GROUP VII ELEMENTS CHALOGENS

Elements	Atomic No.	Electronic configuration	M.P/^{0}C	M.P/^{0}C	Electronegative E.N	A.R
Fluorine	9	$1S^2\ 2S^2\ 2P^5$	-223	-187.9	4	1.36
Chlorine	17	$1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^5$	-108	-34.06	3	1.86
Bromine	35	$1S^2 2S^2 2P^6 3S^2 3P^6 4S^2 3d^{10} 4P^5$	-73	58.8	2.8	1.95
Iodine	53	$nS2nP^7$		154.5	2.5	2.16

CHEMICAL PROPERRTIES OF GROUP VII ELEMENTS.

All the elements have 7 electrons in the outer most shells/nS^2 and nP^5 where n is the quantum No.

All the elements exist as diatomic moleculas i.e F_2, Cl_2, Br_2 and I_2 they form covalent bonds with themselves.

F_2 F——F

Cl_2 Cl——Cl

Their MPs and B.Ps increase down the group.

Explanation:

The simple molecules of the halogens are held together by weak van-der-waal forces. The size of van-der-waal forces increases with increase in the molecular mass down the group. The individual simple molecules are strongly held together down the group.

Fluorine and Chlorine are gases at room temperature. Bromine is liquid at room temp and iodine is solid at room temperature.

The electronegativity of group VII elements decreases down the group

The electron affinity of group VII elements decreases down the group but that of fluorine is abnormally low.

Question.

Briefly explain why fluorine shows some differences in its properties from the rest of other elements.

- ✓ Fluorine has least atomic radius giving
- ✓ Its more electronegative compared to the rest of other element, also
- ✓ Has low F - F bond dissociation energy because of repulsion between/one pair of electrons on fluoride atoms which closely approach @ other.
- ✓ It also forms strong covalent bonds with other non-metals.
- ✓ Its hydration energy is very high because of high charge density on fluoride ion.
- ✓ High lattice energy with cations due to its high charge density.
- ✓ It lacks empty d orbitals hence cannot expand its octate rule therefore its valency is restricted to -1 while for the rest of other elements they can expand their octate rule thus have a max. valency of $^{+}7$.

<u>To show that fluorine's chemical is different from that of other elements of group VII</u>;

1. Hydrogen fluoride is a weaker acid than hydrogen chloride in aqueous solution.
2. Hydrogen fluoride covalent bond is stronger than hydrogen chloride covalent bond.
3. Fluorine is a more oxidizing agent than chlorine.

CHEMICAL PROPERTIES OF HALOGENS

1. <u>REACTION WITH WATER</u>

Fluorine reacts vigorously with water and is reduced to hydrogen fluoride with oxidation of water to oxygen.

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

Fluorine is a stronger oxidizing agent compared to rest of other elements.

Chlorine reacts moderately with water to form hypochlous acid and hydrochloric

Chlorine water

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

When chlorine water is exposed to sunlight, it decomposes to release bubbles of class gas which rekindles a glowing splint.

$$2HOCl_{(aq)} \xrightarrow{\text{sunlight}} 2HCl_{(aq)} + O_{2(g)}$$

Overall eqn; $2Cl_{(g)} + 2H_2O_{(g)} \xrightarrow{\text{sunlight}} 4HCl_{(aq)} + O_{2(g)}$

Bromine reacts moderately with water to form hypobromous acid and hypobromic acid.

$$Br_{2(s)} + H_2O_{(l)} \longrightarrow HBr_{(g)} + HOBr$$

The mixture of HOBr and HBr is called bromine water.

Hypobromide ion from hypobromous acid under goes disproportionation reaction.

NB. (Disproportionation reaction is spontaneous self oxidation reduction (redxn) leading to the formation of two species with different oxidation states.

$$3\bar{O}Br_{(aq)} \rightleftharpoons 2\bar{Br}_{(aq)} + Br\bar{O}_{3(aq)}$$

Iodine is sparingly soluble in water but more soluble in KI solution.

