The chemistry of Group VII elements and their compounds.

Introduction

- The elements of group VII of the Periodic Table are fluorine, chlorine, bromine, iodine and astatine.
- Astatine is radioactive and little is known about its chemistry.

Summary of some of the physical properties group IV elements

Element	Atomic number	Outer most E.C	Atomic radius (nm)	Ionic radius, X^- (nm)	M.pt (℃)	B.pt (℃)	1st E.A (kJ mol^{-1})	Electronegativity	E^θ(V) for $X_2 \rightarrow X^-(aq)$
F	9	$2s^22p^5$	0.072	0.136	−220	−188	−333	4.00	+2.87
Cl	17	$3s^23p^5$	0.099	0.181	−101	−34.7	−348	2.85	+1.36
Br	35	$4s^24p^5$	0.114	0.195	−7.2	58.8	−340	2.75	+1.09
I	53	$5s^25p^5$	0.133	0.216	−114	184	−297	2.20	+0.54
At	85	$6s^26p^5$							

General remarks about the elements

- The elements are called **halogens**; a Greek word meaning **salt formers**.
- All the halogens are poisonous. Thus, handle them with extra care.
- Fluorine is a pale yellow gas, chlorine is a greenish-yellow gas, bromine is a dark red liquid whose vapour is brown and iodine is a shiny black solid which forms purple or violet vapours even on slight warming.
- All the elements have 7 electrons in their outermost energy levels and thus, their general outer electronic configuration is **ns^2np^5**.
- All the elements have one electron short of the inert gas electronic structure. Thus, the elements complete octet (become stable) by:
  - ✓ forming a single covalent bond. This involves sharing the unpaired electron in the p-subshell. For example, in the elements, X_2 (F_2, Cl_2, Br_2, I_2) and their hydrides HF, HCl, HBr and HI.
  - ✓ gaining an electron to form the monovalent ion, X^- (F^-, Cl^-, Br^-, I^-)
- Large atoms as such those of chlorine, bromine and iodine have empty d orbitals of suitable energy (easily accessible d orbitals) and thus, can form compounds in which the octet of electrons is expanded. This makes them show variable oxidation states/valencies in the compounds they form. For example, iodine shows valencies (oxidation states) of 1 (± 1),3 (+3), 5 (+5) and 7 (+7) in HI or ICl, ICl_3, IF_5 and IF_7 respectively. ICl, ICl_3, IF_5 and IF_7 are called **interhalogen compounds**.

- Fluorine the first member in the group cannot expand its octet and thus, has a fixed oxidation state of -1.

  Reason: Fluorine atom has a small atomic radius and this makes the atom lack d orbitals of suitable energy to expand its octet.
- Oxidation states of ± 1 and 0 are the most stable; -1 is shown in ionic compounds while 0 is shown in X_2 molecules.
- All exist as diatomic molecules. The only force operating between the individual molecules are the weak van der Waals forces. The strength of the van der Waals forces between the molecules increases with increase in molecular mass of the molecules in the order; $F_2 < Cl_2 < Br_2 < I_2$. Thus, great amount of heat energy is required to overcome the increasing strength of the intermolecular forces in the same order.

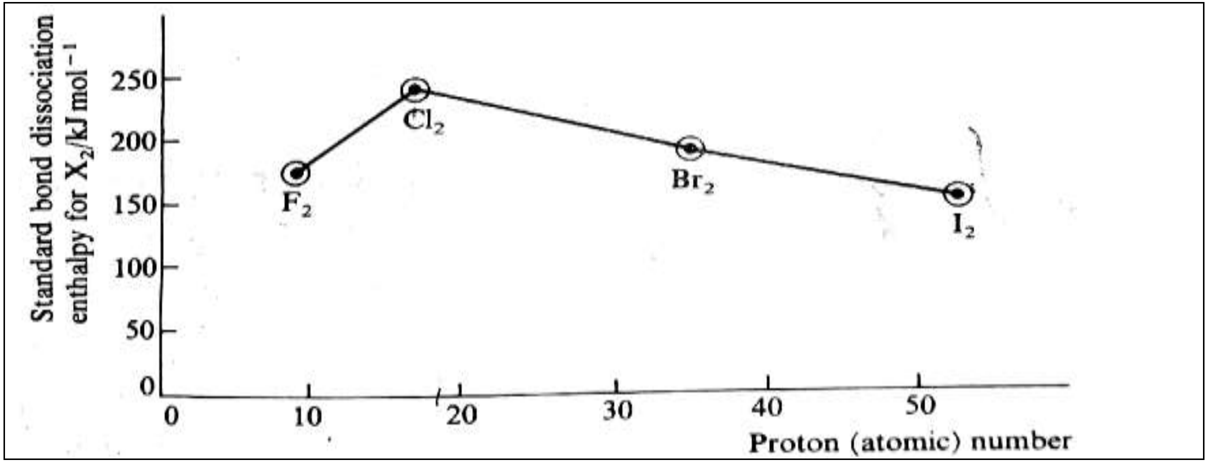
  The increase in the strength of the intermolecular forces from fluorine to iodine explains the:

  (a) trend or order in boiling and melting points.

  (b) gradual change in the physical states from gas through liquid to solid. The changes in the physical states explain the abnormal/unexpected trend in boiling and melting points.
- In iodine, the van der Waals forces are sufficiently strong to bind the individual molecules close together. This makes iodine to exist as a solid at room temperature and pressure. Iodine sublimes on slight warming and this indicates the weak nature of van der Waal's forces.
- On descending down the group from fluorine to iodine, atomic radius increases and thus, electronegativity decreases while electropositivity increases.
- All the members are non-metallic. Metallic character increases with increase in atomic number/atomic radius. Refer to notes on periodicity for the explanation.
- First electron affinity **generally** decreases from fluorine to iodine. The first electron affinity for fluorine atom is much lower than expected. (Refer to notes in periodicity)
- The elements have very high first ionisation energies and this makes them unable to readily form positively charged ions. However, the first ionisation energy decreases from fluorine to iodine as explained before. Fluorine shows appreciably high first ionisation energy than the rest. This is due to very small atomic radius of fluorine atoms.
- As atomic number increases, the bond dissociation energy for $X - X$ bond rises sharply from fluorine to chlorine and decreases from chlorine to iodine.

Element	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Standard bond dissociation energy $X - X$ bond (kJ mol^{-})	79.1	122	111	106

The plot of standard bond dissociation energy for the halogens against atomic number of the halogen takes the following form:



Reason/explanation:

This is because as atomic number increases, atomic radius increases and so does the halogen—halogen bond length. The longer the halogen—halogen bond, the weaker the bond and hence, the observed trend.

Also as atomic radius increases, the effective overlap of atomic orbitals of the bonded atoms reduces. This further causes a reduction in the bond strength.

The unexpected low bond dissociation energy for fluorine—fluorine bond is due to the small atomic radius of fluorine atoms which makes fluorine—fluorine bond length short. The nuclei and the lone pairs of electrons on the two fluorine atoms are brought so closer together than in the other halogen molecules.

