State the reasons for this Unique behaviour.

- It has the smallest atomic radius.
- It has the highest electronegativity value
- ~~It~~ ~~has~~ Carbon does not show inert pair effect.

GROUP (VII) ELEMENTS (HALOGENS)

The general outermost configuration is ns^2np^5

These elements include;

element	Atomic number	colour
F	9	Pale yellow gas
Cl	17	Greenish yellow gas
Br	35	Red liquid
I	53	Black solid

Explain why fluorine and chlorine are gases while Bromine and Iodine are liquid and solid resp. at room temp?

From fluorine to iodine, atomic radius increases, molecular size increases and this increases the magnitude of van der waal's forces of attraction in order $F_2 < Cl_2 < Br_2 < I_2$

∴ The van der waal forces in Bromine and Iodine are stronger and thus molecules are nearer to each other, hence becoming liquids and solid respectively.

Explain why the boiling points/Mpts of halogen increases from Fluorine to Iodine

This is because atomic radius increases from fluorine to Iodine, molecular size increases and this increases the magnitude of Van der waal forces of attraction holding the molecules. Thus more energy is required to break the forces, hence an increase in Bpts

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The table below shows the values of Bond dissociation energies of halogens

Element	F_2	Cl_2	Br_2	I_2
B.D.E ($KJmol^{-1}$)	158.1	242.2	193	151

(a) Differentiate between Bond dissociation energy and Bond energy

- BDE is the heat change that occurs when one mole of a covalent bond is broken down into its (01) constituent gaseous atoms
- Bond energy is the heat change that occurs when one mole of a covalent bond is formed from (01) constituent gaseous atoms.

(b) Explain the trend above in the table.

State the trend: Bond dissociation energy generally decreases from Chlorine to Iodine with fluorine having an abnormally low value.

Explanation: From chlorine to iodine, atomic radius ↑ increases, bond length ↑ increases but bond strength ↓ decreases. resulting into weaker ↓ van der waal forces of attraction holding the molecules, thus less ↓ energy is required to break the bonds.

Fluorine has an abnormally low value of BDE because fluorine has the smallest ↓ atomic ↓ radius and highly electronegative ↑ hence requiring low amount of energy to be broken.

Explain why tin(IV) chloride exists but tin(IV) bromide and tin(IV) iodide donot exist. (03mks)

Bromide and iodide ions have a larger ionic radius than the chloride ion, and are stronger reducing agents, hence they reduce tin(IV) ions to tin(II) ions and themselves are oxidised to bromine and iodine respectively.

Chloride ions can not reduce tin(IV) ions. (03)

$$Sn^{4+}_{(aq)} + 2Br^-_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + Br_{2(l)}$$

Also $$Sn^{4+}_{(aq)} + 2I^-_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + I_{2(s)}$$

METHODS OF PREPARATION OF HALOGENS.

All halogens apart from fluorine are prepared by heating a solid halide salt with concentrated sulphuric acid in presence of manganese(IV) oxide

$$2X^-_{(aq)} + 4H^+_{(aq)} + MnO_{2(s)} \longrightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)} + X_{2(g)}$$

(1½)

$X = Cl, Br, I$

Note Fluorine can be prepared by electrolysis of hydrogen fluoride to which potassium fluoride is added to increase conductivity.

At Anode; $2F^-_{(aq)} \longrightarrow F_{2(g)} + 2e$.

CHEMICAL PROPERTIES.

(a) With water

Fluorine vigorously reacts with water to form oxygen and hydrofluoric acid

$$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow O_{2(g)} + 4HF_{(aq)}$$

Chlorine moderately reacts with water to form chloric(I) acid and hydrochloric acid. – disproportionate rxn

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + HCl_{(aq)}$$

Bromine moderately reacts with water forming bromic(I) acid and hydrobromic acid. disproportionation reaction.

$$Br_{2(l)} + H_2O_{(l)} \rightleftharpoons HOBr_{(aq)} + HBr_{(aq)}$$

Iodine does not react with water.

