure water will dissolve about 1 gram of calcium hydroxide at room temperature.

Barium hydroxide is soluble enough to be able to produce a solution with a concentration of around 0.1 mol dm^{-3} at room temperature.

ii) Solubility of the sulphates

- **The sulphates become *less soluble* as you go down the Group.**

iii) Solubility of the carbonates

- The carbonates tend to become less soluble as you go down the Group.

Carbonates are insoluble in water and therefore occur as solid rock minerals in nature. However, they dissolve in H_2O containing CO_2 due to the formation of bicarbonates.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

Q13. Trends in Thermal Stability of the Carbonates and Nitrates.

Answer

This topic looks at the effect of heat on the carbonates and nitrates of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium. it describes and explains how the thermal stability of the compounds changes as you go down the Group.

The effect of heat on the Group 2 carbonates

All carbonates decompose on heating, at appropriate temperature evolving CO2

$$MCO_3 \longrightarrow CO_2 + MO$$

The stability of the carbonates of these metals increase on moving down the group. This is illustrated by the values of the decomposition temperatures of these carbonates as given below:

$BeCO_3$ = 25°C, $MgCO_3$ = 540°C, $CaCO_3$ = 900°C,
$SrCO_3$ = 1290°C, BaCO3 = 1360°C

The effect of heat on the Group 2 nitrates

All the nitrates in this Group undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen.

The nitrates are white solids, and the oxides produced are also white solids. Brown nitrogen dioxide gas is given off together with oxygen. Magnesium and calcium nitrates normally have water of crystallization, and the solid may dissolve in its own water of crystallization to make a colorless solution before it starts to decompose.

Again, if "X" represents any one of the elements:

$$2X(NO_3)_{2(s)} \longrightarrow 2X0(_s) + 4NO_2(_g) + O_{2(g)}$$

As you go down the Group, the nitrates also have to be heated more strongly before they will decompose.

- The nitrates also become more stable to heat as you go down the Group.

Summary

Both carbonates and nitrates become more thermally stable as you go down the Group. The ones lower down have to be heated more strongly than those at the top before they will decompose.

Q14. How Beryllium Differ from other Members of its Group?

Beryllium, the first elements of the group differs from rest of alkaline earth metals due to its small atomic size and comparatively high electronegativity. The main points of difference are:

1) Hardness. Beryllium is the hardest of all the elements of its group.)

2) Melting and boiling points. The melting and boiling points of beryllium are the highest.

3) Formation of covalent compounds. Beryllium has a tendency to form covalent compounds. Thus, when it reacts with other elements the electronegativity difference is not so large and the bond is therefore covalent.

4) Reaction with water. Beryllium does not react with water even at high temperature. Other alkaline earth metals decompose water liberating H2 gas.

$$Mg + H_20 \longrightarrow Mg0 + H_2$$

5) Reaction with hydrogen. Beryllium does not react with hydrogen directly to form its hydride. Its hydride however has been prepared indirectly. The rest of the alkaline earth metals combine with hydrogen to form hydrides. The hydrides of Be and Mg are covalent, whereas the hydrides of other metals are ionic.

6) Reaction with alkalis. Beryllium reacts with alkalis to form hydrogen.

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$$

Other alkaline earth metals do not react with alkalis.

7) Behaviour of oxides and hydroxides. The oxides and hydroxides of beryllium are amphoteric, i.e. dissolve in both acids and alkalis to form salts.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

8) Behaviour of carbides. Beryllium carbide is decomposed by water to form methane (CH4)

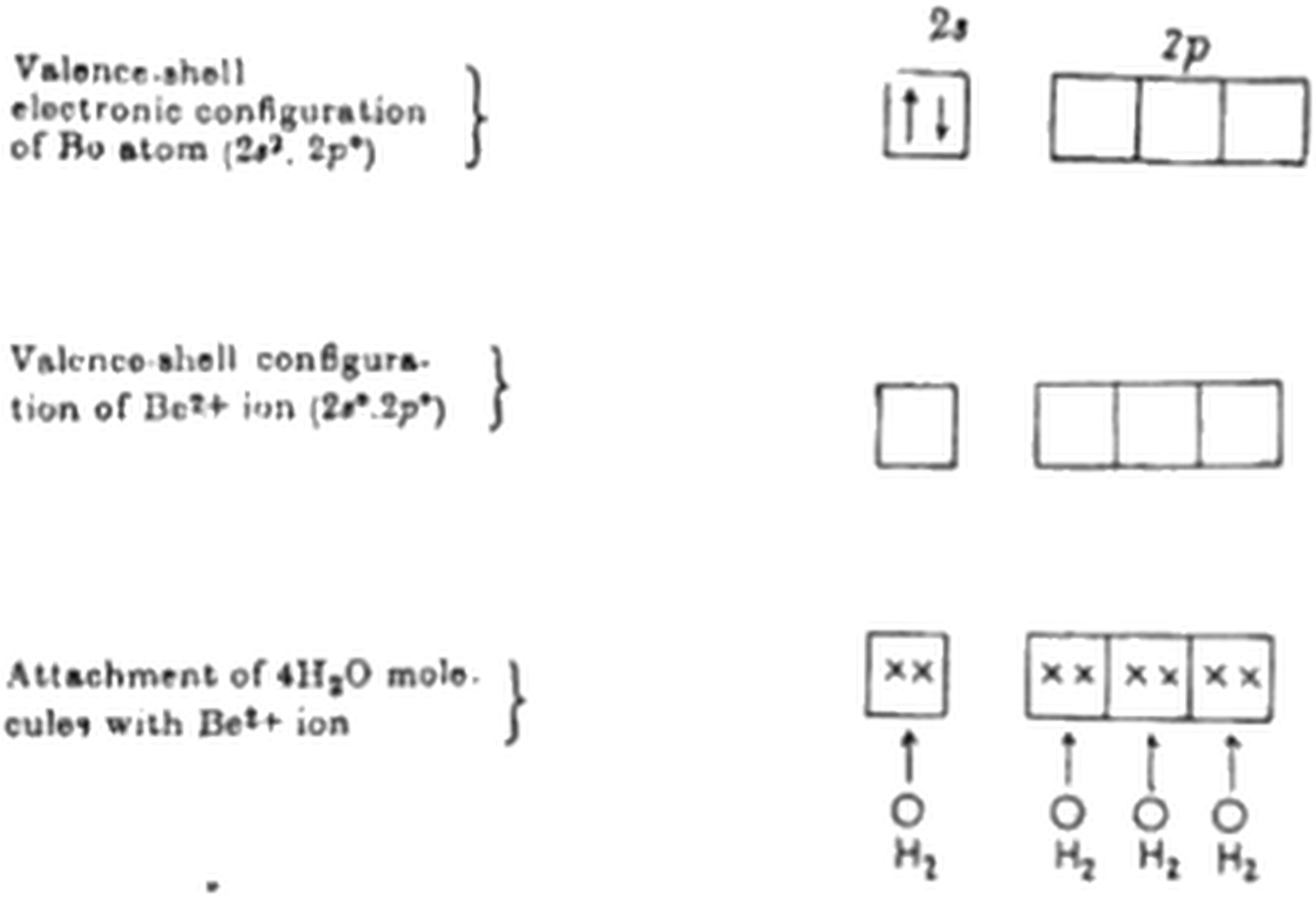
$$Be_2C + 4H_20_4 \longrightarrow 2Be(OH)_2 + CH_4$$

The carbide of other alkaline earth metals is decomposed by water to form acetylene (C_2H_2). For example:

$$CaC2 + 2H_2O \longrightarrow Ca(OH)_2 + C2H2$$

9) Behaviour of nitrides. Be3N2 is volatile while the nitrides of other alkaline earth metals are

10) Number of molecules of water of crystallization. The salts of Be2+ ion cannot have more than four molecules of water of crystallization while other alkaline earth metals have more than four molecules of water of crystallization. This is explained as follows. In case of Be^{2+} ion there are only four orbitals (namely one orbital can accept lone pairs of electrons denoted by 0-atoms on each of the water molecules as shown below.



One the other hand, other alkaline earth metals like Mg can extend their coordination number to six by using one 3s, three 3p and two 3d orbitals belonging to their outermost shell.

11) Formation of complex compounds. Be^{2+} ion, on account of its small size, forms stable complex compounds like $[BeF_3]^-$, $[BeF_3]^{2-}$ while M^{2+} ions derived from other alkaline earth metals form very few complex compounds.

Group 4- Elements

Q 15. Give Physical properties of the elements Group IV-A.

Answer

1) Melting points and boiling points

As we move down the group from C to Pb, the melting points as well as boiling points generally decrease, although the decrease is not in a regular order. This decrease in melting points as well as in boiling points indicates that inter-atomic forces also decrease in the same direction. The melting and boiling points of C and Si are notably high because of the tendencies of these elements to form giant molecules.