This increases the internuclear repulsions and repulsions between lone pairs of electrons of the two atoms. These factors greatly weaken the F–F bond.

- The S.E.P values measure the tendency for the following process to occur (i.e. oxidizing power of the halogen/tendency to accept electrons):

$$X_2 + 2e^- \longrightarrow 2X^-(aq)$$

The more positive the value of S.E.P, the more oxidizing the halogen is. The S.E.P values become less positive from fluorine to iodine and thus, the oxidizing power of the halogens decrease in the same order. Fluorine is the strongest oxidizing agent while iodine is the weakest oxidizing agent.

Fluorine is the strongest oxidant because;

- ✓ Fluorine atom has the smallest atomic radius and is the most electronegative.
- ✓ Fluorine molecule has the lowest bond dissociation energy.
- ✓ Fluoride ion has a very high hydration energy.

Note:
Fluorine is rarely employed as an oxidizing agent because it is difficult to handle.

- Generally the halogens (Cl_2, Br_2, I_2) have low solubility in pure water.

  Reason:

  Their molecules are non-polar and the individual molecules are held by **weak** van der Waals forces. Water molecules are polar with **strong** hydrogen bonds between its molecules. Thus, when mixed, strong repulsions occur between the different molecules and this hinders the association between the halogen molecules and water molecules and hence, dissolution of the halogens in water. Also iodine molecules do not react with water molecules.

  Fluorine does not dissolve in water. It vigorously attacks water forming oxygen and hydrogen fluoride.
- Although iodine is sparingly soluble in water, it readily dissolves in aqueous solution of potassium (or sodium) iodide.

  Reason:

  In aqueous solution of potassium iodide, iodine reacts with iodide ions to form a very stable soluble complex ion, triiodide ion.

$$I_2(s) + \underbrace{I^-(aq)}_{from\ KI} \longrightarrow I_3^-(aq)$$

- The halogens also dissolve in organic solvents in accordance with the rule "like dissolves like". For example, iodine dissolves in benzene and tetrachloromethane to form a purple solution. In ethanol and in aqueous potassium iodide, iodine forms a brown solution.

Anomalous behaviour of fluorine

- Fluorine, the first member in this group, behaves quite differently from the others because of the following reasons:
  - ✓ Fluorine atom has the smallest atomic radius and is the most electronegative.
  - ✓ Fluorine molecule has unexpectedly very low fluorine–fluorine bond dissociation energy.
  - ✓ Fluorine atom lacks easily accessible d-orbitals and thus, cannot expand its octet.
  - ✓ Fluoride ion has very small ionic radius. This causes the ionic fluorides to have higher lattice energies than the corresponding ionic compounds of other halogens.
  - ✓ Fluorine has the highest positive value of electrode potential.
- The above features make fluorine to shows the following differences from other group members:
  - (a) Fluorine shows only one oxidation state in its compounds whereas the other halogens show variable oxidation states in their compounds. For instance iodine shows oxidation states of −1,+3,+5 and +7.
  - (b) Fluorine combines directly with carbon while the others do not.

(c) Fluorine oxidises water with evolution of oxygen whereas the other halogens like bromine and chlorine react with water to form a mixture of acids and no oxygen is evolved. Iodine is insoluble in pure water and thus, no reaction occurs.

(d) The other elements show their highest oxidation states in combination with fluorine. For example; SiF_6, OsF_8, IF_7 and SF_6.

(e) Fluorine reacts with cold, dilute aqueous alkali solution to give oxygen difluoride, fluoride ions and water while the other halogens form the corresponding halide ions, halate(I) ions and water.

(f) Fluorine reacts with hot, concentrated aqueous alkali solution to give oxygen, fluoride ions and water while the other halogens form the corresponding halide ions, halate(V) ions and water.

(g) Calcium fluoride, lithium fluoride and magnesium fluoride are insoluble in water whereas the corresponding chloride, bromide and iodide are soluble. Also silver fluoride is the only soluble silver halide.

(h) Hydrogen fluoride is a liquid at room temperatures, weak acid and has unexpectedly high boiling point whereas the other halogen hydrides are gases, strong acids and have low boiling points. Hydrofluoric acid forms both acid and normal salts whereas the other halogen acids form normal salts only.

(i) Metal fluorides are ionic but the corresponding chlorine, bromine and iodine compounds are essentially covalent. For aluminium trifluoride is ionic whereas aluminium trichloride is covalent.

(j) Potassium manganate(VII) can oxidise HX (X= Cl, Br or I) to form X_2 molecule, but HF is not oxidised by the same reagent.

(k) Fluorine compounds are more stable than the corresponding chlorine, bromine or iodine compounds.

Activity 1

1. Describe **one** general method for preparing halogens (chlorine, bromine and iodine) except fluorine. Your answer should include a relevant reaction equation.
2. Fluorine compounds are very stable whereas the corresponding chlorine, bromine or iodine compounds are not. Explain
3. State **two** reasons why fluorine is;
   (a) more reactive than other halogens in group VII in the Periodic Table.
   (b) the strongest oxidizing agent in group VII in the Periodic Table.
4. Fluorine, chlorine, bromine and iodine some of the elements in Group VII of the Periodic Table.
   (a) Explain the following trends among the Group VII elements.
      (i) Atomic radius (ii) Electronegativity (iii) Boiling points
   (b) Explain why fluorine shows some differences in its properties from the rest of the others elements in the same Group VII.

(c) State
  - (i) the differences between the chemistry of fluorine and the rest of the elements of Group VII of the Periodic Table.
  - (ii) **four** properties in which fluorine differs from the rest of the members of Group VII elements.
  - (iii) **four** properties in which fluorine differs from iodine.

Laboratory preparation of halogens

- Fluorine being extremely very reactive and the strongest oxidizing agent known, cannot be prepared in the laboratory directly by chemical reactions. The gas readily attacks almost anything in contact with it. It is obtained by **electrolysis** of a mixture of anhydrous hydrogen fluoride and molten potassium fluoride.
- The rest (Cl_2, Br_2 and I_2) are prepared by the same fundamental method.
  The method involves **heating** a mixture of the corresponding alkali metal halide, concentrated sulphuric and manganese(IV) oxide (or lead(IV) oxide).
  The general equation leading to the formation of the halogen is:
  $4NaX(s) + 2H_2SO_4(l) + MnO_2(s) \rightarrow X_2(g/l/s) + MnX_2(aq) + 2Na_2SO_4(aq) + 2H_2O(l)$
  Besides NaX, KX can be used. The setup of the apparatus depends on the halogen in question.
- Chlorine can also be obtained by:
  (a) treating bleaching powder with dilute acids.
  (b) oxidizing concentrated hydrochloric acid with **either** potassium manganate(VII) in the cold (room temperature) **or** manganese(IV) oxide/lead(IV) oxide on warning/heating.
  The above methods work only for chlorine because both bleaching powder and concentrated hydrochloric acid are readily available. This is not the case for bromine and iodine.
- Preparation of halogens should be done in an open place or in a fume cupboard because they are very poisonous.