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

Or

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

This is because it forms a stable complex called potassium trio iodide.

Question:

Briefly explain why iodine is more soluble in KI than in water.

Iodine molecule is a non- polar molecule with greater (strong) van-der-waal forces between molecules. It cannot associate with water thru' hydrogen bonding. With KI, it forms a stable complex called KI_3. More I_2 dissolves in KI solution than water because ionic equilibrium favours more KI_3 to be formed.

2. REACTION WITH ALKALI
   a) Dilute Alkali solution (dilute NaOH (aq)

- Fluorine reacts with dilute NaOH to form Oxygen di-fluoride and Fluoride ions.

Eqn. $2F_{2\,(g)} + 2\bar{O}H_{(aq)} \longrightarrow OF_{2\,(g)} + 2F^-_{(aq)} + H_2O_{(l)}$

$2F_{2\,(g)} + NaOH_{(aq)} \longrightarrow OF_{2\,(g)} + NaF_{(aq)} + H_2O_{(l)}$

- Chlorine/bromine and iodine react with dilute sodium hydroxide to form sodium hypohalide and halide ion.

$Cl_{2\,(g)} + 2\bar{O}H_{(aq)} \longrightarrow OCl^-_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$

e.g Chlorine reacts with NaOH (dilute) to form sodium hypochloride and chloride.

for Bromine $Br_{2\,(l)} + 2\bar{O}H_{(aq)} \longrightarrow OBr^-_{(aq)} + Br^-_{(aq)} + H_2O_{(l)}$

Iodine $I_{2\,(s)} + 2\bar{O}H_{(aq)} \longrightarrow OI^-_{(aq)} + I^-_{(aq)} + H_2O_{(l)}$

NB. OBr and OI can undergo disproportionation reaction

b) Hot concentrated alkali (hot conc NaOH)

- Fluorine reacts with hot conc NaOH to form oxygen, fluorine ion and water,

$2F_{2(g)} + 4OH_{(aq)} \longrightarrow 4F^-_{(aq)} + O_{2(g)} + 2H_2O_{(l)}$

- Chlorine, Bromine and iodine react with hot conc NaOH to form halate ions, halide ions and water. e.g Cl_2 reacts with hot conc NaOH to form sodium chlorate, sodium chloride and water

$3Cl_{2(g)} + 6\bar{O}H_{(aq)} \longrightarrow ClO_3^-{}_{(aq)} + 5Cl^-_{(aq)} + 3H_2O_{(l)}$

For Br_2, $3Br_{2(g)} + 6\bar{O}H_{(aq)} \longrightarrow BrO_3^-{}_{(aq)} + 5Br^- + 3H_2O_{(l)}$

Br_2 reacts with hot conc NaOH to form sodium bromate sodium bromide and water as in the equation above. Iodine reacts with hot conc NaOH to form sodium iodate, sodium iodide and water.

Question.

(a) Write the equations to compare the reaction of fluorine and bromine when they react separately with.

(i) Water

(ii) Cold dilute sodium hydroxide.

(iii) Hot concentrated sodium hydroxide.

(b) Compare the oxidizing power of fluorine and iodine using their reaction with water.

3. REACTION WITH HYDROGEN:

Fluorine reacts vigorously with hydrogen even in absence of sunlight,

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

Chlorine reacts with hydrogen in the presence of sunlight.

$$Cl_{2(g)} + H_{2(g)} \xrightarrow{\text{sun light}} 2HCl_{(g)}$$

Bromine reacts with hydrogen which is heated in the presence of platinum catalyst to form hydrogen bromide.

$$Br_{2}^{-}{}_{(l)} + H_{2(g)} \xrightarrow[200^0C]{Pt} 2HBr_{(g)}$$

Iodine reacts with hydrogen which is heated to over 200^0C and in the presence of Pt catalyst.