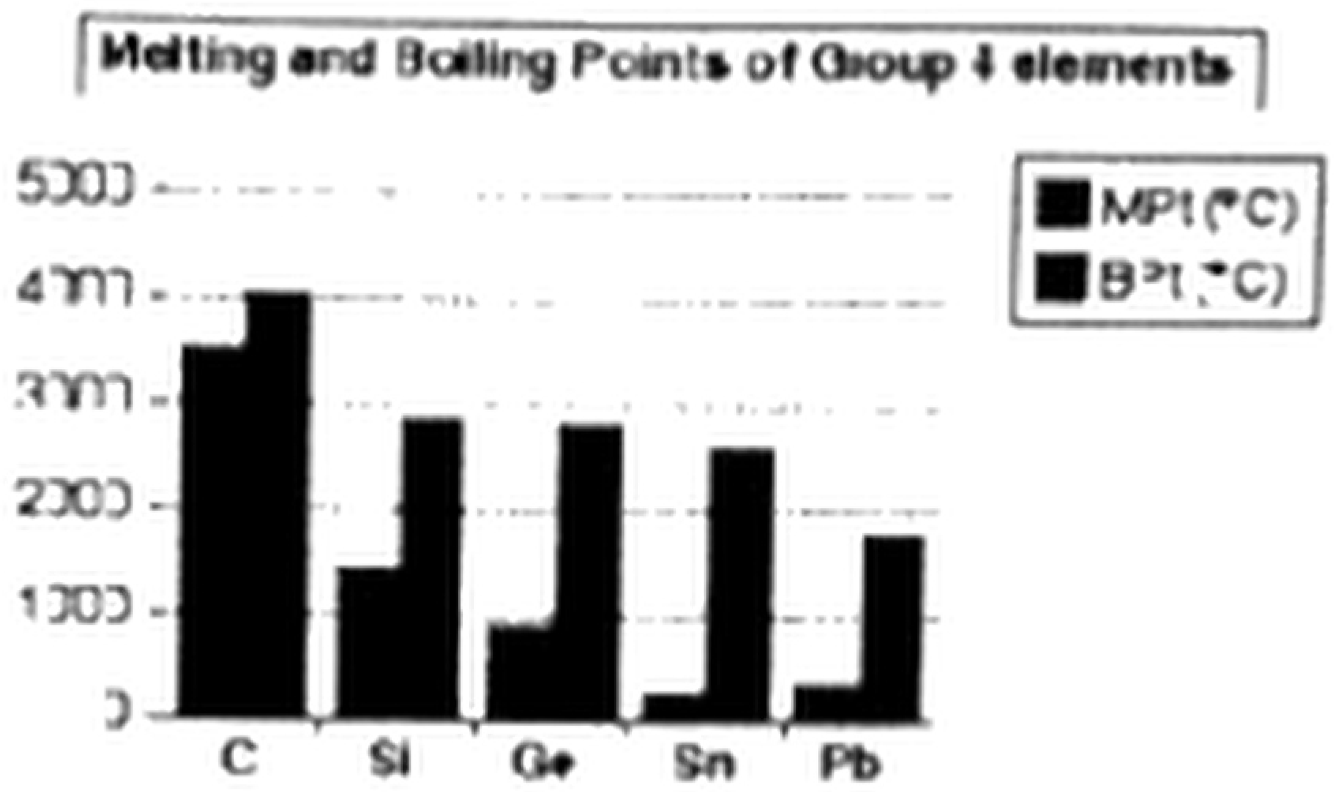


Fig. 13.22 Melting and Boiling Points of Group 4 elements

The low value for tin's melting point compared with lead is presumably due to forming a distorted 12-co-ordinated structure rather than a pure one. The tin values in the chart refer to metallic white tin.

2) Brittleness

Carbon as diamond is, of course, very hard - reflecting the strength of the covalent bonds. However, if you hit it with a hammer, it shatters.

Silicon, germanium and grey tin (all with the same structure as diamond) are also brittle solids.

However, white tin and lead have metallic structures. The atoms can roll over each other without any permanent disruption of the metallic bonds - leading to typical metallic properties like being malleable and ductile. Lead in particular is a fairly soft metal.

3) Electrical conductivity

Carbon as diamond doesn't conduct electricity. In diamond the electrons are all tightly bound and not free to move.

Unlike diamond (which doesn't conduct electricity), silicon, germanium and grey tin are ***semiconductors.***

White tin and lead are normal metallic conductors of electricity.

There is therefore a clear trend from the typically non-metallic conductivity behaviour of carbon as diamond, and the typically metallic behaviour of white tin and lead.

4) Electronegativity

Carbon is the most electronegative elements of this sub-group and the electronegativities decrease with the rise of atomic number but not a regular manner. This is probably due to the filling of the d-orbital in case of Ge and Sn and f-orbitals in case of Pb.

5) Ionization energies

The ionization energy values decrease on moving down the group form C to Pb, although the decrease does not occur in a regular order. The irregularity in the decrease of these values is due to the filling of intervening d-orbitals in case of Ge and Sn and f-orbitals in case of Pb which are not able' to screen the valence electrons effectively in elements following them.

Q16. The Trend from Non-Metal to Metal in the Group 4 Elements.

Answer

This topic explores the trend from non-metallic to metallic behaviour in the Group 4 elements - carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). It describes how this trend is shown in the structures and physical properties of the elements, and finally makes a not entirely successful attempt to explain the trend.

Structures and Physical Properties

Structures of the elements

The trend from non-metal to metal as you go down the Group is clearly seen in the structures of the elements themselves.

Carbon at the top of the Group has giant covalent structures in its two most familiar allotropes - diamond and graphite.

Diamond has a three-dimensional structure of carbon atoms each joined covalently to 4 other atoms. The diagram shows a small part of that structure.

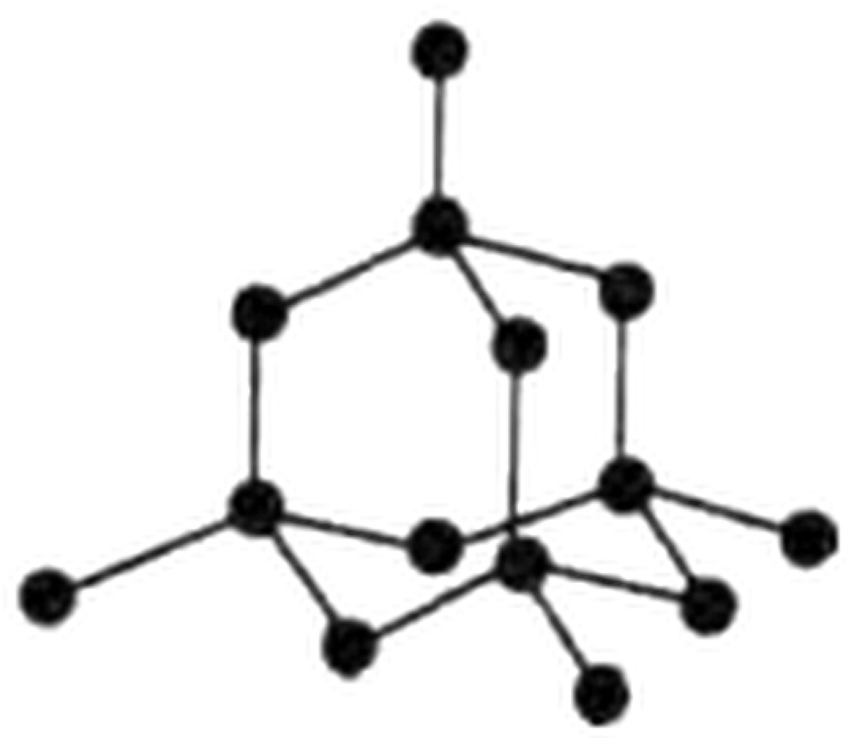


Fig. 13.23

Exactly this same structure is found in silicon and germanium and in one of the allotropes of tin - "grey tin" or "alpha-tin".

The common allotrope of tin ("white tin" or "beta-tin") is metallic and has its atoms held together by metallic bonds. The structure is a distorted dose-packed arrangement. In close-packing, each atom is surrounded by 12 near-neighbors.

There is therefore a clear trend from the typical covalency found in non-metals to the metallic bonding in metals, with the change-over obvious in the two entirely different structures found in tin.

Q 17. Discuss Oxidation State of Group IV- A elements.

Answer

This topic explores the oxidation states (oxidation numbers) shown by the Group IV elements - carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). It looks at the increasing tendency of the elements to form compounds in which their oxidation states are +2, particularly with reference to tin and lead.

a) Inert pair effect and positive oxidation states

Carbon and silicon show +4 oxidation states while occurrence of +2 and +4 oxidation states in case of Ge, Sn and Pb is explained as follows: when only two np electrons from the ns^2p^2 configuration are lost. We get the elements in +2 oxidation states remain inert and hence are not lost in the formation of M^{2+} cations. This pair of ns^2 electrons is called inert pair of electrons. Since the group the stability of +2 oxidation state also increases from Ge^{2+} to Pb^{2+} i.e. $Ge^{2+} < Sn^{2+} < Pb^{2+}$

When all the four ns^2p^2 electrons are lost we get the elements in +4 oxidation state, i.e. M^{4+} cations are formed. On descending the group stability of +4 oxidation state decrease i.e. the stability of M^{4+} cations decrease from Ge^{4+} to Pb^{4+} i.e. $Ge^{4+} > Sn^{4+} > Pb^{4+}$

Compounds of Ge^{2+} are less stable than those of Ge^{4+} and hence the compounds of Ge^{2+} are readily changed oxidized into those of Ge^{4+}. In other words, compounds of $Ge^{e)}$ act as strong reducing agents while those of Ge^{4+} act as oxidizing agents.

Ge^{e+} compounds $\longrightarrow$ Ge^{4+} compounds

Less stable More stable

Reducing agent Oxidizing agent

On similar and rounds it can be shown that the compounds of Sn^{2+} are less stable than those of Sn^4 into those of Sn^{4+}. In other words, compounds of Sn^{2+} act as strong reducing agents while those of Sn^{4+} act as oxidizing agents.

Sn^{2+} compounds $\longrightarrow$ Sn^{4+} compounds

Less stable More stable

Reducing agent Oxidizing agent

When we compare the stability of the compounds of Pb^{2+} and Pb^{4+} ions, we find that Pb^{2+} compounds are more stable than those of Pb^{4+} ($PbC1_4$) and hence the compounds of Pb^{4+} are readily changed (reduced) into those of Pb^{2+}. In other words, compounds of Pb^{4+} act as strong oxidizing agents while those of Pb^{2+} act as reducing agents.