Reaction of the halogens

- Fluorine is the most reactive of all elements. It forms compounds under appropriate conditions with every other element in the Periodic Table except with some inert gases.
- Reactivity decreases from fluorine to iodine.

Note

The halogens react by gaining electrons thus, forming negative ions.

$X(g) + e^- \rightarrow X^-(g)$

The tendency to gain electrons decreases as the group is descended. This is due to increase in atomic radius which in turn reduces the nuclear attraction for the incoming electrons.

A. Reaction with Water

- Fluorine readily oxidises cold water to hydrofluoric acid and oxygen. Some ozone and hydrogen peroxide are also produced.
  $2F_2(g) + 2H_2O(l) \rightarrow 4HF(aq) + O_2(g)$
- Chlorine and bromine are moderately soluble in water and react slowly react with it to form a pale yellow solution which is a mixture of acids. Chlorine forms chloric(I) acid and hydrochloric acid while bromine forms bromic(I) acid and hydrobromic acid.
  $X_2(g/l) + H_2O(l) \rightarrow HX(aq) + HOX(aq)$; X= Cl or Br
  Bromine is less soluble in water and reacts less readily with water than chlorine.

Note:

- ✓ A mixture of chloric(I) acid and hydrochloric acid is called **chlorine water** while that of hydrobromic acid and bromic(I) acid is **bromine water**.
  The aqueous solutions turn colourless when exposed to sunlight due to decomposition of the unstable halic(I) acid. Oxygen gas is evolved.
  $2HOCl(aq) \rightarrow 2HCl(aq) + O_2(g)$; $2HOBr(aq) \rightarrow 2HBr(aq) + O_2(g)$
- ✓ Chlorine dissolves in water to a much greater extent in the presence of hydroxide ions (i.e. alkaline solution).
  Chlorine reversibly reacts with pure water according to the following equation.
  $$Cl_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$
  In an alkaline solution, the hydroxide ions react with hydrogen ions form the acids formed in solution to form water. Equilibrium concentrations of hydrogen ions reduce and this disturbs the equilibrium position. In order to restore the equilibrium position, more chlorine molecules hydrolyse. This causes the solubility of chlorine in alkaline solutions to increase.
- ✓ A similar reaction occurs with aqueous solution of bromine.

- Iodine is sparingly soluble in water. Thus, there is hardly any reaction with water. Iodine is very soluble in water containing with potassium iodide.

- Aqueous solutions of the halogens (except iodine) turn blue litmus paper to red. This indicates the acidic nature of the resultant solution of the halogens. The litmus paper turns white for the case of chlorine and bromine due to their bleaching action.

Activity 2

1. Explain the bleaching action of chlorine.

Bleached shirt

2. Give reasons for each of the following observations.
   (a) Dry chlorine has no effect on dry litmus paper.
   (b) Chlorine has no effect on printer's ink.
   (c) Iodine has no bleaching action.
3. Chlorine is more soluble in aqueous sodium hydroxide than in pure water. Explain this observation.

B. Reaction with Alkalis

- The reaction products depends on upon the reaction conditions and concentration of the alkali.

  (i) With cold dilute alkalis (e.g. cold dilute sodium hydroxide solution)

  - ✓ Fluorine reacts vigorously and forms oxygen difluoride gas and sodium fluoride together with water.
    $F_2(g) + 2NaOH(aq) \rightarrow 2NaF(aq) + OF_2(g) + H_2O(l)$
    Ionic equation is………………………………………………………………………………………………………
  - ✓ Chlorine and bromine react and produce a pale yellow solution. The solution contains a halate(I), a halide and water.
    $X_2(g/l) + 2NaOH(aq) \rightarrow NaX(aq) + NaOX(aq) + H_2O(l)$
    Ionic equation is………………………………………………………………………………………………………
  - ✓ The pale yellow solution formed by bromine readily decomposes to give a colourless solution containing sodium bromate(V), sodium bromide and water. While that formed by chlorine requires sunlight or a catalyst to accelerate its decomposition.
    This type of reaction is called a **disproportionation** reaction.
    For example: $\underbrace{3BrO^-(aq)}_{bromate(I)\ ion} \rightarrow \underbrace{BrO_3^-(aq)}_{bromate(V)\ ion} + 2Br^-(aq)$

- ✓ Iodine dissolves and reacts to form iodate(I) ions, iodide ions and water.
  $I_2(s) + 2OH^-(aq) \rightarrow I^-(aq) + IO^-(aq) + H_2O(l)$
  Molecular equation is………………………………………………………………………………..
  The iodate(I) ions rapidly decompose even at room temperature to iodate(V) ions and iodide ions.
  The ionic equation is ………………………………………………………………………………………….

(ii) With hot concentrated alkalis

- ✓ Fluorine readily reacts to give oxygen, sodium fluoride and water.
  $2F_2(g) + 4NaOH(aq) \rightarrow O_2(g) + 4NaF(aq) + 2H_2O(l)$
  The ionic equation is
- ✓ Chlorine, bromine and iodine react and produce colourless solutions containing halate(V) ions, halide ions and water.
  $3X_2(g/l/s) + 6NaOH(aq) \rightarrow 5NaX(aq) + NaXO_3(aq) + 3H_2O(l)$; X= Cl, Br or I
  The ionic equation is…………………………………………………………………………………………….

- Chlorine reacts with solid slaked lime at room temperature to produce bleaching powder.
  The equation for the reaction can be simply written as follows:
  $Cl_2(g) + Ca(OH)_2(s) \rightarrow \underbrace{CaOCl_2.H_2O(s)}_{\substack{\text{Calcium chlorate(I)} \\ \text{bleaching powder}}}$
  The bleaching powder liberates chlorine when reacted with dilute acids or when left exposed to the atmospheric carbon dioxide. This explains why the bleaching powder always has a strong smell of chlorine.

C. Reaction with some metals

- Dry halogens react with most metals to form the corresponding metal halides.
- Most of reactions require **heating**. Fluorine readily and directly combines with metals.
- Chlorine and bromine are **strongly oxidizing**. They give products in higher oxidation states for metals that exhibit variable oxidation states, unless it is unstable at the temperature used.
- Iodine is less oxidizing and thus, cannot form compounds in higher oxidation states with metals that exhibit variable oxidation states.
- For example:
  $Mg(s) + X_2(g) \rightarrow MgX_2(s)$; X=Cl or Br
  $2M(s) + 3X_2(g) \rightarrow 2MX_3(s)$; X= Cl or Br and M= Al, Fe or Cr
  $Fe(s) + I_2(g) \rightarrow FeI_2(s)$
  $Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l)$; Both $SnBr_4$ and SnI_4 do not exist.

Note:

- ✓ These reactions provide the best way of preparing certain anhydrous metal halides.
- ✓ Bromine reacts with iron filings at room temperature. This explains why the filings are used to trap escaping poisonous bromine vapours in its manufacture.

