THE CHEMISTRY OF GROUP VII ELEMENTS

Electronic structures/ configurations

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>9</td>
<td>$1s^2 2s^2 2p^5$</td>
</tr>
<tr>
<td>Cl</td>
<td>17</td>
<td>$1s^2 2s^2 2p^6 3s^2 3p^5$</td>
</tr>
<tr>
<td>Br</td>
<td>35</td>
<td>$1s^2 2s^2 2p^6 3s^2 3p^5 3d^{10} 4s^2 4p^5$</td>
</tr>
<tr>
<td>I</td>
<td>53</td>
<td>$1s^2 2s^2 2p^6 3s^2 3p^5 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$</td>
</tr>
</tbody>
</table>

From the above electronic configurations, it can be concluded that the outermost electronic configuration of group VII elements is $ns^2 np^5$

Bonding and structure

<table>
<thead>
<tr>
<th>Element</th>
<th>Bonding</th>
<th>Structure</th>
<th>Physical state and colour at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>All covalent</td>
<td>All simple molecular</td>
<td>Pale yellow gas</td>
</tr>
<tr>
<td>Chlorine</td>
<td></td>
<td></td>
<td>Greenish yellow gas</td>
</tr>
<tr>
<td>Bromine</td>
<td></td>
<td></td>
<td>Red liquid</td>
</tr>
<tr>
<td>Iodine</td>
<td></td>
<td></td>
<td>Grey/ black solid</td>
</tr>
</tbody>
</table>

Qn. Explain why fluorine and chlorine exist as gases whereas bromine and iodine exist as liquid and solid respectively at room temperature

From fluorine to iodine, atomic radius increases, molecular size and molecular mass increases, hence magnitude of Van der Waals’ forces of attraction holding the molecules increases in the order; $F_2 < Cl_2 < Br_2 < I_2$. The Van der Waals’ forces in bromine and iodine are strong enough to hold the molecules closer to each other existing as liquid and solid respectively. Fluorine and chlorine have weaker Van der Waals’ forces due to their small size and low molecular masses. Their molecules are therefore far apart.
VARIATION IN ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

1. Melting points/boiling points

The table below shows the boiling points/melting points of halogens

<table>
<thead>
<tr>
<th>Element</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point(°C)</td>
<td>-187.9</td>
<td>-34.0</td>
<td>58.2</td>
<td>+184.5</td>
</tr>
<tr>
<td>Melting points(°C)</td>
<td>-219.6</td>
<td>-102.4</td>
<td>-7.2</td>
<td>+113.6</td>
</tr>
</tbody>
</table>

Explain the trend in boiling points/melting points of the halogens

Boiling point/melting point increases from fluorine to iodine because atomic radius increases, molecular size and molecular mass increases, hence magnitude of Van der Waals’ forces of attraction holding the molecules increases in the order \( F_2 < Cl_2 < Br_2 < I_2 \). The energy required to break the forces therefore increase from fluorine to iodine.

2. Atomic and ionic radius

The table below shows the atomic radii and ionic radii of the elements in Group VII of the Periodic Table.

<table>
<thead>
<tr>
<th>Element</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic radius(nm)</td>
<td>0.072</td>
<td>0.099</td>
<td>0.114</td>
<td>0.133</td>
</tr>
<tr>
<td>Ionic radius(nm)</td>
<td>0.136</td>
<td>0.181</td>
<td>0.195</td>
<td>0.216</td>
</tr>
</tbody>
</table>

(a) State and explain the trend in atomic radius of the elements

Atomic radius increases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect also increases, because an extra energy level completely filled with electrons is added. Increase in screening effect outweighs increase in nuclear charge, effective nuclear charge decreases, and outermost electrons are far and weakly attracted by the nucleus.
(b) Explain why the ionic radius is larger than the atomic radius of corresponding neutral atom for each element.

The ions are formed by gaining electrons. When the electrons are gained, the number of electrons becomes greater than the number of existing protons. Screening effect increases. Effective nuclear charge reduces. The electrons become more strongly repelled by the nucleus than they are attracted. In the neutral atom, the screening effect is counterbalanced by nuclear charge.

3. First ionization energy

The table below shows the first ionization energies of Group VII elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>F (kJmol⁻¹)</th>
<th>Cl (kJmol⁻¹)</th>
<th>Br (kJmol⁻¹)</th>
<th>I (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First ionisation energy</td>
<td>1681</td>
<td>1255</td>
<td>1142</td>
<td>1007</td>
</tr>
</tbody>
</table>

(a) Define the term first ionisation energy.

The minimum amount of energy required to remove an electron from a gaseous atom to form a unipositively charged gaseous ion.

or

The minimum amount of energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of unipositively charged gaseous ions.

(b) State and explain the trend in ionization energy of the elements

First ionization energy decreases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases, Screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases and outer most electron is far and weakly attracted by the nucleus requiring a low amount of energy to be removed.
4. Electron affinity

The table below shows the first electron affinities and atomic numbers of the elements in Group VII

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number</th>
<th>$F$</th>
<th>$Cl$</th>
<th>$Br$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>9</td>
<td>17</td>
<td>35</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>First electron affinity (kJ mol$^{-1}$)</td>
<td>-354</td>
<td>-370</td>
<td>-348</td>
<td>-320</td>
<td></td>
</tr>
</tbody>
</table>

(a) Explain what is meant by the term first electron affinity

(b) Plot a graph of first electron affinity against atomic number of the elements.

(To be done by student. When plotting the graph, the negative sign may be eliminated since it’s on all values and it just indicates that the process is exothermic. The graph below is just a sketch and not on scale)

(c) (i) Explain the general trend in variation of the first electron affinities

(ii) Explain why fluorine has an abnormal value

(a) This is the energy given out when one mole of electrons combines with one mole of gaseous atoms to form one mole of uninegatively charged gaseous ions

or The energy given out when an electron is added to a gaseous atom to form a uninegatively charged gaseous ion.

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

(b)
(c) (i) Generally, first electron affinity decreases from fluorine to iodine. This is because from fluorine to iodine, nuclear charge increases. Screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases and incoming electron is far and weakly attracted by the nucleus giving off a low amount of energy.

(ii) Fluorine has the smallest atomic radius, highest electron density, strongly repels the incoming electron and energy is consumed to add the electron to its atom.

5. Electronegativity

The tendency of an atom in a molecule to attract bonding electrons towards itself.

The table below shows the electronegativity values of the elements in Group VII of the Periodic Table.

<table>
<thead>
<tr>
<th>Element</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity</td>
<td>4.10</td>
<td>2.83</td>
<td>2.74</td>
<td>2.21</td>
</tr>
</tbody>
</table>

State and explain the trend in electronegativity values of the elements

Electronegativity decreases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases, and the bonding electrons experience a greater repulsion than nuclear attraction.

6. Bond dissociation energy

The table below shows the values of Bond dissociation energy of halogens.