Pb^{2+} compounds	$\longrightarrow$	Pb^{4+} compounds
Less stable		More stable
Reducing agent		Oxidizing agent

Thus, when we compare the stabifty of M^{2+} and M^{4+} cations of Ge, Sn and Pb, we find that their stability is in the order $Ge^{2+}<Ge^{4+}$; $Sn^{2+}<Sn^{4+}$; $Pb^{2+}<Pb^{4+}$

b) Negative oxidation state

Since the electronegativities of these elements are low, they do not have much tendency to form the negative ion. However, carbon forms $C^{4'}$ and C_2^{2-} ions in certain compounds, e. s. $Be4^{2+}C2^{4-}$ or Be_2C(Be^{2+} and C^4 ions), $A14^{2+}$ C_3^{4} ($A1^{3+}$ and C^4ions) Na^+ CH^{3+} (Na^+, C^4 and fr ions), Na^{2+} C_2^{2-} (Na^+ and C_2^{2-} ions), $Ca^{2+}C_2^{2-}$ (Ca^{2+} and C_2^{2-} ions).

The inert pair effect in the formation of ionic bonds

If the elements in Group 4 form 2+ ions, they will lose the p electrons, leaving the e pair unused. For example, to form a lead (II) ion, lead will lose the two 6p electrons, but the 6s electrons will be left unchanged - an "inert pair".

You would normally expect ionization energies to fall as you go down a Group as the electrons get further from the nucleus. That doesn't quite happen in Group 4.

This first chart shows how the total ionization energy needed to form the 2+ ions varies as you go down the Group. The values are all in kJ mol^{-1}.

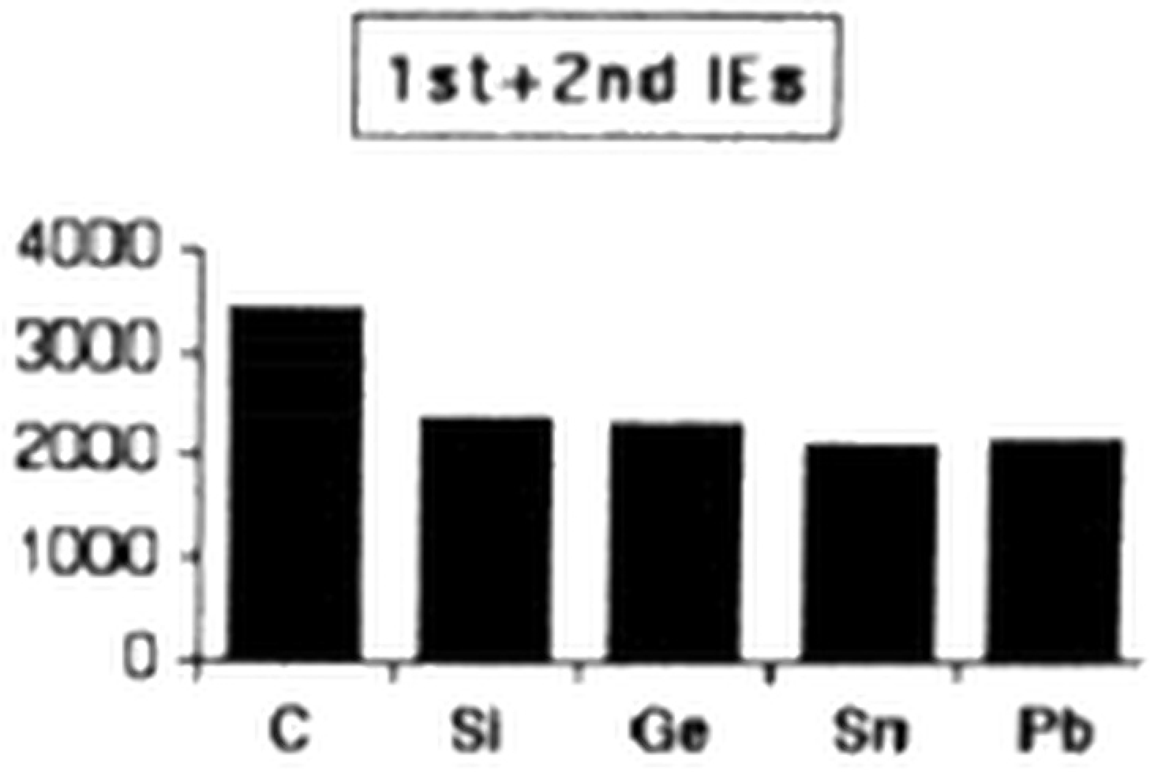


Fig. 13.24

Notice the slight increase between tin and lead.

This means that it is slightly more difficult to remove the p electrons from lead than from tin.

However, if you look at the pattern for the loss of all four electrons, the discrepancy between tin and lead is much more marked. The relatively large increase between tin and lead must be because $6s^2$ pair is significantly more difficult to remove in lead than the corresponding $5s^5$

Pair in tin.

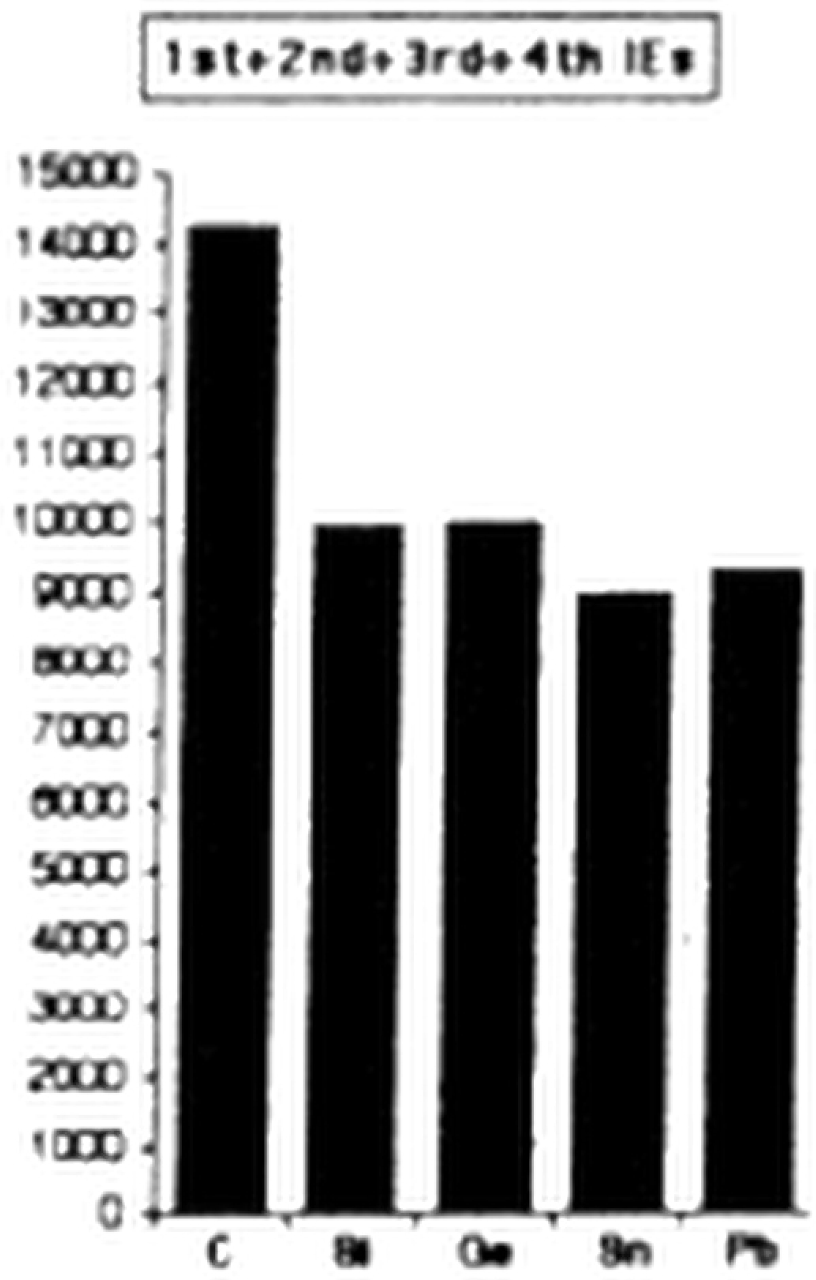


Fig. 13.25

Again, the values are all in kJ mol⁻¹ and the two charts are to approximately the same scale

The reasons for all this lie in the Theory of Relativity. With the heavier elements like lead, there is what is known as a relativistic contraction of the electrons which tends to draw the electrons closer to the nucleus than you would expect. Because they are closer to the nucleus, they are more difficult to remove. The heavier the element, the greater this effect.

This affects s electrons much more than p electrons.

a) In the case of lead, the relativistic contraction makes it energetically more difficult to remove the 6s electrons than you might expect. The energy releasing terms when ions are formed (like lattice enthalpy or hydration enthalpy) obviously aren't enough to compensate for this extra energy. That means that it doesn't make energetic sense for lead to form 4+ ions.

Q18. Discuss the inert pair effect in the formation of covalent bonds.