Activity 3

1. Explain each of the following observations. Illustrate your answers with equations.
   (a) Iron tribromide exists while iron triiodide does not.
   (b) Tin(IV) chloride exists while tin(IV) bromide does not.
2. Dry chlorine was passed over heated aluminium filings. Write equation for the reaction that took place.
3. State the conditions and write equation for the reaction between:
   (a) Chlorine and tin.
   (b) Iron filings and bromine.
4. State how each of the following anhydrous compounds can be prepared.
   (a) Aluminium bromide.
   (b) Iron(III) chloride.

D. Reaction with non-metals

- All the group members do not react directly with oxygen, nitrogen and carbon. Fluorine, however, attacks carbon.
- All react with hydrogen to form the corresponding hydrides. The vigour of the reaction decreases from fluorine to iodine.
  For example;

Reaction equation	**Comments**
$H_2(g) + F_2(g) \rightarrow 2HF(l)$	Occurs at room temperature or even in the dark. Mixture explodes
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	Mixture requires heat or the presence of ultraviolet light (or direct sunlight)
$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$	Mixture explodes requires 200℃ and Pt as a catalyst
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	Mixture explodes requires >400℃ and Pt as a catalyst. Reaction is reversible.

- Dry chlorine and bromine react with molten sulphur to form sulphur monohalide (disulphur dihalide); a red liquid.
  For example; $Cl_2(g) + 2S(l) \rightarrow \underbrace{S_2Cl_2(l)}_{red\ liquid}$
  Iodine does not react with sulphur while fluorine forms gaseous sulphur hexafluoride.

- Silicon combines with all halogens to form the corresponding tetrahalides. Fluorine readily ignites but the rest require heating.
  For example; $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$
  SiF_4 is a gas; $SiCl_4$ and $SiBr_4$ are liquids while SiI_4 is a solid.
- At room temperature, white phosphorus reacts with dry chlorine or bromine to form the corresponding phosphorus trihalides in limited supply of halogen and phosphorus pentahalides with excess supply of the halogen.
  $2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l)$; $\underbrace{Cl_2(g)}_{excess} + PCl_3(l) \rightarrow PCl_5(s)$
  Iodine forms only phosphorus triiodide. Phosphorus pentaiodide does not exist.

  Note:
  Less reactive red phosphorus requires heating/warming.

Activity 4

1. Explain each of the following observations.
   (a) Phosphorus pentabromide exists while phosphorus pentaiodide does not.
   (b) Phosphorus forms phosphorus trichloride and phosphorus pentachloride whereas nitrogen only forms nitrogen trichloride; yet nitrogen and phosphorus belong to the same group in the Periodic Table. ($N = 7$; $P = 15$)
2. State how each of the following anhydrous compounds can be prepared.
   (a) Phosphorus(III) chloride.
   (b) Sulphur monobromide.
   (c) Phosphorus(V) bromide.

E. Oxidising reactions of the halogens

- The halogens are highly electronegative and therefore, readily accept electrons.
- Thus, the halogens act as oxidizing agents and the essential reaction is;

$$X_2(aq) + 2e^- \longrightarrow 2X^-(aq)$$

Note: Oxidation reactions essentially take place in aqueous solution.

- The oxidizing power of the halogens decreases from fluorine to iodine as already explained.
- The following are typical oxidizing actions.
  (i) Chlorine oxidises bromide ions to molecular bromine and iodide ions to molecular iodine.
  Bromine oxidises iodide ions to molecular iodine.
  Iodine has no action on any halide ions in aqueous solution.

$$Cl_2(g/aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + \underbrace{Br_2(aq)}_{reddish-brown}$$

$$Br_2(l/aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + \underbrace{I_2(aq)}_{brown}$$

(ii) Iron(II) ions to iron(III) ions.

This conversion is possible with chlorine or bromine but not iodine.

(iii) Hydrogen sulphide

This conversion is possible with all the halogens.

The colour of the halogen is discharged. Sulphur forms a yellow precipitate.

(iv) Sulphur dioxide, sulphurous acid or any soluble sulphite to sulphate ions.

This conversion is possible with all the halogens. The colour of the halogen is discharged.

(v) Tin(II) salts to tin(IV) salts.

The colour of the halogen is again discharged

(vi) Nitrites to nitrates.

The colour of the halogen is discharged

(vii) Sodium thiosulphate.

- ✓ Chlorine and bromine are strongly oxidizing; the reaction depends on the amount of chlorine and bromine used.

  For example:

  (i) With moderate amount of the chlorine or bromine, the thiosulphate ions are oxidised to sulphate ions. Sulphur is also precipitated as a yellow a solid.

  Ionic equation is……………………………………………………………………………………

  (ii) Large excess of bromine or chlorine oxidises thiosulphate ions to sulphate ions. No sulphur is precipitated.

  Ionic equation is……………………………………………………………………………………
- ✓ The reaction of chlorine with sodium thiosulphate explains why sodium thiosulphate as an antichlor to remove chlorine from a bleached fabric.
- ✓ Iodine dissolved in potassium iodide, is a weaker oxidizing agent and thus, only oxidises thiosulphate ions to tetrathionate ions.

  Ionic equation is……………………………………………………………………………………

Activity 5

1. State the conditions and write equations for the reaction between potassium hydroxide and:

   (a) fluorine. (b) bromine.
2. Compare the oxidizing powers of fluorine and iodine using their reactions with water.
3. Compare the reactivity of fluorine and chlorine with the following compounds (in each case illustrate your answers with equations).

   (a) Water. (b) Concentrated sodium hydroxide solution. (c) Hydrogen.
4. Illustrating your answers with equations (if any) and including conditions, describe the reactions of the group VII elements (fluorine, chlorine, bromine and iodine) with

   (a) water. (a) potassium hydroxide. (c) carbon.

5. (a) Write equation for the reaction between chlorine and
   (i) Hydrogen sulphide solution.
   (ii) Hot concentrated potassium hydroxide solution.
   (b) State what was observed in (a)(i) and (a)(ii).
   (c) In which one of the reactions in (a) is chlorine behaving as an oxidizing agent?

Compounds of Group VII Elements

A. Hydrogen halides (HX, X = F, Cl, Br, I)

Preparation

- The method applicable depends on the hydrogen halide in question. Below are some of the methods applicable:
  (a) Direct combination (synthesis)
    - ✓ Direct combinations involves reacting the halogen with hydrogen under suitable conditions. (See reactions of halogens with hydrogen)
    - ✓ This method works well for hydrogen chloride and is employed in the commercial manufacture hydrochloric acid; hydrogen chloride formed is absorbed in water to form the acid.