<table>
<thead>
<tr>
<th>Element</th>
<th>$F_2$</th>
<th>$Cl_2$</th>
<th>$Br_2$</th>
<th>$I_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond dissociation energy(kJmol$^{-1}$)</td>
<td>158.1</td>
<td>242.2</td>
<td>193</td>
<td>151</td>
</tr>
</tbody>
</table>

(a) State the difference between bond dissociation energy and bond energy.
(b) Explain the trend, stating any anomalies in the bond dissociation energy of the halogens.
(a) Bond dissociation energy is the heat change that occurs when one mole of a covalent bond is broken down into its constituent gaseous atoms whereas Bond energy is the standard enthalpy change that occurs when one mole of a covalent bond is formed from its constituent gaseous atoms.

(b) Bond dissociation energy decreases from chlorine to iodine but with fluorine having an abnormally low value of bond dissociation energy.

This is because from one chlorine to iodine, atomic radius increases, bond length increases and bond strength decreases, resulting into weaker attraction between the atoms in the molecule, requiring a low amount of energy to break the bonds.

Fluorine has an abnormally low value of bond dissociation energy because fluorine has the smallest atomic radius, and the non-bonding electrons in the molecule repel each other strongly. This strong repulsion tends to force the fluorine atoms far apart thus weakening the F-F bond, requiring low amount of energy to break it.

7. Electrode potential

The table below shows the standard electrode potential values of Group VII elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard electrode potential(E^\circ) (Volts) for (\frac{1}{2}X_2/X^-) (aq)</td>
<td>+2.80</td>
<td>+1.36</td>
<td>+1.07</td>
<td>+0.54</td>
</tr>
</tbody>
</table>

(a) State;
   (i) the strongest oxidising agent
   (ii) order of oxidising strength of the halogens

(b) Explain the trend in standard electrode potential of the elements

(c) State what would be observed when;
   (i) Chlorine is bubbled through potassium bromide solution
   (ii) Chlorine is bubbled through potassium iodide solution

(d) Explain your observations in c(i) and (ii) basing on the table above

(e) Explain why tin(IV) chloride exists but tin(IV) bromide and tin(IV) iodide do not exist.

(a)(i) Fluorine or \(F_2\) (but not F)
(ii) $F_2 \gg Cl_2 > Br_2 > I_2$

(b) Standard electrode potential becomes less positive (increases) from fluorine to iodine because ionic radius increases, electron affinity decreases, bond dissociation energy generally decreases and hydration energy also decreases. However, the decrease in electro affinity and bond dissociation energy is more rapid than decrease in hydration energy.

(c) (i) The greenish-yellow gas dissolves and the colourless solution forms a red liquid.  
    (ii) The greenish-yellow gas dissolves and the colourless solution turns dark brown finally forming a black solid deposit.

(d) The standard electrode potential for $Cl_2/Cl^-(aq)$ is more positive than that of $Br_2/Br^-(aq)$ or $I_2/I^-(aq)$ and the chloride ion has a smaller ionic radius than bromide and iodide ions respectively. Chlorine therefore a stronger oxidising agent than bromine or iodine. Chlorine oxidises bromide and iodide ions to bromine and iodine respectively.

\[
\begin{align*}
Cl_2(g) + 2Br^-(aq) & \rightarrow 2Cl^-(aq) + Br_2(l) \\
Cl_2(g) + 2I^-(aq) & \rightarrow 2Cl^-(aq) + I_2(s)
\end{align*}
\]

(e) Bromide ions and iodide ions have a larger ionic radius than chloride ion. The ions are therefore strongly reducing. They reduce tin(IV) ions to tin(II) ions, as they are oxidised to bromine and iodine respectively. Chloride ions cannot reduce tin(IV) ions.

\[
\begin{align*}
Sn^{4+}(aq) + 2Br^-(aq) & \rightarrow Sn^{2+}(aq) + Br_2(l) \\
Sn^{4+}(aq) + 2I^-(aq) & \rightarrow Sn^{2+}(aq) + I_2(s)
\end{align*}
\]
METHODS OF PREPARATION OF HALOGENS

Qn. Describe the general method of preparing halogens except fluorine

All halogens apart from fluorine are prepared by;

Heating a solid halide salt with concentrated with concentrated sulphuric acid in presence of manganese(IV) oxide.

\[ 2X^- (aq) + 4H^+(aq) + MnO_2(s) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + X_2(g/l \text{ or } s) \]

Where \( X = Cl, Br \text{ or } I \)

*N.B. The Chemistry in action here is that concentrated sulphuric acid acts upon the halide salt (KCl/KBr/KI or NaCl/NaBr/NaI) to form a hydrogen halide (HCl or HBr or HI) which is then oxidised to the halogen by manganese(IV) oxide.*

Qn. Describe the reactions, stating the conditions and under which chlorine can be prepared in the laboratory. State any observations made.

1. Chlorine can be prepared by the reaction between cold concentrated hydrochloric acid and potassium manganate(VII).
   *The purple solution turns colourless and bubbles of a greenish yellow gas.*

\[ 2MnO^-_4(aq) + 16H^+(aq) + 10Cl^-(aq) \rightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l) \]

or \[ 2KMnO_4(s) + 16HCl(aq) \rightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g) \]

2. Chlorine can also be prepared by heating concentrated hydrochloric acid with manganese(IV) oxide.
   *The black solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.*

\[ MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l) \]

or \[ MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l) \]

3. Chlorine can also be prepared by heating concentrated hydrochloric acid with lead(IV) oxide.
   *The dark brown solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.*
4. Chlorine can as well be prepared by heating concentrated hydrochloric acid with Dilead(II) lead(IV) oxide. The red solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.

\[
PbO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Pb^{2+}(aq) + Cl_2(g) + 2H_2O(l)
\]

or

\[
PbO_2(s) + 4HCl(aq) \rightarrow PbCl_2(aq) + Cl_2(g) + 2H_2O(l)
\]

5. Chlorine can be prepared by heating solid sodium chloride with concentrated sulphuric acid in presence of manganese(IV) oxide.

\[
Pb_3O_4(s) + 8H^+(aq) + 2Cl^-(aq) \rightarrow 3Pb^{2+}(aq) + Cl_2(g) + 4H_2O(l)
\]

or

\[
Pb_3O_4(s) + 8HCl(aq) \rightarrow 3PbCl_2(aq) + Cl_2(g) + 4H_2O(l)
\]

6. Chlorine is also prepared by the reaction between bleaching powder (Calcium hypochlorite with dilute nitric acid or dilute hydrochloric acid or dilute sulphuric acid. No heat is required.

\[
CaOCl_2(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + Cl_2(g) + H_2O(l)
\]

or

\[
CaOCl_2(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + Cl_2(g) + H_2O(l)
\]

or

\[
CaOCl_2(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + Cl_2(g) + H_2O(l)
\]

or

\[
CaOCl_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + Cl_2(g) + H_2O(l)
\]
CHEMICAL PROPERTIES OF THE ELEMENTS