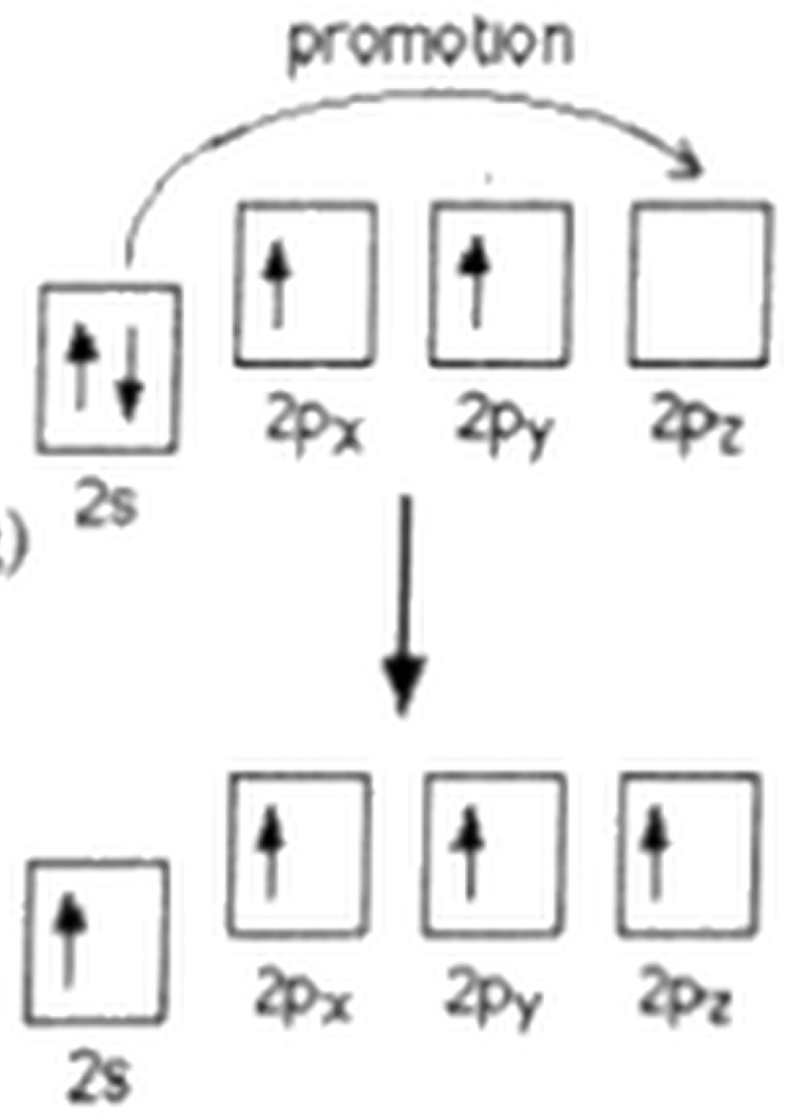
Answer

You need to think about why carbon normally forms four covalent bonds rather than two.

Using the electrons-in-boxes notation, the outer electronic structure of carbon looks like this:

There are only two unpaired electrons. Before carbon forms bonds, though, it normally promotes one of the s electrons to the empty p orbital.

g)



That leaves 4 unpaired electrons which (after hybridization) can go on to form 4 covalent bonds.

It is worth supplying the energy to promote the s electron, because the carbon can then form twice as many covalent bonds. Each covalent bond that forms releases energy, and this is more than enough to supply the energy needed for the promotion.

One possible explanation for the reluctance of lead to do the same thing lies in falling bond energies as you go down the Group. Bond energies tend to fall as atoms get bigger and the bonding pair is further from the two nuclei and better screened from them.

For example, the energy released when two extra Pb-X bonds (where X is H or Cl or whatever) are formed may no longer be enough to compensate for the extra energy needed to promote a 6s electron into the empty Op orbital.

This would be made worse, of course, if the energy gap between the 6s and by orbitals was increased by the relativistic contraction of the 6s orbital.

Q19. Discuss the Chlorides of Carbon, Silicon and Lead.

Answer

This topic takes a brief look at the tetrachloride's of carbon, silicon and lead, and also at lead (II) chloride, it looks at their structures, stability and reactions with water.

1) Structures and Stability

Structures

Carbon, silicon and lead tetrachloride

These all have the formula XC14.

They are all simple covalent molecules with a typical tetrahedral shape. All of them are liquids at room temperature. (Although at room temperature, lead (IV) chloride will tend to decompose to give lead (II) chloride and chlorine gas - see below.)

Lead (II) chloride, $PbCl_2$

Lead (II) chloride is a white solid, melting at 501°C. It is very slightly soluble in cold water, but more soluble in hot water. You can think of lead (II) chloride as being mainly ionic in character.

Stability

At the top of Group 4, the most stable oxidation state shown by the elements is +4. This is the oxidation state shown by carbon and silicon in CCl_4 and $SiCl_4$. These therefore have no tendency to split up to give dichloride.

However, the relative stability of the +4 oxidation state falls as you go down the Group, and the +2-oxidation state becomes the most stable by the time you get to lead.

Lead (IV) chloride decomposes at room temperature to give the more stable lead (II) chloride and chlorine gas.

easy reduction of lead from +4 to +2

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

2) Reaction with water (hydrolysis)

Actually, the hydrolysis of tetra halides takes place through the following two steps:

1st step.

In this step oxygen atoms of H_2O which acts as a donor attacks the central atoms of the halide to form a coordinate bond with it and thus produces an unstable intermediate compound

$$MX_4.H_20$$

2nd step.

In this step four HX molecules are eliminated from this unstable intermediate compound and hydroxide of the central element is formed. Thus X atoms of MX4 molecule are replaced by $0H^-$ ions.

Why the tetrahalides of C are not hydrolyzed while those of Si, Ge and Sn get readily hydrolyzed can be explained as follows:

We know that C atom being a member of 2nd period of the periodic table, has no d-orbitals in it valance shell and hence is unable to accommodate the lone pair donated by the donor oxygen atom of H_2O molecule to form an unstable intermediate compound. Thus, the tetrahalides of C are not hydrolyzed. On the other hand, Si, Ge and Sn have vacant d-orbitals which can accept the lone pair and thus this tetrahalides get readily hydrolyzed.

The ease with which the tetrahalides are hydrolyzed by H_2O decreases from Si to Sn as the metallic character of the central atom increase in this order. Thus, GeX_4 and SnX4 tetrahalides are less readily hydrolyzed than SiX_4 tetrahalides.

it may be mentioned here that empty orbitals are always available with any atom and they can be utilized if sufficient energy is provided for the reaction to occur, e.g., CCl4 undergoes hydrolysis when superheated steam is used.

$$CCl_4 + H_2O \text{ (superheated steam)} \longrightarrow COCl_2 + 2HCl$$

Hydrolysis of tetrahalides of Pb follows essentially the same pattern but due to the instability of tetravalent compounds of Pb, some decomposition of $PbCl_4$ to PbCl2 also takes place.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

Cl_4 is hydrolyzed by H_2O as follows:

$$PbCl_4 + 2H_20 \longrightarrow Pb0_2 + 4HCl$$

Excepting the tetrahalides of C, those of Si, Ge, Sn and Pb react with halide ions and form the hexahalo complex ins like $[SiF_6]^{2-}$, $[GeX6]^{2-}$. For example

$$SiF_4 + 2F \longrightarrow 4\ [SiF6]^{2-}$$

Q20. Discuss Oxides of Group IV-elements.

Answer

This topic takes a brief look at the oxides of carbon, silicon, germanium, tin and lead. It concentrates on the structural differences between carbon dioxide and silicon dioxide, and on the trends in acid-base behaviour of the oxides as you go down Group 4.

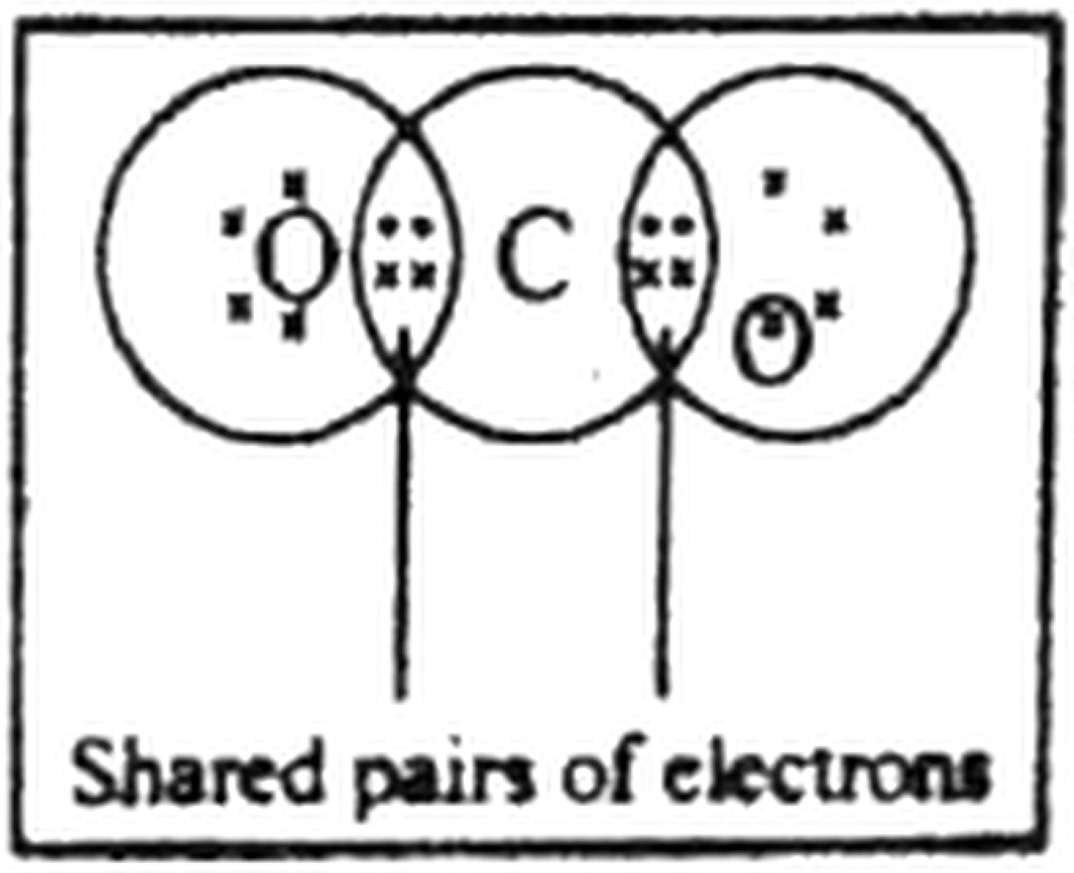
The structures of carbon dioxide and silicon dioxide

There is an enormous difference between the physical properties of carbon dioxide and silicon dioxide (also known as silicon(IV) oxide or silica). Carbon dioxide is a gas whereas silicon dioxide is a hard high-melting solid. The other dioxides in Group 4 are also solids.