Explain why iodine is insoluble in water but soluble in potassium iodide solution (05mks)

Iodine is a non-polar yet water is polar. Intermolecular forces of attraction between individual molecules of water and individual molecules of iodine are stronger than intermolecular forces of attraction between molecules of water and molecules of iodine. When the two are combined, repulsion occurs.

Iodine reacts with potassium iodide to a soluble complex of potassium triiodide.

$$I_{2(aq)} + I^-_{(aq)} \rightleftharpoons I_3^-{}_{(aq)}$$ ✓ 05

OR $I_{2(aq)} + KI_{(aq)} \rightleftharpoons KI_{3(aq)}$.

(b) With cold dilute NaOH solution

Fluorine reacts with cold dilute NaOH solution forming oxygen difluoride, fluoride ions and water.

$$2F_2(g) + 2\bar{O}H(aq) \longrightarrow OF_2(g) + 2F^-(aq) + H_2O(l)$$

Chlorine disproportionates in cold dilute sodium hydroxide solution forming chlorate(I) ions, chloride ions and water.

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

For $X_2(l)$ / $X_2(s)$:

$$X_2 + 2\bar{O}H(aq) \longrightarrow X^-(aq) + X\bar{O}(aq) + H_2O(l)$$

$X = Br$, or I

With hot concentrated NaOH solution

$$F_2(g) + 4\bar{O}H(aq) \longrightarrow 4F^-(aq) + O_2(g) + H_2O(l)$$

Chlorine, Bromine and iodine react with hot concentrated sodium hydroxide solution forming corresponding halides, halates and water

$$3X_2(g) + 6\bar{O}H(aq) \longrightarrow 5X^-(aq) + XO_3^-(aq) + 3H_2O(l)$$

X is Cl or Br or I

Sample Question

Qn; Chlorine was bubbled through potassium manganate(VI) solution. State what was observed

Green solution turns to a purple solution.

$$2MnO_4^{2-}(aq) + Cl_2(g) \longrightarrow 2MnO_4^-(aq) + 2Cl^-(aq)$$

(green) (purple)

Chlorine is an oxidising agent in this case.

(c) Reaction with hydrogen.

$F_{2(g)} + H_{2(g)} \longrightarrow 2HF_{(l)}$

$Cl_{2(g)} + H_{2(g)} \longrightarrow 2HCl_{(g)}$ — on heating

$Br_{2(l)} + H_{2(g)} \longrightarrow 2HBr_{(g)}$ — on heating

$I_{2(s)} + H_{2(g)} \longrightarrow 2HI_{(g)}$ — On heating.

HYDRIDES OF GROUP (VII)

HF (liquid), HCl (gas), HBr (gas), HI (gas).

Explain why hydrogen fluoride is a liquid at 19°C whereas hydrogen bromide is a gas at the same temperature.

Fluorine is more electronegative than bromine atom. The fluoride ion in hydrogen fluoride has a smaller ionic radius than the bromide ion in Hydrogen bromide. This makes the hydrogen–fluorine bond more polar than Hydrogen–bromine bond. Molecules of Hydrogen fluoride are held together by Stronger Intermolecular hydrogen bonds while molecules of Hydrogen bromide are held by weak van der Waal's forces of attraction that keep the molecules apart.

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METHODS OF PREPARATION OF THE HYDRIDES.

(a) Reaction between Concentrated sulphuric acid and halide salts

For HF; $CaF_{2(s)} + H_2SO_{4(l)} \xrightarrow{\text{(Cold Conc.)}} CaSO_{4(aq)} + 2HF_{(g)}$

For HCl; $NaCl_{(s)} + H_2SO_{4(l)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)}$

Note; HBr and HI can not be prepared by above method because they are stronger reducing agents than HCl. hence can reduce sulphuric acid to sulphur dioxide and they are oxidised to bromine and iodine respectively

eg $HBr_{(g)} + H_2SO_{4(l)} \longrightarrow Br_{2(g)} + SO_{2(g)} + 2H_2O_{(l)}$

(b). Direct combination of the elements with hydrogen.