1. Describe the reactions of Group VII elements react with hydrogen. State the conditions for the reactions.

   Fluorine explodes in hydrogen even in darkness forming hydrogen fluoride
   \[ F_2(g) + H_2(g) \rightarrow 2HF(l) \]
   Chlorine does not react with hydrogen in the dark or at room temperature but the mixture explodes on heating or presence of sunlight or ultraviolet light to form hydrogen chloride
   \[ Cl_2(g) + H_2(g) \rightarrow 2HCl(g) \]
   Bromine reacts with hydrogen only on heating or in the presence of platinum catalyst at 300 °C forming hydrogen bromide
   \[ Br_2(l) + H_2(g) \rightarrow 2HBr(g) \]
   Iodine reacts with hydrogen in the presence of platinum catalyst at 400 °C forming hydrogen iodide
   \[ I_2(s) + H_2(g) \rightarrow 2HI(g) \]

2. Describe the reactions of halogens with water.

   Fluorine reacts vigorously with water, oxidising it to oxygen/ozone and itself reduced to hydrofluoric acid.
   \[ 2F_2(g) + 2H_2O(l) \rightarrow O_2(g) + 4HF \text{ (aq)} \]
   \[ 3F_2(g) + 3H_2O(l) \rightarrow O_3(g) + 6HF \text{ (aq)} \]
   Chlorine disproportionates in water to form chloric(I) acid and hydrochloric acid
   \[ Cl_2(g) + H_2O(l) \rightarrow HOCl(aq) + HCl \text{ (aq)} \]
   Bromine disproportionates in water to form bromic(I) acid and hydrobromic acid
   \[ Br_2(l) + H_2O(l) \rightarrow HOBr(aq) + HBr \text{ (aq)} \]
   Iodine is insoluble in water.

3. Explain why iodine is insoluble in water but soluble in potassium iodide solution.

   Iodine is non-polar yet water is polar. Intermolecular forces of attraction between individual molecules of water and individual molecules of iodine are on average stronger than intermolecular forces of attraction between molecules of water and molecules of iodine. When the two are combined, repulsion occurs. However, iodine reacts with potassium iodide to a soluble complex of potassium triiodide.
4. Describe how fluorine, chlorine, bromine and iodine react with sodium hydroxide under various conditions.

(i) Cold dilute sodium hydroxide

Fluorine reacts with cold dilute sodium hydroxide solution to form oxygen difluoride, fluoride ions and water

\[ 2F_2(g) + 2\overline{OH}(aq) \rightarrow OF_2(g) + 2F^-(aq) + H_2O(l) \]

\[ or \quad 2F_2(g) + 2NaOH(aq) \rightarrow OF_2(g) + 2NaF(aq) + H_2O(l) \]

Chlorine disproportionates in cold dilute sodium hydroxide to form chloride ions, chlorate(I) ions and water

\[ Cl_2(g) + 2\overline{OH}(aq) \rightarrow Cl^-(aq) + Cl\overline{O}(aq) + H_2O(l) \]

\[ or \quad Cl_2(g) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l) \]

Bromine also disproportionates in cold dilute sodium hydroxide to form bromide ions, bromate(I) ions and water

\[ Br_2(l) + 2\overline{OH}(aq) \rightarrow Br^-(aq) + Br\overline{O}(aq) + H_2O(l) \]

\[ or \quad Br_2(l) + 2NaOH(aq) \rightarrow NaBr(aq) + NaBrO(aq) + H_2O(l) \]

Iodine disproportionates in cold dilute sodium hydroxide to form iodide ions, iodate(I) ions and water

\[ I_2(s) + 2\overline{OH}(aq) \rightarrow I^-(aq) + IO\overline{O}(aq) + H_2O(l) \]

\[ or \quad I_2(s) + 2NaOH(aq) \rightarrow NaI(aq) + NaIO(aq) + H_2O(l) \]

N.B; The chlorate(I) ions and bromate(I) ions formed by the above reactions undergo further disproportionation if heated/warmed to form chlorate(V) ions and chloride ions, bromate(V) ions and bromide ions respectively. The yellow solution turns colourless during this reaction

\[ 3Cl\overline{O}(aq) \rightarrow ClO_5^-(aq) + 2Cl^-(aq) \]

\[ or \quad 3NaClO(aq) \rightarrow NaClO_3(aq) + 2NaCl(aq) \]

\[ 3Br\overline{O}(aq) \rightarrow BrO_5^-(aq) + 2Br^-(aq) \]

\[ or \quad 3NaBrO(aq) \rightarrow NaBrO_3(aq) + 2NaBr(aq) \]

(ii) Hot concentrated sodium hydroxide.

Fluorine reacts with hot concentrated sodium hydroxide to form oxygen, fluoride ions and water.
Chlorine disproportionates in hot concentrated sodium hydroxide to form chloride ions, chlorate(V) ions and water.

\[
2F_2(g) + 4\overline{OH}(aq) \rightarrow O_2(g) + 4F^-(aq) + 2H_2O(l)
\]

\[
\text{or } 2F_2(g) + 4NaOH(aq) \rightarrow O_2(g) + 4NaF(aq) + 2H_2O(l)
\]

Bromine also disproportionates in hot concentrated sodium hydroxide to form bromide ions, bromate(V) ions and water.

\[
3Cl_2(g) + 6\overline{OH}(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)
\]

\[
\text{or } 3Cl_2(g) + 6NaOH(aq) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)
\]

Iodine also disproportionates in hot concentrated sodium hydroxide to form iodide ions, iodate(V) ions and water.

\[
3I_2(s) + 6\overline{OH}(aq) \rightarrow 5I^-(aq) + IO_3^-(aq) + 3H_2O(l)
\]

\[
\text{or } 3I_2(s) + 6NaOH(aq) \rightarrow 5NaI(aq) + NaIO_3(aq) + 3H_2O(l)
\]

**OXIDISING ACTION OF HALOGENS**

1. State what would be observed and explain your observations when;

   (i) chlorine and bromine are separately added to iron(II) chloride solution.

   (ii) chlorine is bubbled through potassium nitrite solution and silver nitrate solution followed by excess ammonia added to the resultant solution.

   (i) **Observation:** In each case, the green solution turns brown

   **Explanation:** chlorine and bromine oxidise iron(II) ions to iron(III) ions as they are reduced to chloride ions and bromide ions respectively.

   \[
   2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)
   \]

   \[
   2Fe^{2+}(aq) + Br_2(l) \rightarrow 2Fe^{3+}(aq) + 2Br^-(aq)
   \]

   \[
   \text{or } 2FeCl_2(aq) + Cl_2(g) \rightarrow 2FeCl_3(aq)
   \]

   (ii) **Observation:** Greenish yellow gas dissolves and the colourless solution formed a white precipitate soluble in excess ammonia to form a colourless solution.