  (b) Displacement from salts
    - ✓ This method involves reacting any ionic (or metallic) halides with concentrated sulphuric acid at room temperature or on heating.
      For example:
      $CaF_2(s) + H_2SO_4(l) \longrightarrow CaSO_4(s) + 2HF(g)$; on heating
      $NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HCl(g)$; in the cold
      $2NaCl(s) + H_2SO_4(l) \longrightarrow Na_2SO_4(s) + 2HCl(g)$; on heating
    - ✓ Concentrated sulphuric acid is used in this preparation because it is less volatile than halogen acids.
    - ✓ Preparation of hydrogen bromide and hydrogen iodide by the use of similar methods is complicated by secondary reactions.
      Reason
      Hydrogen bromide and hydrogen iodide are very strong reducing agents which are readily oxidised by the unreacted hot concentrated sulphuric acid to molecular bromine and molecular iodine respectively.
      $2KX(s) + H_2SO_4(l) \longrightarrow Na_2SO_4(s) + 2HX(g)$; on heating…………(i); X= Br or I
      $2HX(g) + H_2SO_4(l) \rightarrow X_2(g) + SO_2(g) + 2H_2O(l)$……………………….(ii)
      Overall equation is ……………………………………………………………………………………………

Both hydrogen fluoride and hydrogen chloride are not attacked by concentrated sulphuric acid.

- ✓ The conveniently used ionic halides in the lab to prepare hydrogen chloride are NaCl, KCl or NH_4Cl.

Observations when NaX, KX or NH_4X is treated with concentrated sulphuric acid.

- ❖ NaCl, KCl or NH_4Cl; dissolves, effervescence occurs and misty fumes are evoved.
- ❖ NaBr, KBr or NH_4Br; dissolves, effervescence occurs and reddish-brown fumes are evolved.
- ❖ NaI, KI or NH_4I; dissolves, effervescence occurs and purple vapours are evolved.

(c) Hydrolysis of phosphorus trihalides

- ✓ Phosphorus trihalides are readily hydrolysed by water to form phosphonic acid and the corresponding hydrogen halides.

This method is often employed to obtain hydrogen bromide and hydrogen iodide.

$PBr_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HBr(g)$

$PI_3(s) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HI(g)$

Activity 6

1. When hot concentrated sulphuric acid was added separately to solid sodium iodide and solid sodium chloride, purple vapours were observed with solid sodium iodide but no greenish-yellow gas was seen with solid sodium chloride. Explain this observation.
2. State what would be observed and write equation(s) for the reaction(s) that would take place if
   (a) Iodine is added to hot aqueous solution of sodium hydroxide.
   (b) Solid potassium iodide is heated with concentrated sulphuric acid.
   (c) Chlorine is bubbled into cold dilute aqueous sodium hydroxide solution and mixture warmed.

Properties of the hydrides

Physical properties

Summary of some physical properties of the hydrogen halides

Hydrogen halides (state at r.t.p)	**Period number of halogen that forms the hydride**	**Molecular mass of hydride ($g\ mol^{-1}$)**	**Boiling point (℃)**	**Bond dissociation energy for H-X bond ($kJ\ mol^{-1}$)**
HF (l)	2	20.0	+19.9	+560
HCl (g)	3	36.5	−85.0	+430
HBr (g)	4	81.0	−66.7	+370
HI (g)	5	128.0	−35.4	+300

Activity 7

(a) Draw a graph to show how the boiling points of the hydride vary with
  (i) period number of the halogens.
  (ii) molecular mass of hydrides.

(b) Explain the shape of each of the graphs you have drawn in (a)(i) and (a)(ii).

(c) The table shows the boiling points of hydrides of group IV and group VII elements.

Period number	2	3	4	5
Hydrides of group IV elements	CH_4	SiH_4	GeH_4	SnH_4
Boiling point (℃)	-161	-112	-95	-52
Hydrides of group VII elements	HF	HCl	HBr	HI
Boiling point (℃)	+20	−85	−67	−35

  (i) Draw on the same axes, draw graphs to show how the boiling points of the hydrides vary with the period number of the element that forms the hydride.
  (ii) Explain the shapes of the graphs you have drawn in (c)(i).

- The hydrogen halides;
  - ✓ have pungent odour
  - ✓ are colourless gases (except hydrogen fluoride which is a liquid) at room temperature.

Explanation

Fluorine atom has smaller atomic radius and is highly/strongly electronegative. Hydrogen—fluorine is highly polarized. Thus, molecules of hydrogen fluoride are associated via strong hydrogen bonds. This makes the compound exist as a liquid at room temperature and pressure.

The other hydrides are gases at room temperature since their individual molecules are associated via weak van der Waals forces. This because the halogen atoms have larger atomic radii and are less electronegative than fluorine atom. The hydrogen-halogen bonds are less polar.

- ✓ fume in moist air.
- ✓ hydrogen halides are covalent (i.e. are made up of discrete molecules) when pure and dissolve in organic solvents. Their solutions are in organic solvents, are non-electrolytes, do not show acidic properties, and give negative tests with silver nitrate and lead(II) nitrate solutions. This is because the non-polar solvents suppress the ability of hydrogen halides to ionise, consequently the compound remains in molecular form.
- ✓ form **azeotropic mixtures** with water which have maximum boiling points.

- The boiling points of the hydrogen halides are in the order: $HF > HCl < HBr < HI$.

Explanation

Molecules of hydrogen fluoride possess a highly polar hydrogen–fluorine bond. This is because the fluorine atom has smaller atomic radius and is highly/strongly electronegative. Hydrogen fluoride molecules associate through **strong** hydrogen bonding which requires a lot of heat energy to break.

Hydrogen chloride, hydrogen bromide, and hydrogen iodide are discrete molecules with **weak** van der Waal's forces of attraction between their individual molecules. This because the halogen atoms have larger atomic radii and are less electronegative than fluorine atom. The hydrogen–halogen bonds are less polar.

The strength of the forces increases with increase in the molecular mass in the order $HCl < HBr < HI$ and hence the observed trend.

- Thermal stability of the hydrides decreases from hydrogen fluoride to hydrogen iodide.

Explanation

Thermal stability depends on the bond strength and bond energy of the hydrogen–halogen bond, and the atomic radius of the halogen atom.

As atomic radius of the halogen atoms increases from fluorine to iodine, the hydrogen–halogen bond length increases and the effective overlap of the atomic orbitals of the bonded atoms decreases.

The bond strength and bond energy for hydrogen–halogen bond decrease in the order $HF > HCl > HBr > HI$. Hence the observed trend.

Chemical properties

- Acidity of the hydrogen halides
  - ✓ In aqueous solution, the hydrogen halides are almost completely ionized.
    $HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$
    Or simply we can write; $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$
    Thus, their aqueous solutions show the usual properties of acids, conduct electric current (i.e. are electrolytes) and form precipitates with acidified silver nitrate solution and acidified lead(II) nitrate solution.
  - ✓ Hydrofluoric acid is a weak acid. It ionises slightly in aqueous solution as follows:
    In a dilute aqueous solution: $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
    In concentrated solution, $2HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HF_2^-(aq)$
    Thus, hydrofluoric acid forms both normal and acid salts unlike the other halogen acids (HCl, HBr and HI) which only form normal salts.
    $KOH(aq) + HF(aq) \rightarrow \underbrace{KF(aq)}_{normal\ salt} + H_2O(l); KF(aq) + HF(aq) \rightarrow \underbrace{KHF_2(aq)}_{acid\ salt}$
  - ✓ Hydrofluoric acid is a stronger acid when concentrated than when it is in dilute form.