$F_{2(g)} + H_{2(g)} \longrightarrow 2HF_{(g)}$

$Cl_{2(g)} + H_{2(g)} \longrightarrow 2HCl_{(g)}$

$Br_{2(l)} + H_{2(g)} \longrightarrow 2HBr_{(g)}$

$I_{2(s)} + H_{2(g)} \longrightarrow 2HI_{(g)}$

(c) $PX_{3(s)} + 3H_2O_{(l)} \longrightarrow 3HX_{(l)} + H_3PO_{3(aq)}$ (X is Br or I)

BOILING POINTS / MELTING POINTS OF THE HYDRIDES

Hydride	HF	HCl	HBr	HI
Boiling point (°C)	+19.9	−85.0	−66.7	−35.4

Expla State the trend in Boiling points of the hydrides

Boiling points generally increase from Hydrogen fluoride to hydrogen iodide (01)

Explain the variation.

The increase in boiling point from hydrogen chloride to hydrogen iodide is because these have simple molecular structures held together by weak van der Waal's forces whose magnitude increases with the increase in molecular size. Thus more energy is required to break the stronger forces.

Hydrogen fluoride has an abnormally high melting point because the fluorine atom has a very high (highest) electronegativity value, the fluoride ion has the smallest ionic radius. This makes the hydrogen-fluorine bond highly polar, and thus molecules of hydrogen fluoride are held by strong intermolecular hydrogen bonds that require high energy to be broken hence a very high amount of energy to break. (05)

Similar question;

Explain why hydrogen fluoride has a higher boiling point than hydrogen iodide.

(Hydrogen bonding; Van der Waal forces)

The fluorine atom is more electronegative than iodine atom. Also, the fluoride ion in hydrogen fluoride has a smaller ionic radius than the iodide ion in hydrogen bromide.

This makes the hydrogen-fluorine bond more polar than the hydrogen-bromine bond.

Molecules of hydrogen fluoride are held together by stronger intermolecular hydrogen bonds that require high amount of energy to be broken, hence higher Boiling point.

Molecules of hydrogen iodide are held by weak Van der waal forces of attraction that require less energy to be broken, hence a lower Boiling point.

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ALTERNATIVE Y

Explain why the thermal stability of the hydrides of group (VII) decreases in the order HF > HCl > HBr > HI

This is because the atomic radius of the halogen atoms increases from fluorine to iodine. This makes the hydrogen–halogen bond length longer, reducing the bond strength, thus less energy is required to break the bond.

ACID STRENGTH.

Hydride	HF	HCl	HBr	HI
Ka Value at 25°C ($mol dm^{-3}$)	6.6×10^{-4}	1.3×10^{6}	1×10^{9}	3.2×10^{9}

(a) State the trend in acid strength of the hydrides. (01)

⇒ The acid strength increases in the order HF < HCl < HBr < HI

(b) Explain the trend

This is because ionic radius of the halide ions increase from fluoride to iodide ion. This makes the hydrogen–halogen bond length longer, decreasing the bond strength from hydrogen fluoride to hydrogen iodide, releasing many hydrogen ions in solution hence acid strength increases.

Explain why hydrofluoric acid is a weaker acid than hydroiodic acid.

The fluorine atom is more electronegative than the iodine atom, and the fluoride ion in hydrofluoric acid has a smaller ionic radius than the iodide ion in the hydroiodic acid. The hydrogen–fluorine bond is shorter, more polar and stronger than hydrogen–iodine bond in hydroiodic acid and not as easily broken to release hydrogen ions

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Explain why hydrofluoric acid is a weak acid in dilute solution but a strong acid in concentrated solutions.

The fluorine atom in hydrogen fluoride is highly electronegative. The fluoride ion in hydrogen fluoride has a very small ionic radius. This makes the hydrogen fluorine bond highly polar and very strong.

In dilute solution:

When dissolved in water, the hydrofluoric acid formed partially ionises releasing few hydrogen ions, hence a weak acid.

$$HF_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$$

In concentrated solution:

In concentrated solution, the fluoride ions released react with hydrofluoric acid to form hydrogen difluoride ion

$$HF_{(l)} + F^-_{(aq)} \rightleftharpoons HF_2^-{}_{(aq)}$$

This reduces the concentration of fluoride ions at equilibrium. The equilibrium shifts from left to right as more hydrogen fluoride dissociates releasing more hydrogen ions increasing the acid strength.