   **Explanation:** chlorine oxidises nitrate ions to nitrite ions and itself reduced to chloride ions.
1. Silver ions react with the chloride ions to form insoluble silver chloride.

\[ \text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s) \]

Silver chloride reacts with excess ammonia to form a soluble complex of diammine silver(I) ion.

\[ \text{AgCl}(s) + 2\text{NH}_3(aq) \rightarrow \text{Ag}(\text{NH}_3)_2^+(aq) + \text{Cl}^-(aq) \]

2. Chlorine gas was bubbled through sodium sulphite solution and to the resultant solution was added barium nitrate solution. State what was observed and explain your answer.

**Observation:** Greenish yellow gas dissolved and the colourless solution formed a white precipitate with barium nitrate solution.

**Explanation:** Chlorine oxidises sulphite ions to sulphate ions and itself reduced to chloride ions.

\[ \text{SO}_3^{2-}(aq) + \text{H}_2\text{O}(l) + \text{Cl}_2(g) \rightarrow \text{SO}_4^{2-}(aq) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq) \]

Barium ions react with sulphate ions to form insoluble barium sulphate.

\[ \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{BaSO}_4(s) \]

3. Describe the reactions of chlorine, bromine and iodine react with:

(i) sodium thiosulphate solution

(ii) hydrogen sulphide.

(i) Chlorine and bromine oxidise thiosulphate ions to sulphate ions as they are reduced to chloride ions and bromide ions respectively.

\[ \text{S}_2\text{O}_3^{2-}(aq) + 4\text{Cl}_2(g) + 5\text{H}_2\text{O}(l) \rightarrow 2\text{SO}_4^{2-}(aq) + 10\text{H}^+(aq) + 8\text{Cl}^-(aq) \]

\[ \text{S}_2\text{O}_3^{2-}(aq) + 4\text{Br}_2(l) + 5\text{H}_2\text{O}(l) \rightarrow 2\text{SO}_4^{2-}(aq) + 10\text{H}^+(aq) + 8\text{Br}^-(aq) \]

Iodine being a weaker oxidising agent oxidises thiosulphate ions to tetrathionate ions and itself reduced to iodide ions.

\[ \text{I}_2(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightarrow \text{S}_4\text{O}_6^{2-}(aq) + 2\text{I}^-(aq) \]

(ii) Chlorine, bromine and iodine oxidise hydrogen sulphide to deposit a yellow solid of sulphur as they are reduced to corresponding hydrides.

\[ \text{Cl}_2(g) + \text{H}_2\text{S}(g) \rightarrow \text{S}(s) + 2\text{HCl}(g) \]

\[ \text{Br}_2(l) + \text{H}_2\text{S}(g) \rightarrow \text{S}(s) + 2\text{HBr}(g) \]

\[ \text{I}_2(s) + \text{H}_2\text{S}(g) \rightarrow \text{S}(s) + 2\text{HI}(g) \]
HYDRIDES OF GROUP(VII) ELEMENTS

1. The table below shows the chemical formulae of the hydrides of Group VII elements and their physical states at room temperature.

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula of hydride</th>
<th>Physical state at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>HF</td>
<td>Liquid</td>
</tr>
<tr>
<td>Chlorine</td>
<td>HCl</td>
<td>Gas</td>
</tr>
<tr>
<td>Bromine</td>
<td>HBr</td>
<td>Gas</td>
</tr>
<tr>
<td>Iodine</td>
<td>HI</td>
<td>Gas</td>
</tr>
</tbody>
</table>

Explain why hydrogen fluoride is a liquid whereas other hydrides are gases at room temperature.

Fluorine has the highly electronegative making the hydrogen-fluorine bond highly polar. The molecules of hydrogen fluoride are held by strong intermolecular hydrogen bonds which keep the molecules closer to each other. Molecules of hydrogen chloride, hydrogen bromide and hydrogen iodide are held by weak Van der Waals’ forces that keep the molecules far apart.

METHODS OF PREPARATION OF THE HYDRIDES.

2. (a) Describe the general methods of preparing the hydrides in above.

The hydrides can be formed by three main general methods;

(i) **Direct combination of the elements with hydrogen.**

Fluorine is reacted with hydrogen forming hydrogen fluoride

\[ F_2(g) + H_2(g) \rightarrow 2HF(l) \]

Chlorine is reacted with hydrogen and the mixture is heated or exposed to sunlight or ultraviolet light to form hydrogen chloride

\[ Cl_2(g) + H_2(g) \rightarrow 2HCl(g) \]

Bromine is reacted with hydrogen in the presence of platinum catalyst at 300 °C to form hydrogen bromide

\[ Br_2(l) + H_2(g) \rightarrow 2HBr(g) \]

Iodine is reacted with hydrogen in the presence of platinum catalyst at 400 °C to form hydrogen iodide

\[ I_2(s) + H_2(g) \rightarrow 2HI(g) \]
In general, the hydrides can be formed by the reaction between hydrogen and the halogen

$$X_2 + H_2(g) \rightarrow 2HX(g \text{ or } l) \text{ where } X = F, Cl, Br \text{ or } I$$

(ii) Reaction between concentrated sulphuric acid and the halide salts

Hydrogen fluoride can **best** be formed by reaction between cold concentrated sulphuric acid calcium fluoride.

$$CaF_2(s) + H_2SO_4(l) \rightarrow CaSO_4(aq) + 2HF(l)$$

Hydrogen chloride is also **best** formed by heating concentrated sulphuric acid with either solid potassium chloride or solid sodium chloride.

$$KCl(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HCl(g)$$
$$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$$

However, this method is inconvenient for preparation of hydrogen bromide and hydrogen iodide which are progressively stronger reducing agents than hydrogen chloride.

(iii) Hydrolysis of corresponding phosphorus trihalides prepared in situ.

This is the best method for preparation of hydrogen bromide and hydrogen iodide.

Hydrogen bromide is formed by adding bromine to a paste of red phosphorus and water forming phosphorus(III) bromide which is then hydrolysed to form hydrogen bromide and phosphorous acid

$$P_4(s) + 6Br_2(l) \rightarrow 4PBr_3(l)$$
$$PBr_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HBr(g)$$

Hydrogen iodide is formed by adding water to a mixture of red phosphorus and iodine forming phosphorus(III) iodide which is then hydrolysed to form hydrogen iodide and phosphorous acid

$$P_4(s) + 6I_2(s) \rightarrow 4PI_3(s)$$
$$PI_3(s) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HI(g)$$

No heat is required in each of these two reactions.

N.B. Note that although the above methods can prepare the hydrides in general, there is a more convenient method to prepare each of the hydrides.

