SUB-TOPIC 11.2: Trends in Properties of Group 17 Elements [Halogens] and their Compounds: [Duration:15 periods]

This is under the Topic Competency; *The learner analyses the trends in the physical and chemical properties of Group 14 elements, Group 17 elements and d-block elements and relates these trends to their applications in industrial and environmental contexts.*

Learning outcomes; The learner should be able to;

(a) examine the trends in electronegativity, boiling point, and reactivity of Group 17 elements and their compounds, relating them to their physical and chemical properties.

(b) evaluate the impact of Group 17 elements in daily life and industry, particularly in disinfection and manufacturing, considering both advantages and environmental concerns.

WHAT THE SYLLABUS REQUIRED;

(a) physical and chemical properties of Group 17 elements

Physical properties of the elements	Chemical properties of the elements
Boiling point Melting point Atomic radius Colour/nature Electronegativity	**Reactions with;** Water Alkalis(disproportionation) Hydrogen metals

(a) Compounds of Group 17 elements

1. Hydrides	• Acid strength • Bond energy • Displacement re-activities
2. Oxo-acids	

(b) practical activities

Test tube experiments to identify $\mathbf{Cl^-}$, $\mathbf{Br^-}$ and $\mathbf{I^-}$ ions

(c) Applications of Group 17 elements and their compounds in daily life (advantages and environmental concerns)

(d) Project work on applications of Group 17 elements and their compounds in real life

#####end of sub-topic#####

THE CHEMISTRY OF GROUP 17 ELEMENTS (THE HALOGENS)

The table below summarizes the physical properties of the elements

Elements	Nature/colour	Boiling point/^{0}C	Melting point/^{0}C	Atomic radius/pm	Electron Affinity	Electronegativity
Fluorine	Gas (Pale yellow)	-188	-220	64	-322.6	4.0
Chlorine	Gas(Greenish-Yellow)	-34	-101	99	-364	3.0
Bromine	Liquid(Reddih-brown)	58	-7	114	-342	2.8
Iodine	Solid (Purple)	183	114	143	-295.4	2.5
Astatine	**RADIOACTIVE ELEMENT**					

Physical properties of the halogens.

The halogens exist as diatomic molecules i.e. F_2, Cl_2, Br_2 and I_2.

Fluorine is a colourless gas, chlorine is a yellowish green gas, bromine is a reddish brown gas while iodine is a black (dark purple) solid at room temperature.

Halogens are highly reactive non-metals. They exist as diatomic molecules X_2 containing a covalent bond. Due to their reactivity, the elements do not occur in the free state but are always combined either among themselves or with other elements.

All the elements have 7 electrons in their outer most shells with general outer most electronic configuration of ns^2np^5 (*n= 2, 3, 4, 5)*

They can complete their octet by either gaining an electron to form an ionic bond or sharing electrons with other elements or themselves in a covalent bond.

The melting and boiling points of the halogens are low but increase down the group.

Explanation

The diatomic molecules of halogens are held by weak intermolecular van der Waals forces of attraction. These forces become stronger with increasing molecular weight/ masses down the group.

In bromine and iodine, the forces are strong enough to bind their molecules to exist as liquid and solid respectively at room temperature. However, in fluorine and chlorine, the forces are not strong enough and as a result they exist as gases at room temperature.

Boiling point / melting point.

Boiling point increases down the group. This is because the simple molecules are held by weak van der waals forces whose magnitude increases with increase in molecular mass.

Fluorine behaves differently from the rest of the members due to:

- High electronegativity
- Small atomic radius
- Low bond energy
- High electrode potential

Special properties of F which indicate how it behaves differently

- It combines directly with carbon at room temperature to form carbontetrafluoride.
- Hydrogen fluoride has a very high boiling point due to formation of hydrogen bonding.
- Hydrofluoric acid is the weakest acid compared to other halogen acid.
- Silver fluoride is soluble in water while the chloride, bromide and iodide of silver are insoluble in water. This is because the small fluoride ions have high hydration energy which exceeds lattice energy hence the enthalpy of solution is negative.
- Fluorine has only one oxidation state.
- Fluorine does not form oxo-acids.
- Calcium fluorine is insoluble in water while the other halides are soluble in water.