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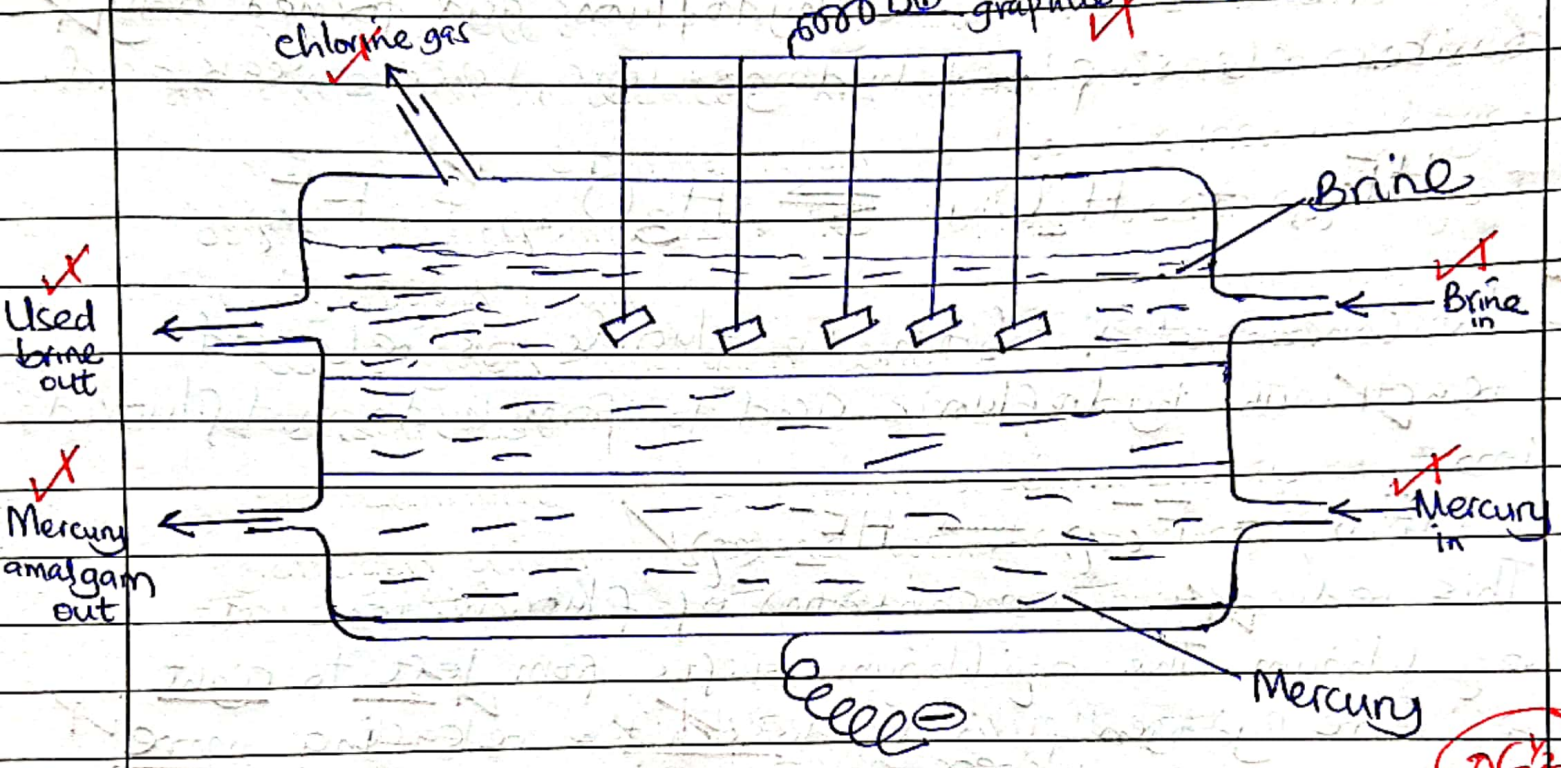
INDUSTRIAL MANUFACTURE OF CHLORINE GAS.

(a) Using Mercury Cathode cell.

Chlorine is manufactured by electrolysis of Concentrated Sodium chloride solution (Brine) using graphite anode and mercury cathode in a mercury cathode cell.