$$I_{2(s)} + H_{2(g)} \xrightarrow[>200^0C]{Pt} 2HI_{(l)}$$

4. HALOGENS AS OXIDISING AGENTS

$$Cl_{2(g)} + 2\bar{e} \longrightarrow 2Cl^-_{(g)} \qquad E^{\ominus} = {}^{+}1.36V$$

$$Br_{2(l)} + 2\bar{e} \longrightarrow 2Br^-_{(g)} \qquad E^{\ominus} = {}^{+}1.09V$$

$$I_{2(s)} + 2\bar{e} \longrightarrow 2I^-_{(g)} \qquad E^{\ominus} = {}^{+}0.54V$$

The standard electrode potential of group VII elements decreases down the group.

The tendency of group VII elements to act as oxidizing agents decreases down the group. Fluorine and chlorine are powerful oxidizing agents while iodine is the least oxidizing

i.e F > Cl > Br > I.

5. REACTION OF IRON (II) CHLOIDE WITH CHLORINE

When chlorine gas is bubbled in a solution containing iron (II) ions, (light green solution), Iron (II) ions are oxidized to iron (III) ions (reddish brown solution)

$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e$

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

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

Light green soln. Reddish brown soln.

6. REACTION OF CHLORINE WITH THIOSULPHATE

Chlorine oxidises sodium thiosulphate to sodium sulphate and sulphur and itself is reduced to chloride ion.

1st half oxidation reaction. $4S_2O_3^{2-}{}_{(aq)} \longrightarrow 3SO_4^{2-}{}_{(aq)} + 5S_{(s)} + 2e$

2nd half reaction; $Cl_{2(g)} + 2e \longrightarrow 2Cl^{-}_{(g)}$

Overall reaction; $4S_2O_3^{2-}{}_{(aq)} + Cl2(g) \longrightarrow 3SO_4^{2-}{}_{(aq)} + 5S_{(s)} + 2Cl^{-}_{(aq)}$

<u>Observation</u>: Yellowish green colour of chlorine is oxidized and a colourless solution with yellow solid deposit.

7. REACTION WITH POTASSIUM IODIDE

When chlorine is bubbled in potassium iodide solution, it displace iodine from its compounds because its more reactive than iodine.

$2KI_{\,(aq)} + Cl_{2\,(g)} \longrightarrow 2KCl_{\,(aq)} + I_{2\,(s)}$

Observation: Brown solid deposit in a colourless solution.

COMPOUNDS OF HALOGENS

1. HYDROGEN HALIDES:

Hydrogen halide	B.D.E	Boiling Point
HF	+556	19.9
HCl	+431	-85.0
HBr	+366	-66.7
HI	+299	-54.4

BOILING POINT:

Trend: B.P of hydrogen halides increases down the group but that of hydrogen fluoride is abnormally high.

Explanation: The increase in B.P from hydrogen chloride to hydrogen iodide is due to increase in molecular mass from HCl to HI gas. The strength of van-de-waal forces increases down the group due to increase in molecular mass. The increase in strength of van-der-wall forces down the group increases in strength of van-der-waal forces down the group increases the B.Ps of hydrogen halides down the group.

The B.P of hydrogen fluoride is abnormally high because fluoride ion is more electronegative, can attract bond electrons towards itself acquiring partial –ve charge and +ve partial charge on hydrogen ion. This makes the molecule polar and thus molecules associate by hydrogen bonding. Hydrogen bonding is more stronger than van-der-waals forces hence hydrogen fluoride has higher boiling point.

2. BOND DISSOCIATION ENERGY.

Trend: It decreases down the group.

Explanation: Electronegativity of group VII elements decreases down the group. Fluorine being more electronegative attracts bond electrons towards itself and polarizes it. The tendency of attracting bond electrons towards halogens in hydrogen halides decreases down the group. Fluorine forms the strongest polarized covalent bond followed by chlorine, Bromine and finally iodine.