Chemical properties of halogens

Reaction with;

(a) Water

Fluorine oxidizes water vigorously to oxygen. Hydrofluoric acid is also formed.

$$2H_2O\,(l) + 2F_2\,(g) \longrightarrow O_2\,(g) + 4HF\,(aq)$$

Chlorine and bromine reacts with water to form halic(I) acids

$Cl_2 (g) + H_2O (l) \longrightarrow HCl (aq) + HOCl (aq)$

$Br_2 (l) + H_2O (l) \longrightarrow HBr (aq) + HOBr (aq)$

Iodine is sparingly soluble in water but highly soluble in potassium iodide solution due to formation of potassium tri-iodide which is a complex salt i.e.

$I_2 (s) + I^- (aq) \longrightarrow I_3^- (aq)$

N.B. In the presence of Sunlight, the halic(I) acid decompose to oxygen.

$2HOCl (aq) \longrightarrow 2HCl (aq) + O_2 (g)$

(b) Alkalis

(i) Cold dilute Alkalis:

Fluorine forms oxygen difluoride, fluoride and water

$2F_2 (g) + 2OH^- (aq) \longrightarrow OF_2 (g) + 2F^- (aq) + H_2O (l)$

Chlorine, Bromine and Iodine form the halide, halite (I) and water.

$Cl_2 (g) + 2 OH^- (aq) \longrightarrow Cl^- (aq) + OCl^- (aq) + H_2O (l)$

$Br_2 (l) + 2OH^- (aq) \longrightarrow Br^- (aq) + OBr^- (aq) + H_2O (l)$

$I_2 (s) + 2 OH^- (aq) \longrightarrow I^- (aq) + OI^- (aq) + H_2O (l)$

(ii) Hot concentrated Alkali:

Fluorine reacts to form oxygen, fluoride and water.

$2F2 (g) + 4OH^- (aq) \longrightarrow O_2 (g) + 4F^- (aq) + 2 H_2O (l)$

Chlorine, Bromine and Iodine forms the Halide, halate (V) and water.

$3X_2 + 6OH^- (aq) \longrightarrow X^- (aq) + XO_3^- (aq) + 3 H_2O (l)$, X= Cl, Br and I

(c) Hydrogen

Fluorine explodes in dry hydrogen even in the dark to form hydrogen fluoride.

$F_2 (g) + H_2 (g) \longrightarrow 2HF (g)$

Chlorine reacts vigorously with hydrogen in presence of sunlight or ultraviolet light to form hydrogen chlorine.

$$Cl_2\,(g) + H_2\,(g) \longrightarrow 2HCl\,(g)$$

Bromine reacts with hydrogen gas at 200°C in presence of platinum catalyst.

$$Br_2\,(l) + H_2(g) \xrightarrow{Pt/\ 200^oC} 2HBr\,(g)$$

Iodine reacts with hydrogen at 400°C to hydrogen iodide and the reaction is reversible.

$$I_2\,(s) + H_2\,(g) \overset{Pt/\ 400^oC}{\rightleftharpoons} 2HI\,(g)$$

(d) metals

Chlorine, Bromine and Iodine Oxidize:

(i) Tin (II) to Tin (IV)

$$Sn^{2+}\,(aq) + Cl_2\,(g) \longrightarrow Sn^{4+}\,(aq) + 2\,Cl^-\,(aq)$$

(ii) Hydrogen sulphide to Sulphur

$$I_2\,(s) + H_2S\,(g) \longrightarrow 2HI\,(g) + S\,(s)$$

$$Br_2\,(l) + H_2S\,(g) \longrightarrow 2HBr\,(g) + S\,(s)$$

(iii) Thiosulphate ions to different products:

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

$$S_2O_3^{2-}\,(aq)\ \ Cl_2\,(g) + H_2O\,(l) \longrightarrow SO_4^{2-}\,(aq) + S\,(s) + 2\,Cl^-(aq) + 2\,H^+\,(aq)$$

$$S_2O_3^{2-}\,(aq) + 4Cl_2\,(g) + 5H_2O\,(l) \longrightarrow 2SO_4^{2-}\,(aq) + 10H^+\,(aq) + 8\,Cl^-\,(aq)$$