06½

At Anode

- Chloride and hydroxide ions migrate to the Anode and chloride ions are preferentially discharged to form chlorine gas.

$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e$

~~$2Cl^-_{(aq)} \longrightarrow$~~

Note

Sodium hydroxide can be prepared on a large scale by the above method

At Anode; $Na^+_{(aq)} + e \longrightarrow Na_{(s)}$

The Sodium then mixes the mercury cathode forming Sodium amalgam

$Na_{(s)} + Hg_{(l)} \longrightarrow Na\text{-}Hg_{(s)}$

The sodium amalgam reacts with water to form Sodium hydroxide solution

$Na\text{-}Hg_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + \frac{1}{2}H_{2(g)} + Hg_{(l)}$

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OXIDATION REACTIONS.

a) With H_2S

$$H_2S_{(g)} + Cl_{2(g)} \longrightarrow S_{(s)} + 2HCl_{(g)}$$

b) With Fe^{2+} ions

$$2Fe^{2+}_{(aq)} + Cl_{2(g)} \longrightarrow Fe^{3+}_{(aq)} + 2Cl^-_{(aq)}$$

(c) Sulphur dioxide in the presence of water or Sulphite ions.

$$SO_3^{2-}_{(aq)} + H_2O_{(l)} + Cl_{2(g)} \longrightarrow SO_4^{2-}_{(aq)} + 2H^+_{(aq)} + 2Cl^-_{(aq)}$$

(d) ~~Oxidation of thiosulphate~~

~~Limited~~ ~~chlorine~~ or ~~Bromine~~ ~~oxidises~~ ~~thiosulphate~~ ~~ions~~ partially to ~~sulphate ion~~

OXIDES AND OXY-ACIDS.

(a) Dichlorine oxide

$$Cl_2O_{(g)} + H_2O_{(l)} \rightleftharpoons 2HOCl_{(aq)}$$

(Yellow gas)

b) Chlorine dioxide

$$ClO_{2(g)} + H_2O_{(l)} \rightleftharpoons HClO_{3(aq)} + HClO_{2(aq)}$$

(Red gas)

c) Dichlorine heptaoxide

$$Cl_2O_{7(g)} + H_2O_{(l)} \longrightarrow 2HClO_{4(aq)}$$

The acids, HOCl, $HClO_2$, $HClO_3$ and $HClO_4$ are called oxyacids of chlorine.

ACID STRENGTH OF OXY-ACIDS.

The acid strength increases in order $HOCl < HClO_2 < HClO_3 < HClO_4$

This is due to the increase in the number of oxygen atoms bonded directly to the chlorine atom.

Oxygen is more electronegative than Chlorine, thus it withdraws electrons away from the chlorine atom in an oxy-acid molecule. This withdraw is transfered through the Chlorine atom to the Oxygen-hydrogen bond which increases the partial positive charge on the hydrogen atom

The Oxygen-hydrogen bond weakens and a proton is easily lost.

The magnitude of the partial positive charge on the hydrogen atom increases with the number of oxygen atoms attached to the chlorine atom.

UNIQUE BEHAVIOUR OF FLUORINE

Why fluorine differs from the rest of group (VII) members.

- It has a ~~very small~~ smallest atomic radius.
- It has the highest electronegativity..
- Lowest bond energy.

Ways in which fluorine differs from the rest of group (VII)

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5 ways in which fluorine differs from the rest of group (VII) members.

- Fluorine reacts directly with Carbon while other members in the group don't
- Fluorine oxidises water to Oxygen and hydrogen fluoride whereas chlorine and bromine form a mixture of hypohalous and hydrohalic acids and iodine does not react with water
- Fluorine reacts with hot concentrated alkalis to form Oxygen, fluorides and water while other elements in the group form halides, halates and water
- Fluorine doesnot form oxyacids while other halogens do.
- Hydrogen fluoride is a weak acid while other hydrogen halides are strong acids
- Hydrogen fluoride is a liquid at room temp while other hydrogen halides are gases.
- Fluorine has only one oxidation state while other halogens have more than one.

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KIBUGO DENNIS