ACIDIC CHARACTERS OF HYDROGEN HALIDES

Pure hydrogen halides are covalent compounds, non-electrolytes and polar molecules.

When dissolved in water, they dissociate to form free mobile ions.

e.g $HX_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + X^-_{(aq)}$ where X is halogen

i.e $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

The acidity of the solution depends on the concentration of hydrogen ions in aqueous solution.

The degree of ionization/dissociation of hydrogen halides in water depends on the strength of covalent bond.

HX acid	**% of ionization**.
HF	8.5
HCl	86
HBr	93
HI	9.5

Trend: The acidity of hydrogen halides increases down the group i.e HF < HCl < HBr < HI.

Explanation The electronegativity of group VII elements decreases down thee group. Fluorine forms a stronger covalent bond with hydrogen because it is more electronegative. The strength of covalent bond between hydrogen and group VII elements decreases in the order of

HF > HCl > HBr > HI.

In water, hydrogen fluorine slightly ionizes because of the strong covalent bond between hydrogen and fluorine.

The degree of ionization in water increases down the group. Hydrogen iodide dissociates in water to release the highest concentration of hydrogen ions while hydrogen fluoride dissociates in water to release least concentration of hydrogen ions.

Question: *Briefly explain why hydrochloric acid is a stronger acid than hydrofluoric acid.*

Fluorine is more electronegative than chlorine in hydrogen chloride. In solution hydrogen fluoride releases the least concentration of hydrogen ions than hydrogen chloride and thus hydrofluoric acid is weaker than hydrochloric acid because the degree of ionization depends on the strength of covalent bond.

CHEMICAL PROPERTIES OF HYDROGEN HALIDES

1. REACTION WITH HOT CONC H_2SO_4

Hot conc H_2SO_4 cannot oxidize hydrogen fluoride gas because hydrogen fluoride is the stronger oxidizing agent than hot concentrated sulphuric acid.
Hot conc sulphuric acid can slightly oxidize hydrogen chloride gas because chloride in hydrogen chloride gas is less electronegative thus hot conc H_2SO_4 is more oxidizing agent than hydrogen chloride gas.
Hot conc sulphuric acid oxidizes hydrogen bromide and hydrogen iodide rapidly

i.e $2HBr_{(g)} + H_2SO_{4(aq)} \longrightarrow Br_{2(l)} + SO_{2(g)} + 2H_2O_{(l)}$

$2HI_{(g)} + H_2SO_{4(aq)} \longrightarrow I_2(s) + SO_{2(g)} + 2H_2O_{(l)}$

Qn. Briefly explain why hot concentrated H_2SO_4 can oxidize hydrogen iodide but not hydrogen fluoride.

OXO – ACIDS OF HALOGENS

Oxo – acids		**Formular**	**Oxidation state**
1.	Hypochlorous/chloric(I) acid	HOCl	+1
2	Chlorous/chloric (III) acid	$HClO_2$	+3

3	Chloric (V) acid	$HClO_3$	+5
4	Chloric (VII) acid	$HClO_4$	+7

The acidic strength of the oxo-acids increases with the increase in No of oxygen atom

(HOCL < $HClO_2$ < $HClO_3$ <$HClO_4$.

Explanation:

Oxygen is more electronegative than chlorine and withdraws electrons from chlorine towards itself (shows –ve inductive effect). This makes chlorine to acquire partial +v charge and oxygen atom patial –ve. The magnitude of partial +ve charge on chlorine increases with increase in h number of oxygen atoms attached to it. The withdrawal of electrons is communicated thru' chlorine atom to O H bond and this weakens O H covalent bond. The strength of O H bond decreases with increase in No. of oxygen atoms. In aqueous solution, hypochlorous acid releases least concentration of H^+ ions < chloric III acid < chloric V acid < chloric VII.