This obviously reflects a difference in structure between carbon dioxide and the dioxides of the rest of the Group.

The structure of carbon dioxide

The dipole moment of carbon dioxide is zero. Therefore, it is a linear molecule.



Fig, Structure of carbon dioxide

Fig. 13.26

The structure of sibcon dkaticle

It is a macromolecular compound, in which silicon and oxygen sums off linked together covalently in tetrahedral basic unit.

In crystobsltc these units are joined as in diamond, *Silk in quartz and tridymite they are arranged spirally around an axis. becomes of its structure silicon dioxide is nonvolatile and hard unlike carbon dioxide,

Triatomic molecules of silicon dioxide and carbon dioxide. carbon and silicon, we similar in having,

1) 4 valence electrons.

ii) 4 covalent bond formation.

But they show a lot of difference in their physical properties. It is due to the fact that

i) Silicon atoms we much larger in sire than carbon wins and thus tend to be surrounded, by nu= oxygen atoms.

ii) Silicon from only single bond with oxygen atoms while carbon forms double bonds.

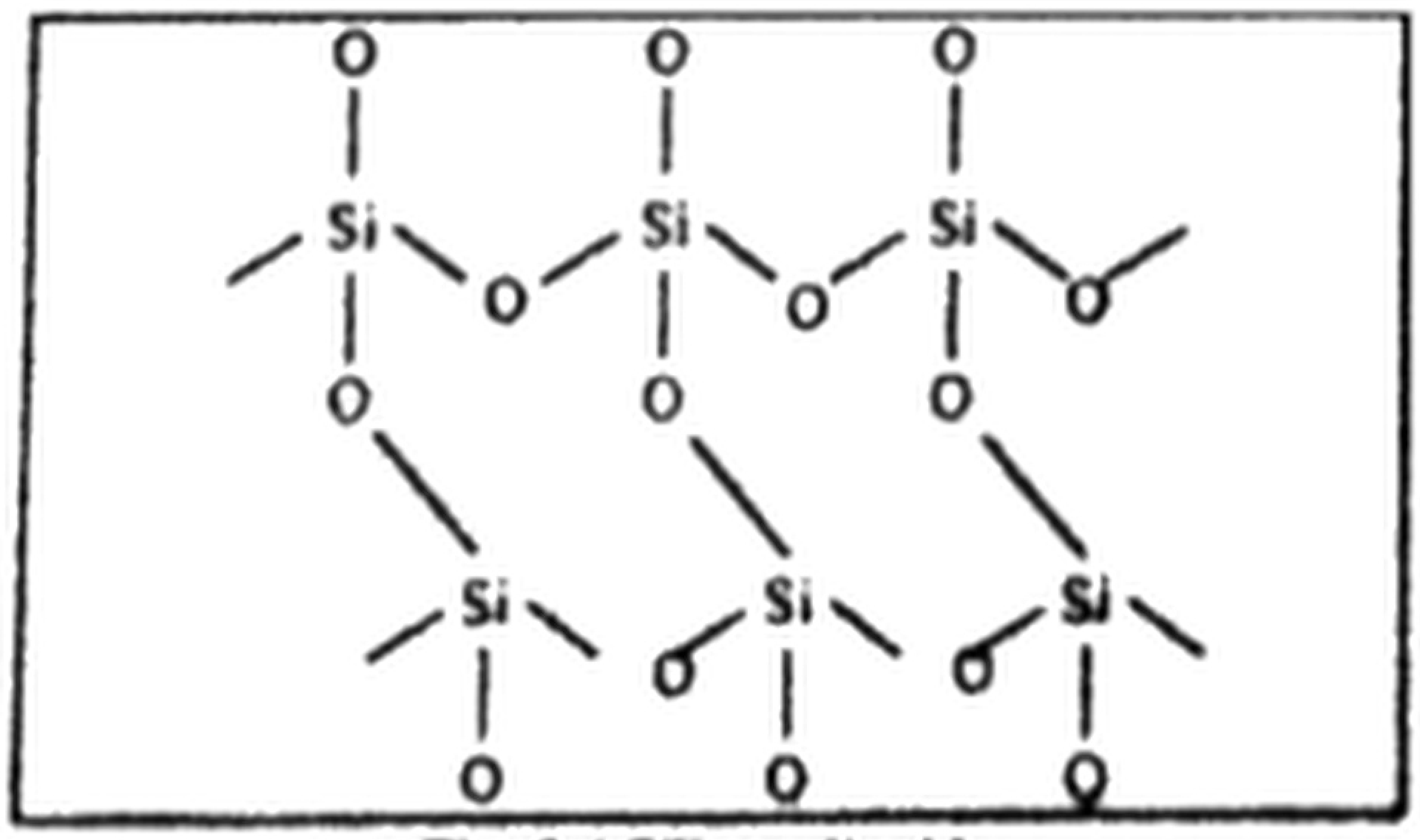


Fig. 3.4 Silicon dioxide

Fig 13.27

iii) Carbon forms a linear molecule of CO, with two oxygen atoms while silicon atom is bound to four oxygen atoms in a tetrahedral structure which result in the formation of silicon dioxide crystal. The simplest formula for series is S_2O_2, However the whole crystal of silicon can be considered as one molecule.

Q21. Discuss the acid-base behaviour of the Group 4 oxides.

Answer

The oxides of the elements at the top of Group 4 are acidic, but acidity of the oxides falls as you go down the Group. Towards the bottom of the Group, the oxides become more basic - although without ever losing their acidic character completely.

An oxide which can show both acidic and basic properties is said to be *amphoteric.*

The trend is therefore from acidic oxides at the top of the Group towards amphoteric ones at the bottom.

Carbon and silicon oxides

Carbon monoxide

Carbon monoxide is usually treated as if it was a neutral oxide, but in fact it is very, very slightly acidic. It doesn't react with water, but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanolate.

$$NaOH + CO \longrightarrow HCOONa$$

The fact that the carbon monoxide reacts with the basic hydroxide ion shows that it must be acidic.

Carbon and silicon dioxides

These are both weakly acidic.

With water

Silicon dioxide doesn't react with water, because of the difficulty of breaking up the giant covalent structure.

Carbon dioxide does react with water to a slight extent to produce hydrogen ions (strictly, hydroxonium ions) and hydrogen carbonate ions.

Overall, this reaction is:

$$H2 + CO_{2(aq)} \longrightarrow H^+_{(aq)} + HCO_{3(aq)}$$

The solution of carbon dioxide in water is sometimes known as carbonic acid, but in fact only about 0.1% of the carbon dioxide has actually reacted. The position of equilibrium is well to the left-hand side.

With bases

Carbon dioxide reacts with sodium hydroxide solution in the cold to give either sodium carbonate or sodium hydrogen carbonate solution - depending on the reacting proportions.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

Silicon dioxide also reacts with sodium hydroxide solution, but only if it is hot and concentrated. Sodium silicate solution is formed.

$$2Na0H + SO_2 \longrightarrow Na_2SiO_3 + H_2O$$

You may also be familiar with one of the reactions happening in the blast furnace extraction of iron (in which calcium oxide (from the limestone which is one of the raw materials) reacts with silicon dioxide to produce a liquid slag, calcium silicate). This is also an example of the acidic silicon dioxide reacting with a base.

$$CaO + SiO_{2(s)} \longrightarrow CaSiO_{3(s)}$$

Germanium, tin and lead oxides

The monoxides

All of these oxides are amphoteric (they show both basic and acidic properties).

The basic nature of the oxides

These oxides all react with acids to form salts.

For example, they all react with concentrated hydrochloric acid. This can be summarized as:

$$XO_{(s)} + 2HCl_{(aq)} \longrightarrow XCl_{2(aq)} + H_2O_{(l)}$$

Where X can be Ge and Sn, but unfortunately needs modifying a bit for lead.

Lead (II) chloride is fairly insoluble in water and, instead of getting a solution, it would form an insoluble layer over the lead (II) oxide if you were to use *dilute* hydrochloric acid - stopping the reaction from going on.

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

However, in this example we are talking about using *concentrated* hydrochloric acid.

The large excess of chloride ions in the concentrated acid react with the lead(II) chloride to produce soluble complexes such as $PbCl_4^{2-}$. These ionic complexes are soluble in water and so the problem disappears.

$$PbCl_{2(s)} + 2Cl^-_{(aq)} \longrightarrow PbCl_4^{2-}{}_{(aq)}$$

The acidic nature of the oxides

All of these oxides also react with bases like sodium hydroxide solution.

$$XO_{(s)} + 2OH^-_{(aq)} \longrightarrow XO_2^{2-}{}_{(aq)} + H_2O_{(l)}$$

Lead (II) oxide, for example, would react to give PbO_2^{2-} - plumbate (II) ions.

The dioxides

These dioxides are again amphoteric - showing both basic and acidic properties.

The basic nature of the dioxides

The dioxides react with concentrated hydrochloric acid first to give compounds of the type XCl_4:

$$XO_2 + 4HCl \longrightarrow XCl_4 + 2H_2O$$

These will react with excess chloride ions in the hydrochloric acid to give complexes such as XCl_6^{2-}.

$$XCl_4 + 2Cl^- \longrightarrow XCl_6^{2-}$$

In the case of lead (IV) oxide, the reaction has to be done with ice-cold hydrochloric g acid. If the reaction is done any warmer, the lead (IV) chloride decomposes to give lead (11) chloride and chlorine gas. This is an effect of the preferred oxidation state of lead being +2 rather than +4.

Q22.Write note on the acidic nature of the dioxides of Group IV-A elements.

Answer

The dioxides will react with hot concentrated sodium hydroxide solution to give soluble complexes of the form $[X(OH)_6]^{2-}$.

$$XO2_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow [X(OH)_6]^{2-}_{(aq)}$$

Some sources suggest that the lead (IV) oxide needs molten sodium hydroxide. In that case, the equation is different.