Explanation

In a concentrated solution of hydrogen fluoride, there is a high concentration of un-ionised hydrogen fluoride molecules. The fluoride ions react with hydrogen fluoride molecules to form hydrogen difluoride ions.

$$HF(aq) + F^- \rightleftharpoons HF_2^-(aq)$$

Equilibrium concentration of fluoride ions decreases and equilibrium position is disturbed. In order to restore to the equilibrium, more hydrogen fluoride molecules ionize. This increases the hydrogen ion concentration in solution and hence, solution becomes more acidic.

In a dilute solution, formation of hydrogen difluoride ions is not possible. The concentration of hydrogen ions is very low and this makes the solution less acidic.

  - ✓ The acid strength increases in the order $HF < HCl < HBr < HI$.

The strength of the acid depends on the ease of release of the proton which in turn depends on both the bond strength and bond energy of the hydrogen—halogen and, the atomic radius of the halogen atom.

The bond strength and hence, bond energy decrease is in the order $H–F > H–Cl > H–Br > H–I$ due to increase in the atomic radius of the halogen atoms in the order $F < Cl < Br < I$.

The larger the atomic radius of the halogen atom, the longer and the weaker is the hydrogen–halogen bond and hence, the stronger is the acid.

Therefore hydrogen fluoride is the weakest acid and hydrogen iodide is the strongest acid.
The ionisation of hydrofluoric acid to form H_3O^+ and F^- ions in a dilute solution lies mainly to the left (i.e. hydrogen fluoride does not easily in a dilute solution). This is because the fluorine atom has a smaller atomic radius and is highly electronegative. This makes the hydrogen—fluorine bond to be shorter and stronger. Also the hydrogen fluoride molecules associate via strong hydrogen bonds which must be broken first before the acid molecules ionize.

Activity 8

1. Explain the following observations.
   (a) Hydrogen fluoride has a higher boiling point and is a weaker acid than hydrogen chloride.
   (b) Hydrogen fluoride is a liquid while hydrogen bromide is a gas at room temperature and pressure.
   (c) The boiling points of the hydrides of group VII elements; fluorine, chlorine, bromine and iodine are in the order; $HF < HCl < HBr < HI$.
   $[HF = 20;\ HCl = 36.7; HBr = 81;\ HI = 128]$
   (d) The acid strength increases in the order $HF < HCl < HBr < HI$.
2. (a) Write equation to show how each of the following hydrides can be prepared.
      (i) Hydrogen fluoride. (b) Hydrogen iodide.
   (b) Compare the thermal stabilities of hydrogen fluoride and hydrogen iodide. (Include equations of reactions if any.)
   (c) Write equation to show how hydrogen fluoride ionizes in a;
      (i) dilute aqueous solution.
      (ii) concentrated aqueous solution.
   (d) Which of the solutions in (c)(i) and (c)(ii) is more acidic? Explain your answer.
   (e) Write equation to show how
      (i) hydrofluoric acid reacts with silicon(IV) oxide.
      (ii) hydrogen iodide reacts with acidified hydrogen peroxide solution.
   (f) State what would be observed in reaction in (e)(ii). Give a reason for your observation.
   (g) Explain why hydrofluoric acid is a weaker acid than hydriodic acid.

- **Reducing properties**
  - ✓ The reducing power of the hydrogen halides increases from hydrogen fluoride to hydrogen iodide.
  - ✓ Thus, hydrogen fluoride is the weakest reducing agent while hydrogen iodide is the strongest reducing agent.
  - ✓ The half equation for the reduction action is: $2X^- \rightarrow X_2 + 2e^-$

Explanation
The ability for the halide ion to reduce increases from fluoride ion to iodide ion. This because from fluoride ion to iodide ion, the ionic radius increases and thus the outermost electrons are less strongly attracted by the nucleus and, this makes ion easily lose electrons. Also the bond energy and bond strength for the hydrogen—halogen bond decreases from hydrogen fluoride to hydrogen iodide. This makes the hydrides easily lose the hydrogen atoms.

- ❖ Hydrogen fluoride shows no reaction with any ordinary oxidizing agent.
- ❖ Hydrogen chloride in concentrated form (i.e. concentrated hydrochloric acid) is easily oxidised by to molecular chlorine by **strong** oxidizing agents such as acidified potassium manganate(VII), lead(IV) oxide and manganese(IV) oxide. Use of lead(IV) oxide and manganese(IV) oxide requires heating but acidified potassium manganate(VII) acts at room temperature.
- ❖ Hydrogen bromide requires **milder** oxidising agents such as hydrogen peroxide, concentrated sulphuric acid, chlorine, acidified potassium dichromate(VI) and oxygen.
  For example; $Cl_2(g) + 2HBr(aq) \rightarrow Br_2(aq) + 2HCl(aq)$
- ❖ Hydrogen iodide (usually in the form of hydriodic acid/potassium iodide solution) is a vigorous reducing agent. It is readily oxidised to molecular iodine by **many** oxidizing agents, e.g. chlorine, bromine, iron(III) salts, oxygen, acidified hydrogen peroxide solution, hot concentrated sulphuric acid, nitric acid, acidified potassium dichromate(VI) solution, acidified potassium manganate(VII) solution and copper(II) salts.
  For example:
  $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$; $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$
  Aqueous solutions of hydriodic acid are stable in the absence of oxygen (air) but quickly turn brown (due to formation of iodine) when exposed to air. This reaction is accelerated by sunlight.
  $4HI(aq) + O_2(g) \rightarrow 2I_2(aq) + 2H_2O(l)$
  For similar reasons, potassium iodide solutions turn yellow when exposed to air.

The half equations involved are:

$2I^{-}(aq) \longrightarrow I_2(aq) + 2e^{-}; \quad O_2(aq) + 2H_2O(l) + 4e^{-} \longrightarrow 4OH^{-}(aq)$

The overall equation is……………………………………………………………………………………………………

Activity 9

1. Explain each of the following observations.
   (a) An aqueous solution of hydriodic acid turns brown when left standing in an open container.
   (b) Aqueous solutions of potassium manganate(VII) for volumetric analysis are never acidified using hydrochloric acid.
   (c) When potassium iodide solution is added to copper(II) sulphate solution, the blue solution turns brown and a white precipitate is formed. On addition of sodium thiosulphate solution to the resultant mixture, the brown solution turns colourless and a white precipitate remains.
   (d) When dry hydrogen iodide is bubbled warm concentrated sulphuric acid, purple vapours are evolved while similar treatment of the acid with dry hydrogen chloride, gives no observable change.
   (e) When acidified potassium dichromate(VI) solution is added to aqueous solution of potassium iodide, the solution turns brown.
2. The hydrides of group(VII) elements of the Periodic Table are: HF, HCl, HBr and HI.
   Using equations where possible, explain what happens when concentrated sulphuric acid is mixed with each of the hydrides.