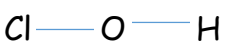
***Question**: Briefly explain why chloric (III) acid is a stronger acid than chloric acid.*

Chloric acid (III) has more oxygen atoms than chloric acid.

Therefore the chlorine atom in chloric acid (III) experiences greater –ve inductive effect than chlorine in chloric acid (I). The O H bond in chloric (III) acid is weakened more than in chloric acid (I) thus in aqueous solution, chloric acid (III) donates more hydrogen ions than chloric (I) acid.

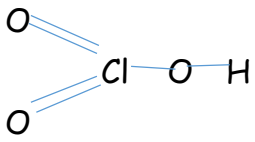
Structures

Chloric I acid:



Chloric (III) acid

Chloric VII acid



Fluorine lacks oxo acids while all other halogens have oxo acids.

Explanation:

Fluorine atom is very small, lacks empty 3d-orbitals hence cannot accommodate/one pair of electrons from oxygen atom. It also cannot expand its octet rule. This restricts its valency to only one. While for the rest of group VII elements. They poses vacant 3d-orbitals for accommodating one pair of electrons from oxygen to have (ligand). They can expand their octet rule in order to have variable oxidation states ranging from $^{+}1$ to $^{+}7$.

USES OF CHLORINE GAS

- Purification of water (use) in water treatment.
- For manufacture of bleaching agents
- For manufacture of organic solvents such as carbon tetra chloromethane.
- For manufacture of sodium chloride salt.

USES OF BROMINE

- Used in manufacture of dyes.
- Used in manufacture of black and white photographic papers and films.

TEST FOR Cl^- Br^- and I^- IONS

1. *Silver nitrate solution/dilute Nitric acid*

   Observation.

   With Cl^-, A white ppts insoluble in the acid.

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

   With Br^-, A pale yellow ppt insoluble in the acid (dilute HNO_3)

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

   With iodide ion, yellow ppt insoluble in dilute Nitric acid.

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

2. *Concentrated sulphuric acid and manganese (IV) oxide.*

   Observation

   With Cl^-;

   Efflorescence with yellowish green gas is given out.

   $Cl^-_{(aq)} + H_2SO_{4(l)} \longrightarrow HCl_{(aq)} + HSO_4^-{}_{(aq)}$

$4HCl_{(aq)} + MnO_{2(s)} \longrightarrow MnCl_{2(aq)} + 2H_2O_{(l)} + Cl_{2(g)}$

With Br^-

Efflorescence with reddish brown gas.

$Br^-_{(aq)} + H_2SO_{4(l)} \longrightarrow HBr_{(aq)} + HSO_4^-{}_{(aq)}$

$4HBr_{(aq)} + MnO_{2(s)} \longrightarrow MnBr_{2(aq)} + 2H_2O_{(l)} + Br_{2(g)}$

With iodide ion,

A dark brown solution is formed.

$I^-_{(aq)} + H_2SO_{4(l)} \longrightarrow HI_{(aq)} + HSO_4^-{}_{(aq)}$

$4HI_{(aq)} + MnO_{2(s)} \longrightarrow MnI_{2(aq)} + 2H_2O_{(l)} + I_{2(aq)}$

3. *Lead (II) nitrate solution, then warming.*

Observation.

With Cl-

A white ppt soluble on warming and precipitates on cooling.

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

With Br-

A pale yellow ppt soluble on warming and precipitates on cooling.

$Pb_2^+{}_{(aq)} + 2Br^-_{(aq)} \longrightarrow PbBr_{2(s)}$

A pale yellow ppt.

With Iodine ion

A yellow ppt soluble on warming and precipitates on cooling.

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

Yello ppt

REVISION QUESTIONS.

1. a) State four properties in which fluorine differs from bromine.
   b) State the conditions and write equations for the reaction btn $NaOH_{(aq)}$
   (i) Flourine

(ii) Bromine

c) Compare the oxidizing powers of Fluorine and Bromine using their reaction with water.