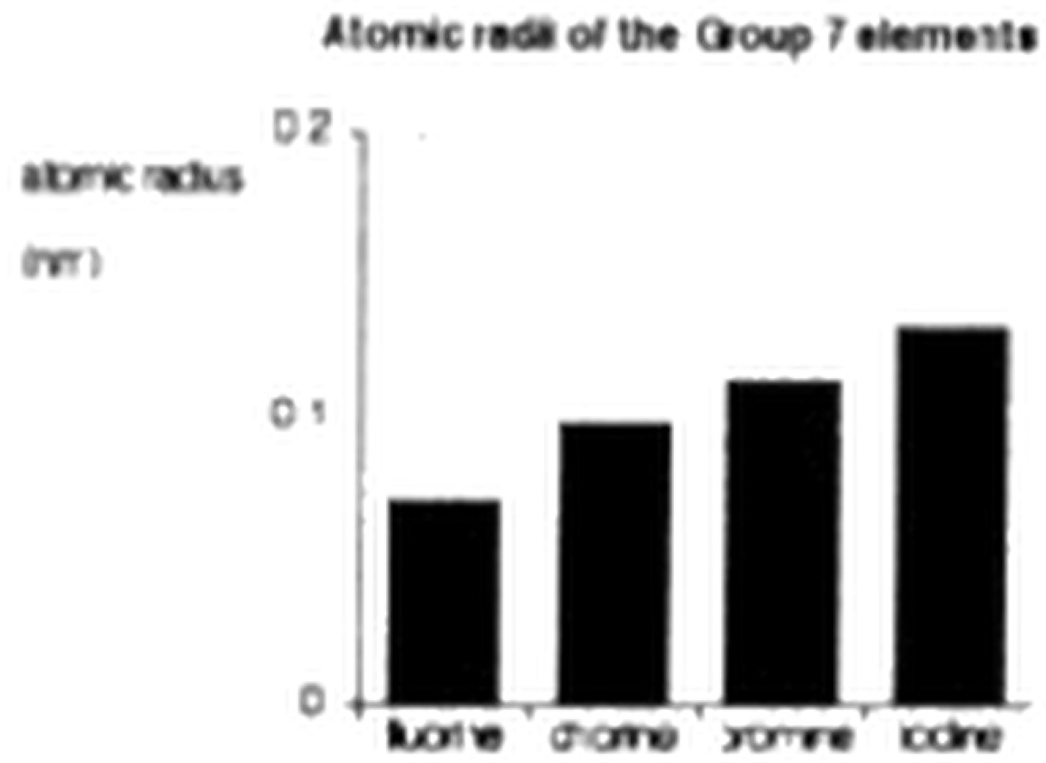
$$PbO_{2(s)} + 2NaOH_{(l)} \longrightarrow Na_2PbO_{3(s)} + H_2O_{(g)}$$

Group 7-Elements: (Halogens)

Atomic and Physical Properties

This article explores the trends in some atomic and physical properties of the Group 7 elements (the halogens) - fluorine, chlorine, bromine and iodine. You will find separate sections below covering the trends in atomic radius, electronegativity, electron affinity, melting and boiling points, and solubility. There is also a section on the bond enthalpies (strengths) of halogen-halogen bonds (for example, Cl-Cl) and of hydrogen-halogen bonds (e.g. H-Cl)

1) Trends in Atomic Radius



Trend,

Atomic radius increases as we go down the group due to increase number of shell greater shielding effect and less nuclear change.

2) Trends in Electronegativity

Halogens have large values of electronegativity. These values decrease as we proceed from F to I in the group. Large electronegativities values of halogen atoms indicate that X atoms have a strong tendency to form X-ions.

3) Trends in First Electron Affinity

Electron affinity values decrease from Cl to I. why the electron affinity value of F is less than that of Cl has already been explained.

4) Trends in Melting and Boiling Points

The melting and boiling points of the halogens regularly increase form F to I. This indicates that the attractive forces between molecules become progressively more prominent as the molecules increase in halogens. F and Cl are gases at ordinary temperature Br is a heavy liquid while I is a solid.

5) Bond enthalpies (bond energies or bond strengths)

Bond enthalpy is the heat needed to break one mole of a covalent bond to produce individual atoms, starting from the original substance in the gas state, and ending with gaseous atoms.

So, for chlorine, $C12_{(3)}$, it is the heat energy needed to carry out this change per mole of bond:

$$Cl - Cl_{(g)} \longrightarrow 2Cl_{(g)}$$

For bromine, the reaction is still from *gaseous* bromine molecules to separate gaseous atoms.

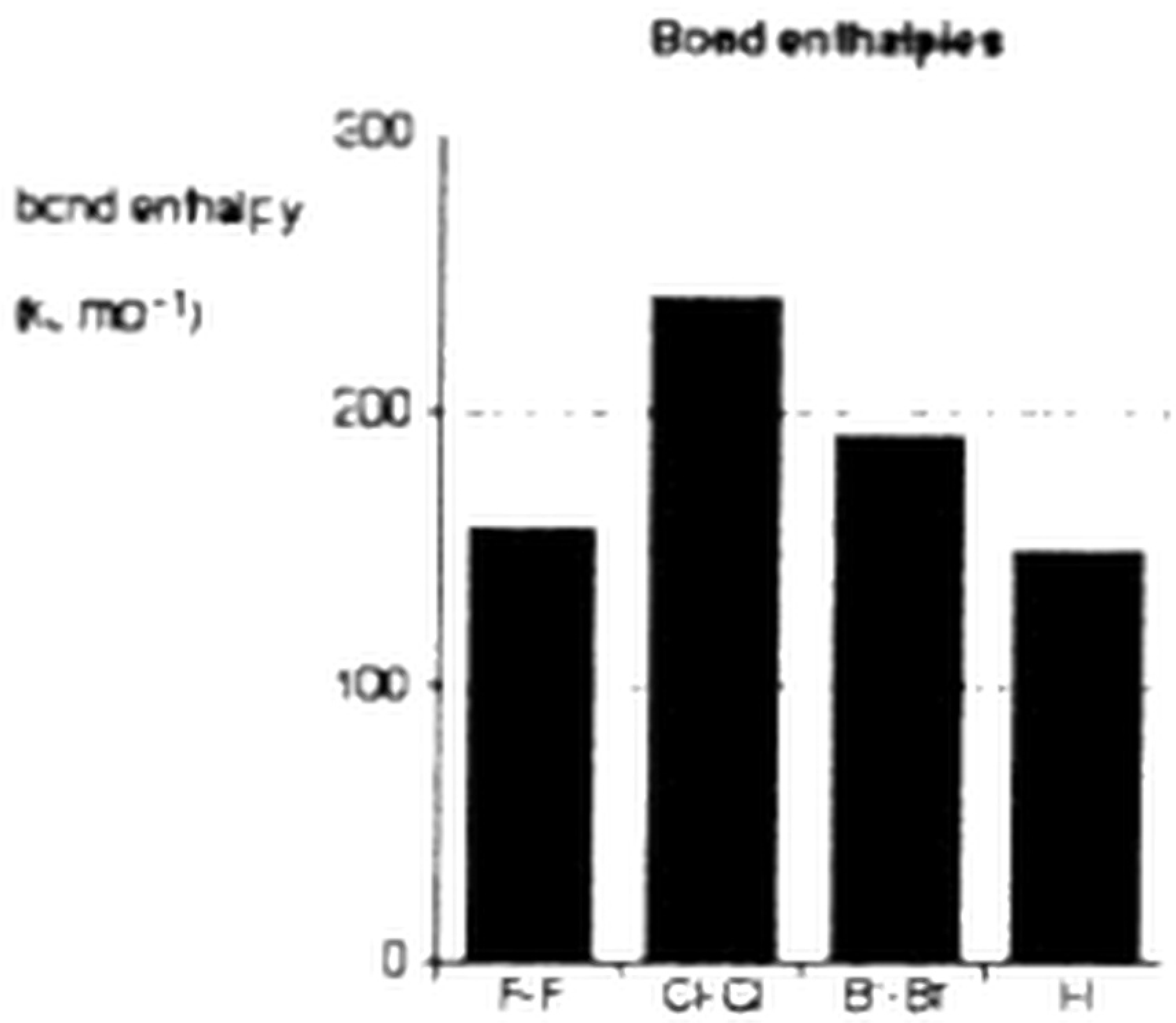
$$Br - Br_{(g)} \longrightarrow 2Br_{(g)}$$

Note gas not liquid

Q23. Discuss Bond enthalpy in the halogens, X2(9).

Answer

Look at following figure



The both enthalpies of the Cl-C1, Br-Br and bonds fall just as you would expect, but

the F-F bond is deviated from the sequence.

This is because of:

Due to very small F-F bond length very large as compared to other X-X bond lengths. This makes the F atoms in F2 molecule repel each other and helps the dissociation of F2 molecule into F atoms. (ii) X-X bond in Cl_2, Br_2 and I_2 molecules is stronger than F-F bond in F2 molecule. This is due to the possibility of the existence of multiple bonds in X-X bond involving d- orbitals.

Q24. Discuss Bond enthalpies in the hydrogen halides, $HX_{(g)}$

Answer

Where the halogen atom is attached to a hydrogen atom, this effect doesn't happen.

There are no lone pairs on a hydrogen atom.