(In excess Cl_2)

COMPOUNDS OF GROUP 17 ELEMENTS (HALOGENS)

(a) Hydrides/ Halogen acids

	HF	**HCl**	**HBr**	**HI**
Bond Energy ($KJmol^{-1}$)	556	431	336	229
Boiling point (^oC)	+19.9	-85	-66.7	-35.4

Boiling point

The boiling point increases from HCl to HI. This is because they are simple molecules held by van der -waals forces of attractions whose magnitude increases with increase in molecular mass. However, HF has extremely high boiling point because the molecules associate by hydrogen bonding due to small ionic radius of the fluoride ions. The small ionic radius of fluoride (F^-) allows for strong attraction between the hydrogen atom in HF and the fluoride ion. This strong attraction leads to formation of hydrogen bonds which are strong.

Bond energy

It decreases from HF to HI due to:

- Increased atomic radius which increases the bond length
- Decrease in electronegativity down the group thus the bonds become less polar.

Acidic Strength

The acid strength depends on the degree of dissociation of the acid thus the concentration of the hydrogen ion in aqueous solution.

Since electronegativity decreases down the group due to increase in atomic radius therefore the bond strength is in the order HF > HCl > HBr > HI thus HF is H-F bond is not easily broken hence it does not easily release a proton in aqueous solution thus it is the weakest acid. The H-I bond is the weakest bond therefore in aqueous solution it easily releases a proton, hence it is the strongest acid.

HF slightly ionizes in dilute solution as:

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

N.B. When concentrated, HF is a weaker acid than in dilute solution due to hydrogen bonding which reduces the concentration of hydrogen ions. i.e.

$$2HF(aq) \rightleftharpoons H^+(aq) + HF_2^-(aq)$$

REACTIONS OF HALOGEN ACIDS

- In aqueous solutions, they behave as strong acids except HF e.g.

$2HBr (aq) + Mg (s) \longrightarrow MgBr_2 (aq) + H_2 (g)$

i.e. Liberates hydrogen gas when reacted with electropositive metals.

- HF and HCl don't react with concentrated sulphuric acid. HBr and HI are strong reducing agents therefore are oxidized to bromine and iodine by conc. Sulphuric acid. i.e.

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

- However, Conc. Hydrochloric acid can be oxidized by the stronger oxidizing agents such as MnO2 , PbO2 and KMnO4

$MnO_2 (s) + 4HCl (aq) \longrightarrow Cl_2 (g) + 2H_2O (l) + MnCl_2 (aq)$

$PbO_2 (s) + 4HCl (aq) \longrightarrow Cl_2 (g) + 2H_2O (l) + PbCl_2 (aq)$

$2MnO_4^- (aq) + 10 Cl^- (aq) + 16H^+ (aq) \longrightarrow 5Cl_2 (g) + 8H_2O (l) + 2Mn^{2+} (aq)$

N.B. Hydroiodic acid (acidified Potassium Iodide) is the strongest reducing agent thus it is easily oxidized.

Hydrofluoric acid reacts with silicon (IV) Oxide to form Hexafluoro silicic acid

$6HF (aq) + SiO_2 (s) \longrightarrow H_2SiF_6 (aq) + 2H_2O (l)$

(b) Oxo- acids / ions

All halogens except fluorine form oxo-ions and oxo-acids e.g. Hypochlorous acid, HOCl, Chlorous acid, $HClO_2$, Chloric acid, $HClO_3$ and Perchloric acid, $HClO_4$

Acid Strength

The acidic strength depends on the number of oxygen atoms in the acid molecule. Since oxygen is more electronegative than chlorine, it pulls the bonding electrons towards itself and this negative inductive effect is transmitted to the O-H bond weakening it thus hydrogen ions are released in solution. The greater the number of oxygen atom, the greater the effect and the weaker the O-H bond. Thus the strength of the acid is in the order of;

$HClO_4 > HClO_3 > HClO_2 > HClO$

Chloric (I) acid is obtained by bubbling chlorine through water.