2. a) Explain each of the following observations.
   (i) Iodine is more soluble in potassium iodide than water.
   (ii) Hydrobromic acid is a stronger acid than hydroflourine acid.
   (iii) Chloric (v) acid is stronger than chloric (III) acid.
   (iv) The bond dissociation energy of hydrogen halides decreases in the order of HF>HCl>HBr>HI.
   (v) Chlorine is a gas at room temperature while iodine is a solid at room temperature.
   (vi) Hydrogen fluoride has a higher melting point and is a weaker acid than hydrogen chloride.
3. a) Explain why fluorine shows some differences in its properties from the rest of the other group VII elements of periodic table.
   b) State the differences between the chemistry of fluorine and the rest of group VII elements of periodic table.
   c) Write equation to compare the reactions of fluorine and chlorine when they react separately with.
      (i) Water
      (ii) Cold dilute sodium hydroxide solution
      (iii) Hot concentrated sodium hydroxide.
   d) Write equation for the reaction between hydrogen bromide gas and conc sulphuric acid.

4. a) Explain what is meant by disproponation reaction.
   b) Write equation to illustrate disproponation reaction.
   c) Explain why fluorine cannot form FO_3^- while chlorine can form ClO_3^-

5. a) Write equations to show how each of fluorine iodine reacts with.
      i) Water
      ii) Hot conc NaOH solution.

iii) Dilate KOH solution

6. a) Describe industrial manufacture of chlorine gas from concentrated brone.

b) Discus the reaction between elements of group VII in periodic table with

i) Water

ii) Sodium hydroxide solution.

7. a) Describe one general method of preparing the halogens in the laboratory and write an equation for the reaction.

b) Describe the reactivity of fluorine and bromine with.

i) Water

ii) Sodium hydroxide solution.

c) Name the reagent that can be used to distinguish the following pairs of ions.

i) Cl^- and Br^-

ii) Cl^- and I^-

In each case state what would be observed and then equation of reaction.

8. a) Briefly explain why the electronegativity of group VII elements decreases down the group.

SOLUTIONS.

1. a) Fluorine is a gas at room temp while Bromine is a liquid.
Fluorine lacks oxo-acid while bromine has
Hydrofluoric acid is a weaker acid than hydrobromic acid.
Fluorine is a stronger oxidizing agent than Bromine.
Fluorine is more electronegative than bromine

b) i) Fluorine reacts with cold dilute sodium hydroxide solution to form oxygen difluoride, fluoride ion and water.

$2F_{2(g)} + 2\bar{O}H_{(aq)} \longrightarrow OF_{2(g)} + 2F^-_{(aq)} + H_2O_{(l)}$

It also reacts with hot conc NaOH solution to form oxygen fluoride ion and water.

$F_{2(g)} + 4OH_{(aq)} \longrightarrow O_{2(g)} + 2F^-_{(aq)} + 2H_2O_{(l)}$

ii) Bromine reacts with cold dilute NaOH solution as in equation below:

$Br_{2(s)} + 2NaOH_{(aq)} \longrightarrow NaOBr_{(aq)} + NaBr_{(aq)} + H_2O_{(l)}$

Bromine reacts with hot concentrated NaOH solution as in equation below:

$3Br_{2(l)} + 6NaOH_{(aq)} \longrightarrow NaBrO_{3(aq)} + 5NaBr_{(aq)} + 3H_2O_{(l)}$

(b) Fluorine is a stronger oxidizing agent and fully oxidises water to oxygen and itself reduced to hydrogen fluoride.

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

Bromine however is a weak oxidizing agent and partially oxidises water to form a mixture of hypobromous acid and hypobromide acid.

$Br2(g) + H2O(l) \longrightarrow HOBr(aq) + HBr(aq)$

The hypobromide ion in HOBr can under go a disproponation reaction.

