9.3 Group VII

Content

9.3.1 The similarities and trends in the physical and chemical properties of chlorine, bromine and iodine

- (i) Characteristic physical properties
- (ii) The relative reactivity of the elements as oxidising agents
- (iii) Some reactions of the halide ions
- (iv) The reactions of chlorine with aqueous sodium hydroxide

Learning Outcomes

Candidates should be able to:

(a) describe the trends in volatility and colour of chlorine, bromine and iodine

(b) analyse the volatility of the elements in terms of van der Waals' forces

(c) describe and deduce from $E^{\ominus}$ values the relative reactivity of the elements as oxidising agents

(d) describe and explain the reactions of the elements with hydrogen

(e) (i) describe and explain the relative thermal stabilities of the hydrides

(ii) interpret these relative stabilities in terms of bond energy

(f) describe and explain the reactions of halide ions with:

(i) aqueous silver ions followed by aqueous ammonia,

(ii) concentrated sulfuric acid

(g) describe and analyse in terms of changes of oxidation number the reaction of chlorine with cold, and with hot, aqueous sodium hydroxide

9.3.1 The similarities and trends in the physical and chemical properties of chlorine, bromine and iodine

fundamental questions

Example 1

(a) Define halogens.

(b) Describe the types of bonding that halogens take part in.

(c) State and explain if all the halogens can expand their octet configuration.

Solution:

(a) **Halogens** are defined as the chemical elements either individually or collectively that constitute Group VII of the Periodic Table. They are also commonly known as *p*-block elements. (ans)

(b) The halogens have seven electrons in their outermost shell, with a configuration of ns^2np^5. Halogens will complete the octet by accepting an electron to form a halide ion, X^-, or by sharing an electron to form a covalent bond. (ans)

(c) With the exception of fluorine, all halogens can expand their octet configuration. Fluorine does not have energetically accessible *d* orbitals for expansion of octet configuration to take place. All other halogens are able to promote electrons into the *d* orbitals and thus are able to form more than one bond. (ans)

Example 2

(a) State the colours of chlorine, bromine and iodine in their respective states at room temperature.

(b) Describe the trend in volatility of the halogens, with reference to chlorine, bromine and iodine.

Solution:

(a) Chlorine – yellowish green gas

Bromine – dark red liquid

Iodine – black solid (ans)

(b) The boiling points of the halogens increase down the group as the number of electrons increases, resulting in an increase in the strength of the Van der Waal's forces. Chlorine has the smallest number of electrons, thus it has the lowest boiling point, followed by bromine and iodine. This also explains the change in physical state of the halogens down the group – from gas to solid. Chlorine is a gas, bromine is a liquid and iodine is a solid. (ans)

Example 3

Explain why iodine is more soluble in aqueous potassium iodide than in water.

Solution:

Iodine dissolves in aqueous potassium iodide solution to give a reddish-brown solution of soluble I_3^- ions.

$$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq) \quad \text{(ans)}$$

Example 4

(a) Halogens are oxidizing agents. Explain why the relative strength of oxidizing powers decreases down the group.

(b) Explain how $E^\ominus$ values can be used to deduce the relative reactivity of the halogens as oxidizing agents.

(c) State and explain what is seen when chlorine gas is passed through colourless potassium bromide.

(d) Explain why the strength of the oxo-acids increases in the order $HClO < HClO_2 < HClO_3 < HClO_4$.

Solution:

(a) This is because the halogens become less reactive and the electron affinity decreases, thus decreasing their tendency to oxidize other elements. Thus fluorine is the strongest oxidizing agent while iodine is the weakest. (ans)

(b) The weaker the oxidizing strength, the less positive the $E^\ominus$ values. For example, bromine has an $E^\ominus$ value of +1.07 V while iodine, which is lower in the group, has an $E^\ominus$ value of +0.54 V. (ans)

(c) The solution turns reddish brown. The chlorine gas is a stronger oxidising agent than bromine and thus it displaces the bromine from potassium bromide to form aqueous potassium chloride and bromine. Bromine is reddish brown in colour and gives the solution its colour. (ans)

(d) All four oxo-acids dissociate in water to form protons and the corresponding anions. The strength of the O–H bond in the molecule determines the acid strength. The additional oxygen atoms exert an electron-withdrawing effect, weakening the O–H bond. Thus the acid strength is in the order: $HClO < HClO_2 < HClO_3 < HClO_4$. (ans)

Example 5

(a) State whether bromine or iodine is a stronger oxidizing agent.

(b) Suggest an experiment to prove the answer above.