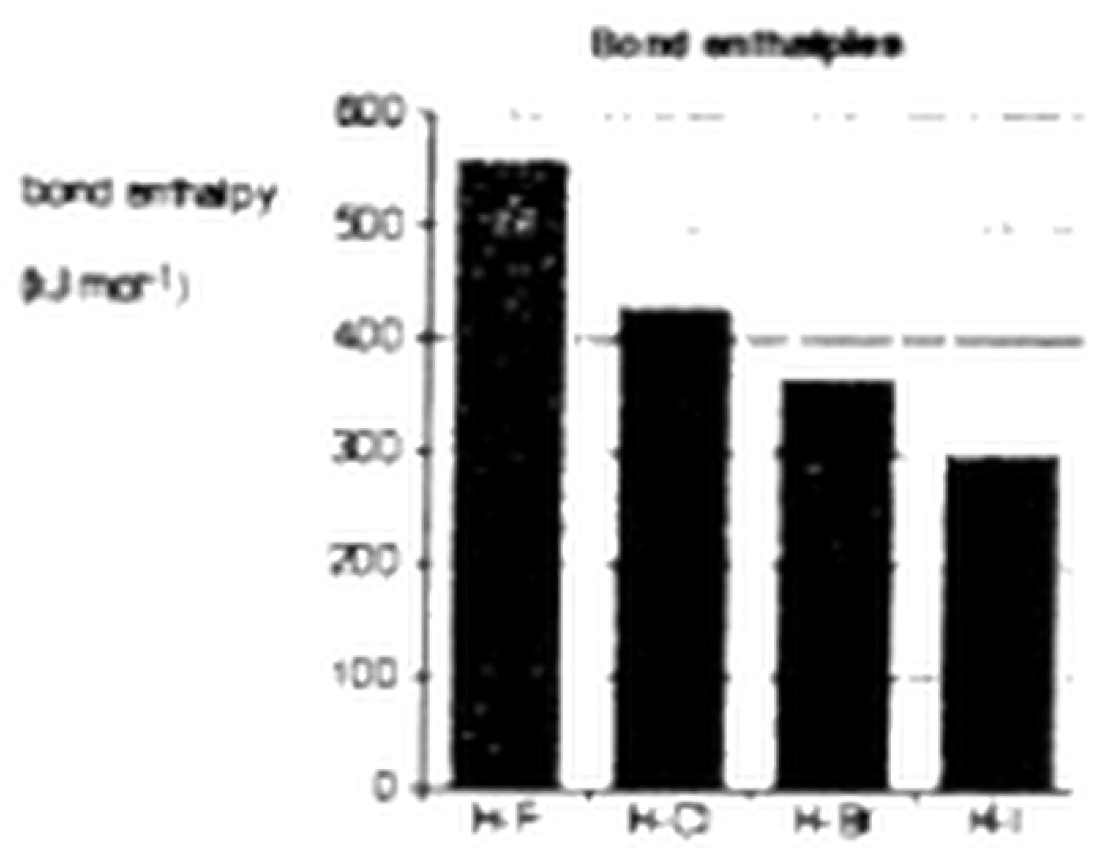


Fig. 13.28

As the halogen atom gets bigger, the bonding pair gets more and more distant from the nucleus. The attraction is less, and the bond gets weaker, exactly what is shown by the data. There is nothing complicated happening in this case.

Q25. Discuss Strength of Halogens as Oxidizing Agents: F2>Cl2>Br2>I2.

Answer

This section explores the trend in oxidizing ability of the Group 7 elements (the halogens) - fluorine, chlorine, bromine and iodine. We are going to look at the ability of one halogen to oxidize the ions of another one, and how that changes as you go down the Group.

Facts:

A substance that has a tendency to accept one or more electrons is said to show oxidising property. The halogens due to high electron affinity values have a great tendency to accept electron and hence act as strong oxidising agent: The oxidising property of a halogen molecule, X2 is represented by:

The above reaction is accompanied by the release of energy which is made up of many energy terms like that of fusion, vaporization etc. it has been seen that the values of E are decreasing from F2 to 12 the oxidising power of halogens is also decreasing in the same direction i.e. the oxidising power of halogen is in the or F2>C12>Br2>I2 (weakest oxidising agents). Since F2 is the strongest oxidising agent in the series, it will oxidise other halide ions to halogens in solution or when dry, F2, displaces other halogens from their corresponding halides. For example.

$$F_2 + 2X^- \rightarrow 2F^- + X_2$$

Similarly, Cl_2 will displace Br'' and 1- ins from their solutions and Bi_2 will displace 1- ions from their solutions.

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2$$

$$Br_2 + 2X^- \rightarrow 2Br^- + X_2$$

Q26. *Discuss* the Acidity of The Hydrogen Halides.

Answer

This topic looks at the acidity of the hydrogen halides - hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide.

The acidity of the hydrogen halides

Hydrogen chloride as an acid

All the halogen acids in the gaseous states are essentially covalent but in the aqueous solution they ionize to give solvated proton (H_30) and hence acts as acids.

$$H_2O + HX \rightarrow H_3O + X^-$$

HF ionizes only slightly while HCl, HBr, and HI ionize completely. Hence HF is the weakest acid and strength of these acids increases from HF to HI, i.e. HF (weakest acid)<HCl<HBr<HI

of H-F bond is HF molecule is the highest and hence this molecule has least tendency to splits up into Fr and F ions in aqueous solution. Another explanation of the above order of the acidic strength of HX acids can be given by finding out the relative order of the basicity of the conjugate bases viz F, CF, Brand I of these acids. The hydrides show no acidic character when perfectly dry.

Q27. Discuss Halide Ions as Reducing Agents and Trends in Reducing Strength Ability of Halide Ions.

Answer

The redox reactions between halide ions and concentrated sulphuric acid

This section describes and explains the redox reactions involving halide ions and concentrated sulphuric acid. It uses these reactions to discuss the trend in reducing ability of the ions as you go from fluoride to chloride to bromide to iodide.

Fluorides and Chlorides do not reduce concentrated sulphuric acid.

1) With bromide ions

The bromide ions are strong enough reducing agents to reduce the concentrated sulphuric acid. In the process the bromide ions are oxidized to bromine.

$$2Br^- \rightarrow Br_2 + 2e^-$$

The bromide ions reduce the sulphuric acid to sulphur dioxide gas. This is a decrease of oxidation state of the sulphur from +6 in the sulphuric acid to +4 in the sulphur dioxide.

$$H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$$

You can combine these two half-equations to give the overall ionic equation for the reaction:

$$H_2SO_4 + 2H^+ + 2Br^- \rightarrow Br_2 + SO_2 + 2H_20$$

2) With iodide ions

Iodide ions are stronger reducing agents than bromide ions are. They are oxidized to iodine by the concentrated sulphuric acid.

The reduction of the sulphuric acid is more complicated than before. The iodide ions are powerful enough reducing agents to reduce it

3) first to sulphur dioxide (sulphur oxidation state = +4)

4) then to sulphur itself (oxidation state = 0)

5) and all the way to hydrogen sulphide (sulphur oxidation state = -2).

The most important of this mixture of reduction products is probably the hydrogen sulphide. The half-equation for its formation is:

$$H_2SO_4 + 8H^+ + Be^- \rightarrow H_2S + 4H_2O$$

Combining these last two half-equations gives:

$$H_2SO_4 + 8H^+ + 81^- \rightarrow 412 + H_2S + 4H_20$$

Summary of the trend in reducing ability

Fluoride and chloride ions won't reduce concentrated sulphuric acid.

. Bromide ions reduce the sulphuric acid to sulphur dioxide. in the process, the bromide ions are oxidized to bromine.

:. Iodide ions reduce the sulphuric acid to a mixture of products including hydrogen sulphide. The iodide ions are oxidized to iodine.

i. Reducing ability of the halide ions increases as you go down the Group.

Explaining the trend

1) When a halide ion acts as a reducing agent, it gives electrons to something else. That means that the halide ion itself has to lose electrons.

2) The bigger the halide ion, the further the outer electrons are from the nucleus, and the more they are screened from it by inner electrons. It therefore gets easier for the halide ions to lose electrons as you go down the Group because there is less attraction between the outer electrons and the nucleus.

Q28.Write a note on: Food and Beverage Canning.

Answer

As early as 1940, can manufacturers begin to explore adapting cans to package carbonated soft drinks. The can had to be strengthened to accommodate higher internal can pressures created by carbonation (especially during warm summer months), which meant increasing the thickness of the metal used in the can ends. Otherwise, distortion of the end would strain the seal, creating potential leaks or making cans unstack able for storage and transit.

Another concern for the new beverage can was its shelf life. Even small amounts of dissolved tin or iron from the can could impair the drinking quality of both beer and soft drinks. Fortunately, beer, which is only mildly acidic, is relatively noncorrosive. In addition, beer ages naturally, so it has a limited shelf life of about three months in any package. In contrast, the food acids, including carbonic, citric and phosphoric, in soft drinks present a risk for rapid corrosion of exposed tin and iron in the can. The consequences of off-flavors, color changes and leakage through the metal needed to be addressed. At this point, the can was upgraded by improving the organic coatings used to line the inside, making cans heavier and more encasing.

The use of cans for carbonated beverages was delayed because of wartime material limitations mandated by the U.S. government. When the restriction ended in 1953 after the Korean War, the improved can was introduced and marketed nationwide. The can manufacturers then embarked on a program of material and cost savings by reducing both the amount of steel and the amount of coatings used in can making. These efforts were in part inspired by a new competitor — aluminum.

Q29. Write a note on Mining and Extraction of metals.

Answer

Different elements/metals are not obtained such rather these are obtained after passing through different steps.

These steps are discussed as follows:

I. **Mining and enrichment**
2. **Reduction**
3. **Refining and Casting**

In fact, some special methods are used to obtain each metal from its ores and to develop it into useful articles, yet few steps are common in the metallurgy of every metal. These are follows.

1. Mining

i) Crushing

Obtaining ores by digging the rocks and hills is called mining. This work is done by engineers and laborers with the help of machines. But prior to this work it is confirmed by survey and analysis that obtaining metals from this is economical or not.

ii) Grinding

Breaking of rocks and larger stones into smaller size stones is called crushing. This is done by jaw crushers.

iii) Hand Picking, *Jugging and* Shaking

In Pakistan and other underdeveloped countries where labor is cheap, metallic stones are picked and separated by hands. Heavy metals are separated from useless material i.e. gangue, by shaking with "chaage". In some countries this process is done by pressurized water.

iii) Magnetic Separation

The ground ore is passed over a magnetic belt which separates the magnetic metal from gangue. This process is sued for metals which have magnetic properties like iron.