(b) Hydrogen chloride can be prepared by the action of concentrated sulphuric acid on potassium chloride but hydrogen iodide and hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on potassium iodide and potassium bromide respectively.
Potassium chloride reacts with concentrated sulphuric acid to form hydrogen chloride gas which is a weak reducing agent due to the smaller ionic radius of chloride ion.

\[ KCl(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HCl(g) \]

On the other hand, hydrogen iodide and hydrogen bromide that would be formed are strong reducing agents due to the large ionic radius of iodide and bromide ions. They reduce sulphuric acid to sulphur dioxide as they are oxidised to iodine and bromine respectively. The iodine is observed as purple vapours and bromine as reddish brown vapours.

\[ 2Br^- (aq) + 4H^+ (aq) + SO_4^{2-} (aq) \rightarrow Br_2 (g) + SO_2 (g) + 2H_2O(l) \]
\[ 10I^- (aq) + 14H^+ (aq) + 2SO_4^{2-} (aq) \rightarrow 5I_2 (g) + SO_2 (g) + H_2S(g) + 6H_2O(l) \]

### BOILING POINTS/ MELTING POINTS OF THE HYDRIDES

3. The table below shows both boiling points of group VII hydrides.

<table>
<thead>
<tr>
<th>Hydride</th>
<th>HF</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point(°C)</td>
<td>+19.9</td>
<td>-85.0</td>
<td>-66.7</td>
<td>-35.4</td>
</tr>
</tbody>
</table>

Explain the variation in melting/ boiling points, including any anomalies involved.

Boiling points generally increase from hydrogen fluoride to hydrogen iodide. However, hydrogen fluoride has an abnormally high value of boiling point. The increase in melting point from hydrogen chloride to hydrogen iodide is because the three hydrides have simple molecular structures held by weak Van der Waals’ forces whose magnitude increases with the increasing molecular weight leading to an increase in amount of energy required to break the forces. Hydrogen fluoride has an abnormally high melting point because fluorine has the highest electronegativity, making the hydrogen-fluorine highly polar. The hydrogen fluoride molecules are therefore held by strong intermolecular hydrogen bonds which require a high amount of energy to break.
ACID STRENGTHS

4. The table below shows acid dissociation constants, $K_a$, of group VII hydrides.

<table>
<thead>
<tr>
<th>Hydride</th>
<th>$K_a$ ($mol dm^{-3}$) at 25°C</th>
<th>$HF$</th>
<th>$HCl$</th>
<th>$HBr$</th>
<th>$HI$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$6.6 \times 10^{-4}$</td>
<td>$1.3 \times 10^6$</td>
<td>$1.0 \times 10^9$</td>
<td>$3.2 \times 10^9$</td>
</tr>
</tbody>
</table>

Explain the trend in $K_a$ values of the hydrides.

The $K_a$ values increase in the order $HF < HCl < HBr < HI$ indicating that acid strength increases in the same order. This is because atomic radius of the halogen atoms increases from fluorine to iodine. This makes the hydrogen-halogen bond length longer, reducing the bond strength from hydrogen fluoride to hydrogen iodide, releasing many hydrogen ions in solution.

Hydrofluoric acid is a very weak acid because it dissociates to a considerably smaller extent and also the fluoride ions produced tend to combine with the undissociated hydrogen fluoride molecules especially in concentrated solutions.

In dilute solution; $HF(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

In concentrated solution; $HF(l) + F^-(aq) \rightleftharpoons HF_2^-(aq)$

THERMOSTABILITY

5. Explain the trend in thermostability of the hydrides.

REDUCING ACTION

6. State and explain the trend in reducing action of the hydrides

Reducing strength increases in the order $HF < HCl < HBr < HI$ because ionic radius halide ions increases and electronegativity decreases from fluorine to iodine. Hydrogen fluoride has no reducing action.
ANOMALOUS BEHAVIOUR OF FLUORINE AND HYDROGEN FLUORIDE

7. Although fluorine is an element in group VII of the Periodic Table, it behaves differently from other members of the group.
(a) State the reasons why fluorine behaves differently from the other members of the group.
(b) State the differences between the Chemistry of fluorine as an element and other halogens

Reasons / causes for anomalous behaviour of fluorine
(a)
- Fluorine has the smallest atomic radius compared to other elements
- Fluorine has the highest electronegativity among the elements
- Fluorine has an abnormally low value of bond dissociation energy of the $F—F$ bond
- Unlike other elements, fluorine cannot expand its octet
- Fluorine has the most positive standard electrode potential among the elements
- High exothermic hydration energy of the fluoride ion
(b)
- Fluorine oxidises water to oxygen and itself reduced to hydrofluoric acid. Iodine does not react with water and other halogens disproportionate in water
- Fluorine oxidises cold dilute sodium hydroxide solution to oxygen difluoride gas, itself reduced to fluoride ions. Other halogens disproportionate to form halide ions and halate(I) ions and water.
- Fluorine oxidises hot concentrated sodium hydroxide solution to oxygen gas, itself reduced to fluoride ions. Other halogens disproportionate to form halide ions and halate(V) ions and water.
- Fluorine combines directly with carbon. Other halogens do not react directly with carbon.

Note with concern that the chemistry of compounds of fluorine is not required here as the question is specific to fluorine.
8. Although hydrogen fluoride is a group VII hydride, it behaves differently from hydrides of other members in the group. 
(a) State the reasons why hydrogen fluoride behaves differently from the hydrides of other members of the group.

(b) State the differences between the properties on hydrogen fluoride and other group VII hydrides. 
(a)
- Hydrogen fluoride is strongly hydrogen bonded unlike other hydrides
- It has a very low value of acid dissociation constant at room temperature
- The fluoride ion in it has the smallest ionic radius compared to other halide ions
- The fluorine atom, to which hydrogen is bonded, has the highest electronegativity among the halogen atoms

(b)
- Hydrogen fluoride is a liquid at room temperature whereas other hydrides are gases
- Hydrogen fluoride has an abnormally high value of boiling point compared to other hydrides
- Hydrofluoric acid is a very weak acid in contrast to hydrochloric acid, hydrobromic acid and hydroiodic acid which are all strong acids
- Hydrogen fluoride has no reducing action yet other hydrides are reducing

9. The bond angle in phosphorus trifluoride is 96° while that of phosphorus trichloride is 100°. Explain this observation.
Both phosphorus trifluoride and phosphorus trichloride adopt a trigonal pyramidal shape. However, the fluorine atom is more electronegative than the chlorine atom. The fluorine atom therefore draws away the bonded pairs of electrons from the phosphorus atom more than the chlorine atom does. This makes the bonded pairs to be far apart reducing the repulsion between them. Therefore phosphorus trifluoride has a smaller bond angle than phosphorus trichloride.
POLARISABILITY OF HALIDE IONS
As anionic radius of the anions increases, the anions become more polarisable. This increases the tendency forming covalent compounds.

10. Explain why the solubility of lead(II) halides increases in the order;

\[ PbI_2 < PbBr_2 < PbCl_2 \]

The cationic radius and cationic charge are the same in all compounds. However, anionic radius decreases from the iodide ion to the chloride ion. The halide ions therefore become less polarisable and the ionic character increases from lead(II) iodide to lead(II) chloride. Since water is a polar solvent, the compounds become more soluble in that order.