B. Oxides of group VII elements

All the elements form oxides; the most stable being those of iodine and most important being those of chlorine.

Element	Formula and name	Reaction with water if any
F	$F_2O(g)$; Oxygen difluoride	
Cl	$Cl_2O(g/l)$; Dichlorine oxide	$Cl_2O(g) + H_2O(l) \rightarrow 2HOCl(aq)$
	$ClO_2(g)$; Chlorine dioxide	$2ClO_2(g) + H_2O(l) \rightarrow HClO_2(aq) + HClO_3(aq)$
	$Cl_2O_6(l)$; Dichlorine hexoxide	$Cl_2O_6(l) + H_2O(l) \rightarrow HClO_3(aq) + HClO_4(aq)$
	$Cl_2O_7(l)$; Dichlorine heptoxide	$Cl_2O_7(l) + H_2O(l) \rightarrow 2HClO_4(aq)$
I	$I_2O_5(s)$ Iodine pentoxide (iodine(V) oxide)	

Activity 10

Write ionic equations to show how each of the oxides of chlorine reacts with sodium hydroxide solution.

C. Oxo-acids

- Fluorine forms no oxo-acids. The other halogens form several oxo-acids.
- Most important oxo-acids and their salts are:

Oxo-acid	Some important salts it forms	Uses of the salts
Chloric(I) acid, HOCl	Sodium chlorate(I), NaClO	Bleaching agent; present in liquid bleaches
	Calcium chlorate(I) ('bleaching powder'), $Ca(ClO)_2$	Bleaching agent; present in bleaching powder
Chloric(III) acid, $HClO_2$	Sodium chlorate(III), $NaClO_2$	Bleaching agent in textile industries
Chloric(V) acid, $HClO_3$	Sodium chlorate(V), $NaClO_3$	Weed-killer; acts by sterilizing the soil
	Potassium chlorate(V), $KClO_3$	• Source of bromine in volumetric analysis • Oxidising agent in matches and fireworks
Iodic(V) acid, HIO_3	Potassium iodate(V). KIO_3	Primary standard for standardising sodium thiosulphate solution
Chloric(VII) acid/perchloric acid), $HClO_4$	Potassium chlorate(VII), sodium chlorate(VII) and ammonium chlorate(VII)	Manufacture of explosives and detonators

- Both the acids and their salts are powerful oxidising agents in acidic medium.
- For example:
  (a) The half equation for the oxidizing action of chloric(I) acid and its salts is:
  $ClO^-(aq) + 2H^+(aq) + 2e^- \rightarrow Cl^-(aq) + H_2O(l)$
  Thus, they can oxides iron(II) to iron(III), iodide ions in acidified potassium iodide solution to free iodine and sulphites ions to sulphates.
  (b) The half equation for the oxidizing action halic(V) acids and their salts is:
  $XO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow X^-(aq) + 3H_2O(l); \quad (X = Cl, Br\ or\ I)$
  Thus, they oxidise iron(II) ions to iron(III) ions, sulphur dioxide and sulphites to sulphates, iodide ions to molecular iodine, hydrogen sulphide to elemental sulphur.
- The chlorates(I) are unstable in acidic medium. They react with dilute acids (e.g. ethanoic acid or hydrochloric acid) to liberate chlorine:

$$ClO^-(aq) + \underbrace{2H^+(aq) + 2Cl^-}_{acid} \rightarrow \underbrace{Cl_2(g)}_{liberated} + H_2O(l)$$

The above reaction can be used to estimate the percentage of the 'available' chlorine in the bleaches (bleaching powder or bleaching liquids).

The liberated chlorine is used to displace iodine from potassium iodide solution.

$$Cl_2(g) + \underbrace{2I^-(aq)}_{from\ KI} \rightarrow 2Cl^-(aq) + I_2(aq)$$

The liberated iodine is then titrated with a standard solution of sodium thiosulphate using starch indicator.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Bleaching powder **deteriorates** on storage because of the reaction with aerial carbon dioxide and auto-oxidation. All these reactions liberate chlorine and hence reduce the 'available' chlorine content.

		
Some common bleaching agents		
Sodium chlorate(I) widely used as a mild antiseptic and bleaching agent is sold under trade names like Parazone, Milton and Domestos.		

- Potassium iodate(V) is used as a ***primary standard*** in volumetric analysis because the salt:
  (i) can be obtained with a high degree of purity.
  (ii) is stable in aqueous solution and during storage.
  (iii) very soluble in water at ordinary temperatures.
  (iv) has a relatively high molecular mass.

- In acidic medium, potassium iodate(V) reacts with excess potassium iodide to give a quantitative yield of iodine which is then titrated with standard sodium thiosulphate solution using starch indicator.
  Iodine is liberated according to the following equation……………………………………………

Activity 11

1. 10.0 cm^3 of a sample of commercial bleach containing chlorine was diluted to 250 cm^3 with water. 25.0 cm^3 of this solution was transferred into a conical flask and potassium iodide solution added to liberate iodine. The iodine mixture required 23.2 cm^3 of a 0.1 M sodium thiosulphate solution for complete reaction. Sodium thiosulphate reacts with iodine solution according to the following equation.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Chlorine reacts with iodide ions according to the following equation.

$$Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$

Calculate the:

(a) molar concentration of chlorine in the commercial bleach.

(b) percentage of available chlorine in the commercial bleach.

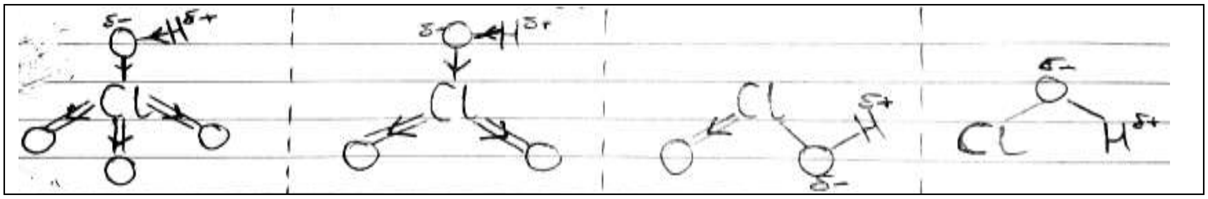
2. Sodium hypochlorite solution was added to an aqueous solution of iron(II) sulphate.
   State what was observed and write equation for the reaction that took place.
3. Briefly describe how the percentage of available chlorine in a liquid bleach commercial bleach can be determined by titrimetric method.
4. State what would be observed and write equation for the reaction that would take place if:
   (a) dilute sulphuric acid is added to a solution containing potassium iodate(V) and potassium iodide.
   (b) potassium chlorate(V) is added to acidified solution iron(II) nitrate.
   (c) sodium chlorate(V) is mixed with acidified sodium iodide solution.
5. 2.0 g of a mixture of potassium chloride and potassium chlorate(V) was dissolved in 250 cm^3 of water.
   10.0 cm^3 of the solution was mixed with excess potassium iodide. The iodine liberated required 8.00 cm^3 of a 0.2 M sodium thiosulphate solution for complete reaction.
   The equations for the reactions taking place are:
   $ClO_3^-(aq) + 6H^+(aq) + 6I^-(aq) \rightarrow I_2(aq) + 6I^-(aq) + 3H_2O(l)$
   $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
   Calculate the percentage of potassium chlorate(V) in the mixture.