2) Reduction

For the complete separation of a metal from gangue, ores are heated at high temperature. At its melting pint, molten metal is separated from solid gangue. It must be remembered that different metals are mixed with different compounds according to the type of impurities present in the metal ore and then they are passed through the process of reduction. The process of reduction is carried out in the blast furnace.

Blast Furnace

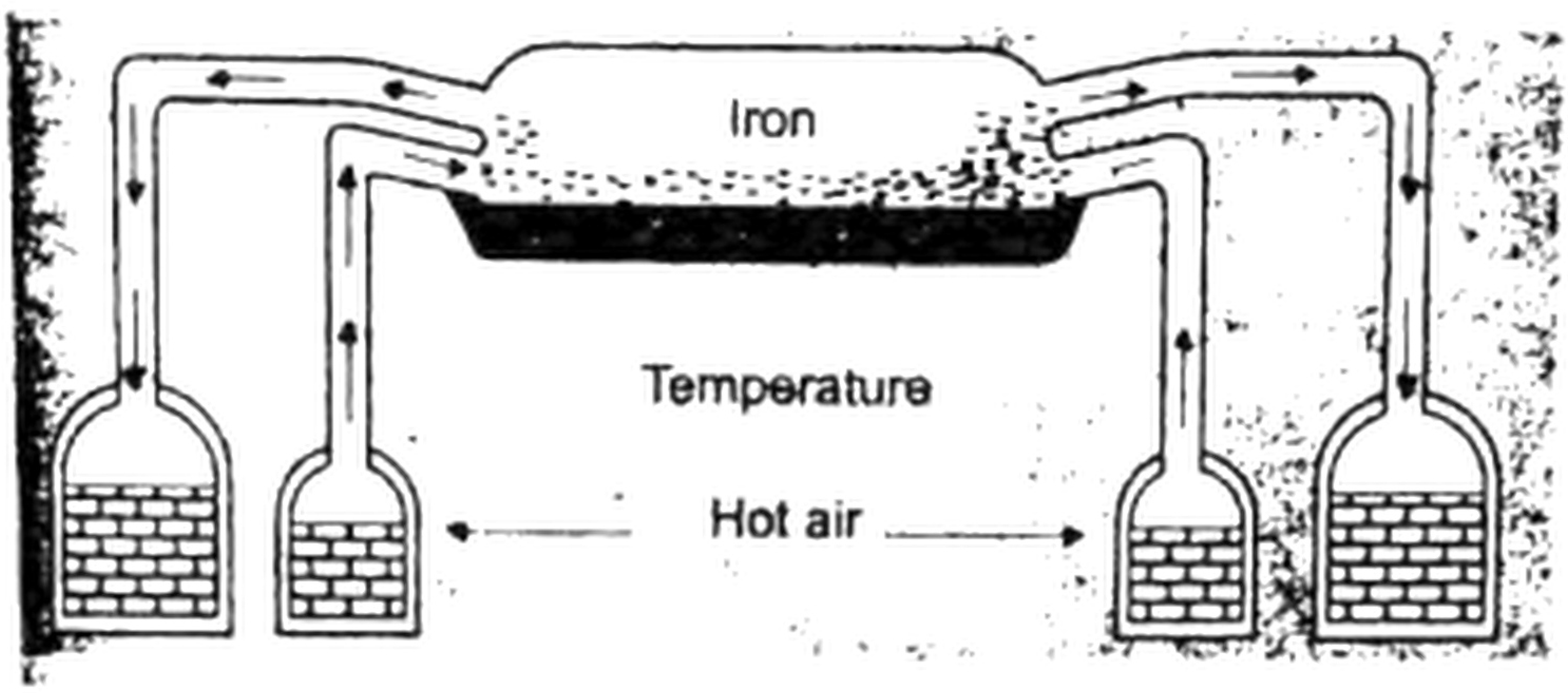
It is lined inside with fire bricks. Its height and capacity are kept according to the requirement. Hot gases enter from lower side and ores are charged from the top of the furnace. Temperature is maintained at 1500°-3000°C. This furnace is usually used for iron and copper metallurgy.

3) Refining of Metals

Metals extracted in the above process are further refined by the following process.

Open-Hearth Process:

A fire furnace is used to remove the impurities of metal. It is lined inside with fire bricks and is just like a room. Burning gases are entered from one side and exhaust gases are removed from the opposite end. The process is operated form opposite ends after an interval. Metals melt in a shorter time by this two-way heating.



Q30. Give applications of bleaching powder.

Answer

Bleaching powder is actually a mixture of calcium hypochlorite ($Ca(OCl)_2$) and the basic chloride CaCl2, H_2O with some slaked lime, Ca(OH)2.

Bleaching powders take time to dissolve in water and longer to work but have a longer shelf life in comparison to liquid bleaches and can be used on items like upholstery, carpet and some delicate fabrics. However, bleaching powder should never be combined with ammonia or used on colored fabrics as it will cause fading.

1) Bleaching powder is highly effective for cleaning inside the home and outdoors. It can be used for removing mildew from fabric, cleaning countertops and for removing mold from grout between tiles, bathmats and shower curtains. Outside, the agent can be used on plastic furniture, unpainted cement, paving and painted surfaces to eliminate mildew and other stubborn stains.

2) Bleaching powder can be used to safely disinfect and sterilize many things around the home including secondhand goods, trash cans, pet accessories and baby toys and furniture.

   Bleaching powder is a highly effective means of returning the luster to white porcelain and glassware. Glassware can regain its sparkle by adding a small amount of powdered bleach to dishwater when washing glasses. Gardening

3) To kill any annoying weeds growing from cracks and crevices in the garden a pang mixture of bleaching powder and water is applied. Moss and algae on garden walkways can be easily eliminated by scrubbing with bleaching powder diluted in water. Powdered bleach is also useful for sanitizing garden tools to avoid diseases spreading between plants. Adding powdered bleach to the water of cut flowers will help to preserve their freshness by preventing the growth of bacteria in the vase.

4) Bleaching powder is used for the disinfection of drinking water or swimming pool water. It is used as a sanitizes in outdoor swimming pools in combination with a as a sanitizes in outdoor swimming pools in combination with a cyanuric acid stabilizer, which reduces the loss of chlorine due to ultraviolet radiation. The calcium content hardens the water and tends to clog up some filters; hence, some products containing calcium hypochlorite also contain anti-scaling agents.

Bleaching powder is used for bleaching cotton and linen. It is also used in bathroom cleaners, household disinfectant sprays, moss and algae removers, and weed killers.

In addition, bleaching powder may be used to manufacture chloroform.

Bleaching powder is used also in sugar industry for bleaching sugar cane juice before its crystallization.

Q31.Give Commercial Uses of Halogens.

Answer

1. Chlorine is used as a cheap industrial oxidant in the manufacture of bromine
2. Iodine is dissolved in alcohol, commonly known as tincture of iodine is used as a mild antiseptic for cuts and scratches. Iodine is also mixed with the detergents used in cleaning diary equipment.
3. Small quantities of fluorine are used in rocket propulsion. Much larger quantities are used make uranium (VI) fluoride for the separation of ^{238}U and ^{235}U:

$$UF_4\ (s) + F2\ (g) \rightarrow UF_6\ (s)$$

4. Fluorine is also used to make a wide range of fluorocarbon compounds for use as refrigerants, aerosol propellants, an aesthetics and fire-extinguisher fluid. One of the most important fluorocarbons is poly (tetrafluoroethene), PTFE, frequently sold under the trade name Fluon or Teflon.

Q32. Write a note on: Iodine Deficiency and Goiter.

Answer

Iodine Deficiency

Iodine is an element that is needed for the production of thyroid hormone. The human body cannot synthesize iodine, so it is an essential element.

1 The deficiency of iodine leads to enlargement of thyroid a condition called goiter. Hypothyroidism and mental retardation in children and infants is observed if their mothers suffered from iodine deficiency during pregnancy.

Before 1920, iodine deficiency was common in Appalachian, north-western US regions, and in most of Canada. Approximately, 40% of the world's population remains at the risk of iodine deficiency.

Goiter

The term goiter refers to the abnormal enlargement of thyroid gland due to deficiency of iodine in diet. It results in swelling in neck. It is important to know that the presence of goiter does not necessarily mean that the thyroid gland is malfunctioning (hypothyroidism). A goiter can also occur in a gland that is producing too much thyroid hormone (hyperthyroidism) or even the correct amount of hormone (euthyroidism). A goiter indicates there is a condition present which is causing the thyroid to grow abnormally.

Q33.What is Fluoride Deficiency and Toxicity?

Answer

Fluoride Toxicity

Fluoride toxicity or fluoride poisoning is a condition in which more fluoride is taken than the amount required for normal growth, development and metabolism. Fluoride toxicity is characterized by a variety of signs and symptoms. Poisoning most commonly occurs following ingestion of conspicuous amount of fluoride entraining products. Symptoms or set usually occurs within minutes of exposure. Fluoride is found in many common household products e.g. toothpaste, dietary supplementary, insecticides, rodenticides etc: ·fluoride toxicity results,

i) Arthritis

ii) Stiff painful joints with or wistful swelling

iii) Asthma, especially after showering

iv) Painful bony lumps where tendons and ligaments attach to bones

Fluoride Deficiency

Fluoride deficiency results when the amount of its tip take is less than required.

Fluoride deficiency results in

Brittle bones or demineralization of bones

Brittle bones or demineralization of bones

Cavities

Weakened tooth enamel

Fluoride deficiency can lead to a higher likelihood of developing bone fractures and possibly even osteoporosis.

Halogens and their compounds are used or bleaching, refrigeration and as aerosols, etc.