OCCURRENCE, EXTRACTION AND UTILISATION OF NATURAL SALT (SODIUM CHLORIDE)

11. Describe the extraction of sodium chloride from natural deposits

<p>| QUALITATIVE ANALYSIS FOR ( Cl^- ), ( Br^- ) AND ( I^- ) IONS |
|---------------------------------|----------------|----------------|----------------|</p>
<table>
<thead>
<tr>
<th>ION</th>
<th>TEST</th>
<th>OBSERVATION</th>
<th>DEDUCTION</th>
<th>EXPLANATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Cl^- )</td>
<td>To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat</td>
<td>White fumes turn blue litmus red and form dense white fumes with concentrated ammonia</td>
<td>( HCl ) gas evolved ( Cl^- ) present</td>
<td>Concentrated sulphuric acid reacts with chloride ions to form hydrogen chloride gas. ( Cl^- (s) + H_2SO_4(I) \rightarrow HCl(g) + HSO_4^-(aq) ) Hydrogen chloride gas reacts with concentrated ammonia to form ammonium chloride ( HCl(g) + NH_3(g) \rightarrow NH_4Cl(s) )</td>
</tr>
<tr>
<td>( Cl^- )</td>
<td>To the solution, add dilute nitric acid followed lead(II) nitrate solution</td>
<td>White precipitate ( C_2O_4^{2-}, SO_3^{2-}, SO_4^{2-}, Cl^- ) probably present</td>
<td>Lead(II) ions react with chloride ions to form insoluble lead(II) chloride ( Pb^{2+}(aq) + 2Cl^- (aq) \rightarrow PbCl_2(s) )</td>
<td></td>
</tr>
<tr>
<td>( Cl^- )</td>
<td>Add lead(II) nitrate followed by dilute nitric acid</td>
<td>White precipitate insoluble in acid ( SO_4^{2-}, Cl^- ) probably present</td>
<td>Lead(II) ions react with chloride ions to form insoluble lead(II) chloride ( Pb^{2+}(aq) + 2Cl^- (aq) \rightarrow PbCl_2(s) )</td>
<td></td>
</tr>
<tr>
<td>Step</td>
<td>Description</td>
<td>Observations</td>
<td>Reaction</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td>--------------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td><strong>To the acidified solution, lead(II) nitrate solution and heat/boil/warm</strong></td>
<td>White precipitate soluble on heating/boiling/warming and reprecipitates on cooling</td>
<td>$Cl^-$ present</td>
<td>Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $\text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow \text{PbCl}_2(s)$</td>
<td></td>
</tr>
<tr>
<td><strong>Add dilute nitric acid followed by silver nitrate solution</strong></td>
<td>White precipitate $C_2\text{O}_4^{2-}$, $\text{SO}_3^{2-}$, $\text{Cl}^-$ probably present</td>
<td></td>
<td>Silver ions react with chloride ions to form insoluble silver chloride $\text{Ag}^{+}(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$</td>
<td></td>
</tr>
<tr>
<td><strong>Add silver nitrate solution followed by dilute nitric acid</strong></td>
<td>White precipitate insoluble in acid</td>
<td>$Cl^-$ present</td>
<td>Silver ions react with chloride ions to form insoluble silver chloride $\text{Ag}^{+}(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$</td>
<td></td>
</tr>
<tr>
<td><strong>Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia dropwise until in excess.</strong></td>
<td>White precipitate soluble in excess ammonia to form a colourless solution $Cl^- \text{ confirmed}$</td>
<td></td>
<td>Silver ions react with chloride ions to form insoluble silver chloride $\text{Ag}^{+}(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$ Silver chloride reacts with excess ammonia to form a soluble complex of diammine silver(I) ion. $\text{AgCl}(s) + 2\text{NH}_3(aq) \rightarrow \text{Ag(NH}_3)_2^+(aq) + \text{Cl}^-(aq)$</td>
<td></td>
</tr>
<tr>
<td><strong>To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand.</strong></td>
<td>Tetrachloromethane layer remains colourless</td>
<td>$Cl^-$ present</td>
<td>The acidified bleaching powder or chlorine water produces Chlorine. The chlorine cannot oxidise chloride ions. hence the tetrachloromethane layer remains colourless</td>
<td></td>
</tr>
<tr>
<td><strong>To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat (the reaction may</strong></td>
<td>Reddish brown vapours $Br^-$ present</td>
<td></td>
<td>Bromide ions are strongly reducing due to their large ionic radius. They reduce hot concentrated sulphuric acid to sulphur dioxide as they are oxidised to bromine.</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Products</td>
<td>Equation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>To the solution, add dilute nitric acid followed lead(II) nitrate solution</td>
<td>White precipitate</td>
<td>( \text{C}_2\text{O}_4^{2-}, \text{SO}_3^{2-}, \text{SO}_4^{2-}, \text{Cl}^- )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{Br}^- ) probably present</td>
<td>( \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq) \rightarrow \text{PbBr}_2(s) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add dilute nitric acid followed by silver nitrate solution</td>
<td>White precipitate (Pale yellow)</td>
<td>( \text{Br}^- ) present</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Ag}^+(aq) + \text{Br}^-(aq) \rightarrow \text{AgBr}(s) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add silver nitrate solution followed by dilute nitric acid</td>
<td>Pale yellow precipitate (Pale yellow precipitate soluble in excess ammonia)</td>
<td>( \text{Br}^- ) present</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Ag}^+(aq) + \text{Br}^-(aq) \rightarrow \text{AgBr}(s) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia dropwise until in excess.</td>
<td>Pale yellow precipitate soluble in excess ammonia</td>
<td>( \text{Br}^- ) present</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Ag}^+(aq) + \text{Br}^-(aq) \rightarrow \text{AgBr}(s) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silver bromide is sparingly soluble in ammonia.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand</td>
<td>Reddish brown liquid in tetrachloromethane layer</td>
<td>( \text{Br}^- ) present</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>The acidified bleaching powder or chlorine water produces Chlorine which oxidises bromide ions to bromine.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Cl}_2(g) + 2\text{Br}^-(aq) \rightarrow 2\text{Cl}^-(aq) + \text{Br}_2(l) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bromine is covalent hence dissolves in tetrachloromethane to form the reddish brown layer.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat (the reaction may take place even before heating)</td>
<td>Purple vapours</td>
<td>( \text{I}^- ) present</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iodide ions are strongly reducing due to their large ionic radius. They reduce hot concentrated sulphuric acid to sulphur dioxide as they are oxidised to iodine. Sometimes oxidation result into formation of hydrogen sulphide gas, as well, with a smell of rotten eggs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 2\text{I}^-(aq) + 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{I}_2(g) + \text{SO}_2(g) + 2\text{H}_2\text{O}(l) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>or ( 10\text{I}^-(aq) + 14\text{H}^+(aq) + 2\text{SO}_4^{2-}(aq) \rightarrow 5\text{I}_2(g) + \text{SO}_2(g) + \text{H}_2\text{S}(g) + 6\text{H}_2\text{O}(l) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Precipitate</td>
<td>Product</td>
<td>Equation</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>-----------------------</td>
<td>-----------------------</td>
<td>--------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>To the solution, add dilute nitric acid followed by lead(II) nitrate solution</strong></td>
<td>Yellow precipitate</td>
<td>$I^-$ present</td>
<td>Lead(II) ions react with iodide ions to form insoluble lead(II) iodide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$</td>
<td></td>
</tr>
<tr>
<td><strong>Add dilute nitric acid followed by silver nitrate solution</strong></td>
<td>Yellow precipitate</td>
<td>$I^-$ present</td>
<td>Silver ions react with iodide ions to form insoluble silver iodide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$</td>
<td></td>
</tr>
<tr>
<td><strong>Add silver nitrate solution followed by dilute nitric acid</strong></td>
<td>Yellow precipitate</td>
<td>$I^-$ present</td>
<td>Silver ions react with iodide ions to form insoluble silver iodide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>insoluble in acid</td>
<td></td>
<td>$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$</td>
<td></td>
</tr>
<tr>
<td><strong>Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia dropwise until in excess.</strong></td>
<td>Yellow precipitate</td>
<td>$I^-$ present</td>
<td>Silver ions react with iodide ions to form insoluble silver iodide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>insoluble in acid</td>
<td></td>
<td>$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Silver iodide is insoluble in ammonia</td>
<td></td>
</tr>
<tr>
<td><strong>To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand</strong></td>
<td>Violet colouration in tetrachloromethane layer</td>
<td>$I^-$ present</td>
<td>The acidified bleaching powder or chlorine water produces Chlorine which oxidises iodide ions to iodine.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iodine is covalent hence dissolves in tetrachloromethane.</td>
<td></td>
</tr>
<tr>
<td><strong>Add copper(II) sulphate solution</strong></td>
<td>White precipitate in a brown solution</td>
<td>$I^-$ present</td>
<td>Copper(II) ions oxidises iodide ions to iodine and itself reduced copper(I) iodide.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$</td>
<td></td>
</tr>
</tbody>
</table>
MISCELLANEOUS TOPICAL QUESTIONS