Solution:

(a) Bromine. (ans)

(b) The relative oxidizing power can be determined using a displacement reaction. When $Br_2(g)$ is mixed with KI(aq), the iodine is displaced to form iodine. However, $I_2(g)$ cannot displace bromine from KBr(aq). This shows that bromine is a stronger oxidizing agent than iodine. (ans)

Example 6

(a) Define disproportionation.

(b) The equation below shows the reaction between chlorine and cold dilute alkali. It is an example of a disproportionation reaction. State the changes in oxidation number of chlorine.

$$Cl_2(g) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

(c) Will the products be different if chlorine has reacted with hot alkali instead? If so, give the equation for the reaction and the corresponding changes in oxidation number.

Solution:

(a) **Disproportionation** is the simultaneous oxidation and reduction of a substance reacting with itself, thereby forming two dissimilar ions, or an ion and an atom or molecule. (ans)

(b) Chlorine (0) is simultaneously oxidized to chlorate(I) ions (+1) and reduced to chloride ions (–1). (ans)

(c) Yes.

$$3Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$$

Chlorine (0) is simultaneously oxidized to chlorate(V) ions (+5) and reduced to chloride ions (–1). (ans)

Example 7

(a) Describe the reaction of halogens with hydrogen gas.

(b) Describe and explain the relative thermal stabilities of the compounds formed from the above reaction.

(c) Describe the effect of heating on hydrogen chloride, hydrogen bromide and hydrogen iodide.

Solution:

(a) Hydrogen halides are formed from the reaction of halogen with hydrogen. Taking X as the halogen,

$$H_2 + X_2 \rightarrow 2HX$$

Hydrogen reacts vigorously with chlorine, less vigorously with bromine and very slowly with iodine. This can be attributed to the higher bond energy value of hydrogen chloride as compared to hydrogen bromide and hydrogen iodide. The heat energy given out by the formation of the hydrogen chloride bond is sufficient to provide the energy needed to break the hydrogen and chlorine gas bonds. However, this is not the case for hydrogen iodide. Thus the reaction does not go to completion. (ans)

(b) Bond energy can be used to compare relative thermal stabilities. The strength of the H–X bond decreases from hydrogen chloride to hydrogen iodide due to the increase in size of the halogen. This causes the thermal stability of the hydrogen halides to decrease down the group. (ans)

(c) Hydrogen chloride does not decompose.

Hydrogen bromide decomposes slightly to produce some $Br_2(g)$.

Hydrogen iodide decomposes most readily to form thick purple fumes of $I_2(g)$. (ans)

Example 8

(a) Name the process that hydrogen halides undergo when concentrated sulfuric acid is added.

(b) Describe what happens when concentrated sulfuric acid is added to sodium chloride, sodium bromide and sodium iodide. Give equations for the reactions that occur.

Solution:

(a) Oxidation. (ans)

(b) For sodium chloride, steamy fumes of $HCl(g)$ are produced, e.g. with $NaCl$.

$$NaCl(aq) + H_2SO_4(aq) \rightarrow HCl(g) + NaHSO_4(aq)$$

For sodium bromide, orange-brown fumes of HBr are produced.

$$NaBr(s) + H_2SO_4(aq) \rightarrow HBr(g) + NaHSO_4(aq)$$

HBr is oxidized to Br_2. Orange-brown fumes of Br_2 are produced.

$$2HBr(aq) + H_2SO_4(aq) \rightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$$

The bromide ion is more easily oxidized than the chloride ion, thus concentrated sulfuric acid is strong enough to oxidize hydrogen bromide to bromine gas but not for hydrogen chloride.

For sodium iodide, purple vapour of iodine is obtained.

$$NaI(s) + H_2SO_4(aq) \rightarrow HI(g) + NaHSO_4(aq)$$

HI is readily oxidized to I_2.

$$8HI(aq) + H_2SO_4(aq) \rightarrow 4I_2(g) + H_2S(g) + 2H_2O(l) \quad \text{(ans)}$$

Example 9

(a) Compare the effect of acidified silver nitrate on sodium chloride, sodium bromide and sodium iodide. State what happens when the precipitate formed is exposed to light.

(b) Describe what happens when aqueous ammonia is added to the precipitates formed in (b).

Solution:

(a) For sodium chloride, a white precipitate of silver chloride is formed.

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$

Upon standing in the light, the white precipitate darkens quickly.

For sodium bromide, a pale yellow precipitate of silver bromide is formed.

$$Ag^{+}(aq) + Br^{-}(aq) \rightarrow AgBr(s)$$

Upon standing in the light, the precipitate darkens slightly.

For sodium iodide, a yellow precipitate of silver iodide is formed.

$$Ag^{+}(aq) + I^{-}(aq) \rightarrow AgI(s)$$

There is no change when the precipitate is exposed to light. (ans)

☺ *The darkening effect is due to the conversion of silver halide to small particles of metallic silver by light.*

(b) Silver chloride dissolves readily to give a colourless solution of diammine silver(I) ion.