Acid strength of the oxo-acids of chlorine

- The acid strength of oxo-acids of chlorine increases with increase in the number of oxygen atoms bonded to the chlorine atom. Thus, the acid strength increases in the order; $HClO < HClO_2 < HClO_3 < HClO_4$.
- Therefore $HClO_4$ is the strongest acid while HClO is the weakest acid.

  Explanation

  Oxygen atom is more electronegative than the chlorine atom. It therefore withdraws/pulls the bonding electrons more towards itself. This withdrawal of bonding electrons is communicated/transmitted through the chlorine atom to the oxygen–hydrogen bond. The magnitude of the partial positive charge on the hydrogen atom increases. This weakens the oxygen–hydrogen bond and consequently a proton is easily lost/released in aqueous solution. The more the number of oxygen atoms bonded to the chlorine atom, the greater the magnitude of the partial positive charge on the hydrogen atom and hence, the weaker the oxygen–hydrogen bond becomes.



Uses of halogens and their compounds

- The halogens and their compounds are of great importance in a number of ways. These include:
  - (i) Fluorine is used to make fluorocarbons for tetrafluoroethane($CF_2=CF_2$) used to make teflon. It is used for fluoridation of water as well. Fluorine is used to make uranium(VI) fluoride (UF_6) to be used for separation of isotopes of uranium, while an aqueous solution of HF is used to clean glasses.
  - (ii) Chlorine is used to manufacture weed killers (for example, $NaClO_3$), antiseptics (for example, NaOCl), solvents (for example, CCl_4, $CHCl_3$), insecticides (for example, DDT), plastics (for example, PVC), hydrochloric acid, bleaches (both for domestic and industrial use). It is used in water treatment (for example, in swimming pools and water plants).

Swimming pool which contains water treated with chlorine although its use is being replaced by chloric(I) acid. *Why do you think this so?*

  - (iii) Bromine compounds for example, AgBr is used to manufacture photographic film paper and $C_2H_4Br_2$ is used as a petrol additive.
  - (iv) Iodine in ethanol is used as a mild antiseptic for cuts and scratches on the skin. Potassium iodate(V) is a primary standard in volumetric analysis.

Detection of chloride, bromide, and iodide ions in a sample

Case 1: Halide ions in solid samples

Reagent	**Expected observations with a sample containing**		
	Chloride ions	**Bromide ions**	**Iodide ions**
Concentrated sulphuric acid and warm/heat	Effervescence occurs and misty fumes are evolved	Effervescence occurs and brown/red vapours are evolved	Effervescence occurs and purple/violet vapours are evolved
Solid manganese(IV) oxide and concentrated sulphuric acid and heat	Effervescence occurs and greenish-yellow gas evolved	Effervescence occurs and reddish-brown fumes/vapours evolved	Effervescence occurs and violet/purple vapours evolved
General equation	$MnO_2(s) + 4H^+(aq) + 2X^-(s) \rightarrow Mn^{2+}(aq) + X_2(g) + 2H_2O(l)$		

Case 2: Halide ions in aqueous solution

Reagent	**Expected observations with a sample containing**		
	Chloride ions	**Bromide ions**	**Iodide ions**
Dilute nitric acid followed by lead(II) nitrate (ethanoate) solution and heat	White ppt soluble on heating (and forms on cooling)	Pale yellow/white ppt slightly soluble on heating	Yellow ppt insoluble on heating
General equation	$Pb^{2+}(aq) + 2X^-(aq) \rightarrow PbX_2(s)$		
Dilute nitric acid followed by silver nitrate (ethanoate) solution and excess ammonia solution	White ppt soluble in excess ammonia solution to form a colourless solution	Pale yellow slightly soluble in excess ammonia solution	Yellow ppt insoluble in excess ammonia solution
Equation(s)	$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$; *X=Cl, Br or I* $AgX(s) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + X^-(aq)$; X= Cl or Br Silver chloride and silver bromide dissolve in excess ammonia solution due to formation of **soluble complex ions**.		
Chlorine water (bleaching powder and dilute nitric acid) followed by choroform/carbon tetrachloride. Shake and allow to stand.	No observable change	Reddish-brown/brown coloration in organic layer	Purple/violet coloration in organic layer

Activity 12

1. Name a reagent that can be used to distinguish between the following pairs of ions/compounds. In each case, state what would be observed if each ion is separately treated with the reagent you have named.
   (a) $Br^-(aq)$ and $Cl^-(aq)$ (b) $I^-(aq)$ and $Cl^-(aq)$ (c) $KBr(aq)$ and $KI(aq)$
2. Explain how each of the following reagents can be used to distinguish chloride, bromide and iodide ions.
   (a) Silver nitrate.
   (b) Silver nitrate and aqueous ammonia solution.
   (c) Bleaching powder, dilute nitric acid and tetrachloromethane.
   (d) Chlorine water and tetrachloromethane
3. Explain each of the following observations.
   (a) Chloric acid a weaker acid than chloric(V) acid.
   (b) Chloride ion is has a larger ionic radius than the chlorine atom.
4. Both chlorine and sodium hydroxide are manufactured by electrolysis of saturated sodium chloride solution
   (a) Name the substance used as the:
      (i) cathode. (ii) anode.
   (b) Write equation(s) for the reaction(s) leading to the formation of
      (i) chlorine. (ii) sodium hydroxide.
   (c) Write equation for the reaction between chlorine and dilute sodium hydroxide solution at room temperature.
   (d) Explain what would happen if the mixture in (c) is warmed/heated.
   (e) State what would be observed and write equation(s) for the reaction(s) that would take place if chlorine is bubbled through;
      (i) sodium iodide solution. (ii) hot concentrated sodium hydroxides solution.
   (f) Give a reason for your answer in (e)(i).
5. The boiling points and reduction potentials of group VII elements in the Periodic Table are given in the table below.

Element	F	Cl	Br	I
Boiling point/$^\circ C$	-187	-35	59	183
Electrode potential/V	+2.87	+1.36	+1.07	+0.54

   (a) Write the general outermost electronic configuration of group VII elements in the Periodic Table.
   (b) State the trend in the boiling points of the elements and explain your answer.
   (c) Which one of the elements is the strongest oxidizing agent? Give a reason for your answer.
   (d) Chlorine was bubbled through a solution containing bromide ions.
      (i) State what was observed and give reasons for your answer.
      (ii) Write equation for the reaction that took place.