Short answer type questions

1. Write equations to show how chlorine and iodine react with;
   (a) Sodium iodide solution. (03 marks)
   (b) Sodium thiosulphate solution (03 marks)
   (c) Cold dilute sodium hydroxide (03 marks)

2. (a) Write equation for the reaction that takes place when hot concentrated potassium hydroxide is added to;
   (i) fluorine. (01 mark)
   (ii) chlorine. (01 mark)
   (b) Write equation(s) for the reaction(s) of
      (i) fluorine and water (1 ½ marks)
      (ii) hydrofluoric acid and silicon(IV) oxide (1 ½ marks)

3. (a) Fluorine, chlorine, bromine and iodine are diatomic molecules of group VII elements of the Periodic Table. Briefly describe how the elements react with;
   (i) Potassium bromide. (02 marks)
   (ii) Hydrogen sulphide (02 marks)
   (c) The hydrides of the elements in (a) above boil at different temperatures shown in the table below.

<table>
<thead>
<tr>
<th>Hydride</th>
<th>HF</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point(°C)</td>
<td>+20</td>
<td>-85</td>
<td>-67</td>
<td>-35</td>
</tr>
</tbody>
</table>
   State and explain the trend in boiling points of the hydrides. (03 marks)
   (d) (i) State the order in reducing strength of the hydrides. (01 mark)
   (ii) Write a general equation for the reaction between aqueous solutions of the hydrohalic acids with sodium carbonate. (01 mark)

4. The table below gives some physical properties of hydrogen halides.

<table>
<thead>
<tr>
<th>Hydride</th>
<th>HF</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point(K)</td>
<td>293</td>
<td>188</td>
<td>206</td>
<td>238</td>
</tr>
<tr>
<td>Bond length(nm)</td>
<td>0.086</td>
<td>0.128</td>
<td>0.142</td>
<td>0.160</td>
</tr>
</tbody>
</table>

   (d) Explain the observed trend in;
   (i) Boiling points (02 marks)
   (ii) Bond length (02 marks)
   (e) Arrange the hydrogen halides in order of the expected increase in acid strength of their aqueous solutions, giving reason for your answer. (02 marks)
5. (a) Draw the structure and name the shape of the following compounds

<table>
<thead>
<tr>
<th>Structure</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>( PH_3 )</td>
<td></td>
</tr>
<tr>
<td>( SF_4 )</td>
<td></td>
</tr>
</tbody>
</table>

(b) Write equation for the reaction between ammonia and aluminium chloride.

(01 mark)

6. State what would be observed and write equation for the reaction that would take place when;
   (i) Copper(II) sulphate solution was added to potassium iodide solution.

(2 ½ marks)
   (ii) Potassium iodide solution is added to chlorine water.

(02 marks)
   (iii) Solid sodium iodide is heated with concentrated sulphuric acid.

(2 ½ marks)
   (iv) Warm concentrated hydrochloric acid is added to manganese(IV) oxide.

(02 marks)
   (v) Sodium iodide is added to acidified sodium chlorate(I) solution.

(02 marks)
   (vi) Sodium iodide solution is added to acidified hydrogen peroxide solution.

(1 ½ marks)

7. (a) The chemistry of fluorine differs from that of chlorine.
   (i) State two differences between the chemistry of fluorine and chlorine apart from their reactions with sodium hydroxide.

(02 marks)
   (ii) Write the equation for the reaction between cold dilute sodium hydroxide and;

   - Fluorine
   - chlorine

(03 marks)
8. (a) The oxidising strength of group VII elements decreases in the order:

\[ F_2 > Cl_2 > Br_2 > I_2 \]

(i) State three reasons to account for the high oxidising strength of fluorine relative to other halogens. (1 ½ marks)

(ii) State two other anomalous properties of fluorine. (02 marks)

(b) Describe the reactions of chlorine and iodine with;

(i) sodium thiosulphate solution. (3 ½ marks)

(ii) iron(II) sulphate. (02 marks)

9. (a) (i) State the condition(s) under chlorine reacts with sulphur dioxide. (01 mark)

(ii) Write equation for the reaction. (01 mark)

(b) Chlorine was bubbled through sodium thiosulphate solution and lead(II) nitrate solution was added to the resultant solution.

(i) State what was observed. (01 mark)

(ii) Write equation(s) for the reaction(s) that took place. (02 marks)

10.(a) State three reasons why fluorine differs in some of its properties from the rest of group VII elements. (03 marks)

(b) Write equations for ionisation of hydrogen fluoride in aqueous solutions that are;

(i) dilute

(ii) concentrated (03 marks)

(c) Explain why hydrogen fluoride is a weaker acid than hydrogen chloride. (03 marks)

11. Name the reagent(s) that can be used to distinguish between the following pair(s) of compounds. In each case state the observations made and write equation(s) for the reaction.