Cl2 (g) + H2O (l) $\longrightarrow$ HOCl (aq) + HCl (aq)

Chlorate (I) salts are obtained when chlorine gas is bubbled through dilute alkali solution.

$$Cl2\ (g) + 2OH^{-}\ (aq) \longrightarrow OCl^{-}\ (aq) + Cl^{-}\ (aq) + H2O\ (l)$$

Aqueous solutions of Chlorate (I) disproportionate at about 75°C to form Chlorate (V) and Chloride.

$$3OCl^{-}\ (aq) \longrightarrow ClO3^{-}\ (aq) + 2Cl^{-}\ (aq)$$

They decompose in presence of sunlight to form oxygen and a chloride

$$2OCl^{-}\ (aq) \longrightarrow O2\ (g) + 2Cl^{-}\ (aq)$$

However, in presence of an acid chlorate (I) ions act as oxidizing agent e.g. it oxidizes iodide ions to iodine

$$2H^{+}\ (aq) + I^{-}\ (aq) + OCl^{-}\ (aq) \longrightarrow I2\ (aq) + Cl^{-}\ (aq) + H2O(l)$$

With concentrated Hydrochloric acid, Chlorate (I) ions liberate chlorine gas

$$ClO^{-}\ (aq) + 2H^{+}\ (aq) + Cl^{-}\ (aq) \longrightarrow Cl_2\ (g) + H_2O\ (l)$$

N.B.

The reaction above is used to determine the percentage of chlorine in bleaching agent.

A disproportionation reaction is a specific type of redox reaction in which a single substance is both oxidized and reduced resulting in the formation of two different products from one reactant.

Chloric (V) acid

This is a powerful oxidizing agent that only occurs in aqueous solution. Its salts are more stable and can be obtained by passing chlorine gas through hot Conc. Alkali.

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

The Chlorate(V) and Chloride are separated by fractional crystallization.

In Acidic medium, Chlorate (V) ions are strong Oxidizing Agents and the reduction half-cell equation is as below.

$$ClO_3^{-}\ (aq) + 6H^{+}\ (aq) + 6e \longrightarrow Cl^{-}\ (aq) + 3H_2O\ (l)$$

It oxidizes Iron (II) to Iron (III), Sulphite ions to Sulphate ions and Iodide ions to Iodine.

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

$$ClO_3^{-}\ (aq) + 3SO_3^{2-}\ (aq) \longrightarrow 3SO_4^{2-}\ (aq) + Cl^{-}\ (aq)$$

$$ClO_3^{-}\ (aq) + 6H^{+}\ (aq) + 6I^{-}\ (aq) \longrightarrow 3I_2\ (aq) + 3H_2O\ (l) + Cl^{-}\ (aq)$$

QUALITATIVE ANALYSIS OF Cl^-, Br^- and I^-

Test for Chlorides, Bromides and Iodides ions

1) Use of silver nitrate solution

Procedure

To the solution containing the unknown anion is added silver nitrate solution.

Observation

a) In the case of chloride ions, a white silver chloride is formed. The precipitate dissolves in excess aqueous ammonia due to the formation of a soluble complex called diammine silver (I) ions.

Equation

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)}$$

white precipitate.

$$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow Ag(NH_3)^{2+}_{(aq)} + Cl^{-}_{(aq)}$$

Soluble complex.

b) In the presence of bromide ions a pale yellow precipitate of silver bromide is formed. The precipitate dissolves in excess aqueous ammonia due to the formation of a soluble complex.

Equation

$$Ag^{+}_{(aq)} + Br^{-}_{(aq)} \longrightarrow AgBr_{(s)}$$

pale yellow precipitate.

$$AgBr_{(s)} + 2NH_{3(aq)} \longrightarrow Ag(NH_3)^{2+}_{(aq)} + Br^{-}_{(aq)}$$

Soluble complex.

c) In the presence of iodide ions, a yellow precipitate of silver iodide is formed. The precipitate is insoluble in excess aqueous ammonia.

Equation

$$Ag^{+}_{(aq)} + I^{-}_{(aq)} \longrightarrow AgI_{(s)}$$

yellow precipitate.