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^{+}(aq) + Cl^{-}(aq)$$

Silver bromide dissolves in concentrated ammonia solution to give a colourless solution.

$$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^{+}(aq) + Br^{-}(aq)$$

Silver iodide is insoluble in aqueous ammonia. (ans)

Example 10

(a) Discuss the manufacture of chlorine.
(b) Write equations for the reaction of chlorine with
   (i) sodium hydroxide;
   (ii) hydrogen sulfide; and
   (iii) potassium iodide.

Solution:

(a) Chlorine is produced in the mercury cathode cell and the diaphragm cell.

Mercury cathode cell – brine is electrolysed using mercury as a cathode and graphite as anode.

- Anode: $2Cl^{-} \rightarrow Cl_2 + 2e^{-}$
- Cathode: $2Na^{+} + 2e^{-} \rightarrow 2Na$
  $Na + Hg \rightarrow Na/Hg$

An unreactive sodium amalgam is formed at the cathode. It will react with water to produce sodium hydroxide and hydrogen gas.

$$2Na/Hg + 2H_2O \rightarrow 2NaOH + H_2 + 2Hg$$

Diaphragm cell

- Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$
- Cathode: $2H^+ + 2e^- \rightarrow H_2$

The anode compartment contains an excess of Na^+ ions while the cathode compartment contains an excess of OH^- ions. The ions in excess are allowed to react as brine flows through the diaphragm, producing sodium hydroxide. (ans)

(b) (i) $Cl_2(g) + 2NaOH(aq) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$

(ii) $Cl_2(g) + H_2S(aq) \rightarrow 2Cl^-(aq) + 2H^+(aq) + S(s)$

(iii) $Cl_2(g) + 2KI(aq) \rightarrow I_2(aq) + 2KCl(aq)$ (ans)

Example 11

(a) Three substances which contain chlorine include polychloroethene, sodium chlorate(I) and tetrachloromethane. State one use of each of these substances and the properties which make them suitable for such use.

(b) Potassium chlorate(V) is used to make fireworks and matchstick heads.

(i) Suggest how it can be obtained from chlorine.

(ii) Suggest what happens when potassium chlorate(V) is added to iron(II) sulfate (aq).

Solution:

(a) Polychloroethene is used to make pipes as it is chemically inert, durable and strong.

Sodium chlorate(I) is used in bleach as it is a strong oxidising agent.

Tetrachloromethane is used as an organic solvent as it is inert and not flammable. (ans)

(b) (i) It is obtained from chlorine by passing chlorine gas into hot aqueous KOH.

$$3Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$$

(ii) From the Data Booklet,

$$ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O \qquad E^\ominus = 1.45\ \text{V}$$

When iron(II) sulfate is added,

$$ClO_3^- + 6H^+ + 6Fe^{2+} \rightarrow Cl^- + 6Fe^{3+} + 3H_2O(l)$$

$$E^\ominus_{cell} = 1.45 - 0.77 = 0.68\ \text{V} > 0$$

Thus the reaction is feasible, and the solution changed colour from pale green to yellow. (ans)

Example 12

[***Examined in*** 2012]

The following two experiments are carried out with anhydrous potassium chloride and observations X and Y are made at the end of each experiment.

Concentrated sulfuric acid is added to the potassium chloride and the fumes produced are bubbled into aqueous potassium iodide solution – observation X.

The potassium chloride is dissolved in aqueous ammonia and this is then added to aqueous silver nitrate – observation Y.

What are the observations X and Y?

	X	Y
A	brown solution	colourless solution
B	brown solution	white precipitate
C	colourless solution	colourless solution
D	colourless solution	white precipitate

Solution:

Answer: **C**

The relevant product of the first reaction is HC*l*.

$$\text{conc } H_2SO_4 + 2KCl \rightarrow K_2SO_4 + 2HCl$$

HC*l* will not react with KI(aq), hence observation X is "colourless solution".

The second reaction was between KC*l* and $AgNO_3$ in the presence of ammonia solution.

$$AgNO_3 + KCl \rightarrow AgCl + KNO_3$$

The expected product, AgC*l*, is soluble in ammonia solution, so observation Y is also "colourless solution".

[Teachers' Comments] The most commonly chosen incorrect answers were B and D. The relevant product of the first reaction (conc H_2SO_4 + KC*l*) is HC*l*. HC*l* will not react with KI(aq), so observation X is "colourless solution". The second reaction was between KC*l* and $AgNO_3$ in the presence of ammonia solution. The expected product, AgC*l*, is soluble in ammonia solution, so observation Y is also "colourless solution".