(i) \( I^- \) and \( Br^- \) (4 ½ marks)

(ii) \( Cl^- \) and \( Br^- \) (4 ½ marks)

(iii) \( I^- \) and \( Cl^- \) (4 ½ marks)
12. (a) (i) What is the electronic configuration of the bromide ion. (01 mark)
(ii) With the aid of a suitable diagram(s), show how the bonding of the chlorate(III) oxo-anion of chlorine. (1 ½ marks)
(b) When iodine is added to aqueous sodium hydroxide, the initial product formed disproportionates. Explain the meaning of this term and write an ionic equation for the changes that take place. (2 ½ marks)
(c) Explain why unlike other halogens, fluorine liberates oxygen from cold water. (02 marks)

13. (a) State what would be observed and write equation for the reaction that would take place if potassium iodide was added to acidified potassium dichromate solution. (2 ½ marks)
(c) Sodium thiosulphate solution was added to the mixture in (a), state what was observed and write equation for the reaction that took place. (2 ½ marks)

14. (a) The table below shows the melting points of magnesium halides.

<table>
<thead>
<tr>
<th>Formula of halide</th>
<th>$MgF_2$</th>
<th>$MgCl_2$</th>
<th>$MgBr_2$</th>
<th>$MgL_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point(°C)</td>
<td>1263</td>
<td>714</td>
<td>711</td>
<td>634</td>
</tr>
</tbody>
</table>

Explain the trend in melting points of the halides. (04 marks)
(b) The values of lattice energies of potassium halides are given below.

<table>
<thead>
<tr>
<th>Formula of halide</th>
<th>$KCl$</th>
<th>$KBr$</th>
<th>$KI$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice energy(kJmol⁻¹)</td>
<td>-710</td>
<td>-643</td>
<td></td>
</tr>
</tbody>
</table>

Explain the trend in these values for the potassium halides. (03 marks)

15. Explain the following observations
(a) Lead(IV) chloride exists but lead(IV) bromide does not. (02 marks)
(b) Tin and lead do not form tetraiodides. (03 marks)
(c) When hydrogen iodide is treated with concentrated sulphuric acid, iodine is liberated, whereas when hydrogen chloride is similarly treated, chlorine is not evolved. (03 marks)
(d) When added separately to copper(II) sulphate solution, potassium iodide forms a white precipitate in a brown solution while potassium chloride gives no observable change. (03 marks)
(e) The boiling point of hydrogen fluoride is higher than that of hydrogen chloride. (03 marks)
(f) Both halogens and oxygen are diatomic. However, halogens react more readily with metals than oxygen. (02 marks)

(g) Iodine is insoluble in water but soluble in potassium iodide solution. (2 ½ marks)

(h) The bond in hydrogen chloride is polar. (1 ½ marks)

(i) Hydrofluoric acid is weaker than hydrobromic acid. (03 marks)

**Long answer type questions**

16. Fluorine, chlorine, bromine and iodine are elements in group VII of the Periodic Table.

(a) Describe the general method of preparing chlorine, bromine and iodine in the laboratory. (02 marks)

(b) Fluorine differs in some of its properties from chlorine, bromine and iodine.

(i) Explain why fluorine differs from other Group VII elements. (02 marks)

(ii) State four properties in which fluorine differs from other Group members. (04 marks)

(c) Describe the reactions of group VII elements with:

(i) Water (04 marks)

(ii) Sodium hydroxide (08 marks)

(d) Hydrofluoric acid is a weaker acid than hydrochloric acid. Explain. (02 marks)

17. (a)(i) Sketch a graph of first electron affinity against atomic number of group VII elements. (3 ½ marks)

(ii) Explain the shape of the graph (6 ½ marks)

(b) State two reasons why fluorine differs in some of its properties from bromine. (02 marks)

(c) State three properties in which fluorine differs from bromine. (03 marks)

(d) Describe the reaction of sulphuric acid with hydrogen bromide. Write the equation for the reaction. (03 marks)
18. (a) The boiling points of group VII elements are in the order $I_2 > Br_2 > Cl_2 > F_2$ whereas the dissociation energy is in the reverse order. Briefly explain this observation. (06 marks)

(b) Discuss the chemical differences between fluorine and bromine with respect to;

(i) Water
(ii) Sodium hydroxide (08 marks)

(c) The oxy-acids of chlorine include; $HOCl, HClO_2, HClO_3$ and $HClO_4$.

(i) Write and name the shapes adopted by the oxy-acids. (04 marks)

(ii) Which of the oxy-acids is the strongest acid. Give a reason for your answer. (02 marks)

19. (a) State and explain the trend in the boiling points of group VII elements. (03 marks)

(b) Explain why hydrogen fluoride;

(i) is a weaker acid in dilute aqueous solution than in concentrated solution. (03 marks)

(ii) has a higher boiling point than hydrogen iodide. (03 marks)

(c) Write equation for the reaction between hydrogen fluoride and silicon(V) oxide. (01 mark)

(d) Describe the reactions of group (VII) elements with sodium hydroxide. (07 marks)

(e) Write the equation for the reaction between sulphuric acid

(i) Sodium chloride
(ii) Potassium bromide
(iii) Sodium iodide (03 marks)

20. (a) The bond energies of halogen acids are given in the table below.

<table>
<thead>
<tr>
<th>$H—X$</th>
<th>$H—F$</th>
<th>$H—Cl$</th>
<th>$H—Br$</th>
<th>$H—I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy (kJmol$^{-1}$)</td>
<td>556</td>
<td>431</td>
<td>336</td>
<td>299</td>
</tr>
</tbody>
</table>

(i) Explain the variation in bond energy. (03 marks)

(ii) State two properties of the halogen acids whose variation is caused by the trend in bond energies. (02 marks)

(b) Describe the reaction of the halogen acids with;

(i) Concentrated sulphuric acid (05 marks)

(ii) Sodium carbonate (2 ½ marks)

(c) Describe the reaction of the halogens with concentrated potassium hydroxide. (7 ½ marks)

21. (a) Describe the industrial preparation of chlorine. (04 marks)
(b) Describe the reaction of chlorine with;
   (i) iron                                           (02 marks)
   (ii) potassium hydroxide                         (04 marks)

(c) Describe the reaction of fluorine with
   (i) Water                                          (02 marks)
   (ii) Potassium hydroxide                          (04 marks)

(d) Explain why hydrogen fluoride is a liquid whereas hydrogen chloride is a
     gas at 18 °C.                                        (04 marks)

22. Explain the following observations.
   (a) When iodine crystals are added to cold dilute sodium hydroxide solution,
       the grey solid dissolves to form a pale yellow solution which turned
       colourless on standing.                                        (04 marks)
   (b) When acidified potassium manganate(VII) solution was added to aqueous
       potassium iodide solution, the solution turns brown.             (03 marks)
   (c) The first electron affinities of the halogens generally decrease down the
       group. However, the first electron affinity of fluorine is abnormally high. (04 marks)
   (d) When a limited amount of chlorine is bubbled through sodium thiosulphate
       solution, a yellow precipitate is formed.                        (05 marks)
   (e) The fluorine molecule has a low bond dissociation enthalpy yet it has a
       short bond length.                                              (04 marks)