2) Use of lead (II) nitrate or lead (II) ethanoate solution.

Procedure

To the solution containing the unknown anion is added lead (II) nitrate or lead (II) ethanoate solution.

Observation

a) In the presence of chloride ions a white precipitate of lead (II) is formed. The precipitate dissolves on heating but reappears on cooling.

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

b) In the presence of bromide ions a white precipitate of lead (II) is formed. The precipitate dissolves on warming but reappears on cooling

$$Pb^{2+}_{(aq)} + 2Br^{-}_{(aq)} \longrightarrow PbBr_{2(s)}$$

c) In the presence of iodide ions a pale yellow precipitate of lead (II) iodide is formed. The precipitate dissolves on warming but reappears on cooling

$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$

3) Use of chlorine water and tetra chloromethane

Procedure

To the solution containing the unknown anion is added Chlorine water followed by 2-3 drops of tetra chloromethane

Observation

a) In the presence of chloride ions, there is no observable change.

b) In the presence of bromide ions, a brown colour appears in the organic liquid.

c) In the presence of iodide ions, a purple/violet colour appears in the organic liquid.

4) Use of concentrated sulphuric acid

Procedure

To a few grams of the solid containing the unknown anion is added concentrated sulphuric acid.

Observation

a) In the presence of chloride ions, hydrogen chloride gas is evolved (white fumes).

b) In the presence of bromide ions, bromine gas (brown) and hydrogen bromide gas is evolved.

c) In the presence of iodide ions, iodine vapour (purple) and hydrogen iodide gas is evolved.

5) Use of copper (II) sulphate solution

Procedure

When the reagent is added to a solution containing iodide ions, a white precipitate of copper (I) iodide and a brown solution of iodine is formed.

Equation

$Cu^{2+}(aq) + 2I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(aq)$

APPLICATIONS OF HALOGENS AND THEIR COMPOUNDS

Fluorine

Applications

- Fluorinated Compounds are used in the production of Teflon (non-stick cookware) and refrigerants (e.g., HFCs).
- Fluoride is added to toothpaste and drinking water to prevent tooth decay.

Advantages

- Enhances dental health.

- Provides non-stick surfaces and efficient refrigeration.

Environmental Concerns

- Some fluorinated gases are potential greenhouse gases and can contribute to ozone depletion.
- Overexposure to fluoride can lead to dental fluorosis.

Chlorine

Applications

- Used in water treatment to disinfect drinking water and swimming pools.
- It is a common bleaching agents used in household bleach and paper production.
- Chlorine is essential in making polyvinyl chloride (PVC), used in plumbing and construction.

Advantages

- Effective in killing harmful pathogens in water.
- Widely used in the production of various consumer goods.

Environmental Concerns

- Chlorine can form harmful byproducts (e.g., trihalomethanes) in drinking water.
- Chlorinated compounds can contribute to environmental pollution and bioaccumulation.

Bromine

Applications

- Used in plastics and textiles to reduce flammability.
- Some bromine compounds are used in agricultural pesticides.
- Used in some swimming pool as disinfectants.

Advantages

- Enhances safety by reducing fire hazards.
- Effective in controlling pests.

Environmental Concerns

- Some brominated flame retardants are persistent in the environment and can accumulate in living organisms.
- Potential health risks associated with exposure to bromine compounds.

Iodine

Applications

- Iodine is essential for thyroid function and is added to table salt (iodized salt) nutritional supplement.
- Used in medical disinfectants (e.g., povidone-iodine).
- Iodine compounds are used in some photographic processes.

Advantages

- Prevents iodine deficiency and related health issues.
- Effective antiseptic properties.

Environmental Concerns

- Excessive iodine can lead to thyroid dysfunction.
- Iodine pollution in water bodies can affect aquatic life.

Astatine

Applications

It has Limited use in targeted alpha-particle cancer therapy due to its radioactivity i.e it is use in medical research.

Advantages

Potential for treating certain types of cancer.

Environmental Concerns

Due to its radioactivity and rarity, astatine has limited environmental impact but poses handling and disposal challenges.