$3OBr_{(aq)} \rightleftharpoons 2Br^-_{(aq)} + BrO_3^-{}_{(aq)}$

2. a) (i) Iodine is a non-polar molecule with high molecular weight. It experiences stronger van-des-waals forces, between its atoms and cannot therefore associate with water through hydrogen bonding hence it is less soluble in water.

With potassium iodide, iodine readily dissolve to form a complex, potassium triodide because ionic equilbreium favous more to I_3 to be formed.

ii) The strength of the acid depends on its degree of dissociation which also depends on the strength of covalent bond. Fluorine in hydrofluoric acid has a small atomic radius and high electronegativity. It therefore forms a strong covalent bond which slightly ionizes releasing less concentration of hydrogen ions. Bromine however is less electronegative,

forms a weak covalent bond with hydrogen hence fully ionizes to release high concn of hydrogen ions hence a stronger acid than hydrofluoric acid.

iii) Chloric (v) acid has more oxygen atoms than chloric (III) acid. The chloride atom in chloric (v) acid experiences higher negative inductive effect than in chloric (III) acid thus the O – H bond is weaker in chloric (v) acid compare to chloric (III) acid. Chloric (v) acid thus readily ionizes releasing high concentration of hydrogen ions than chloric (III) acid.

iv) The atomic size of halogen increases down the group and their electronegativity decrease down the group. Fluorine has greatest electronegativity, attracts bond electrons from hydrogen forming a strong polarized covalent bond. Iodine however has least electronegativity forming weak covalent bond with hydrogen. The strength of covalent bond decreases in the order of HF>HCl>HBr>HI and hence bond dissociation energy decreases in the order of HF>HCl>HBr>HI.

v) Chlorine and iodine both exist as diatomic molecules with iodine having higher molecular weight than chlorine, chlorine therefore experienceses very little van-dar-waals forces of attraction hence melts at a low temperature and becomes a gas at room temp. iodine however experiences high van-das-waals forces of attraction and remains solid at room temperature.

(vi) Related to (ii)

3. a) Fluorine has a very small atomic radius giving it a high electronegativity. Also has low F – F bond dissociation energy due to repulsive forces between two florences atoms approaching each other closely. Hence forms complexes unlike other grou VII elements.

Fluorine als lacks empty d-subshell and cannot therefore expand its octate rule hence restricting its valency to only $^{+}1$ unlike other halogens.

b) Fluorine lacks oxo-acids while other halogens have.
Fluorine is a stronger oxidizing agent than all other halogens.
Hydrogluorine acid is a weaker acid than the acids of other elements.
Fluorine has least melting point than the other halogen ions.

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

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

ii) $2F_{2(g)} + 2NaOH_{(aq)} \longrightarrow OF_{2(g)} + 2NaF_{(aq)} + H_2O_{(l)}$

$Cl_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaOCl_{(aq)} + NaCl_{(aq)} + H_2O_{(l)}$

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

$3Cl_{2(g)} + 6NaOH_{(aq)} \longrightarrow NaClO_{3(aq)} + 5NaCl_{(aq)} + 3H_2O_{(l)}$

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

4. a) Disproportionation reaction refers to the self-oxidation – reduction reaction leading to the formation of two different species of different oxidation states.

b) $3\bar{O}HBr_{(aq)} \rightleftharpoons 2Br^-_{(aq)} + BrO_3^-{}_{(aq)}$

$3OI_{(aq)} \rightleftharpoons 2I^-_{(aq)} + IO_3^-{}_{(aq)}$

c) Fluorine has a very small atomic size as compared to chlorine. It therefore lacks empty d subshell and cannot expand its octate rule to accommodate electrons from oxygen hence cannot form FO_3^-. Chlorine however has empty d subshell can expand its octate rule to accommodate electone from oxygen hence forms ClO_3^-

5. Similar to No 3 (c)

No. 7 (c) (i) silver nitrate and hydro dilute nitric acid.
With Cl-, a whilte ppt insoluble in the acid.

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

With Br- a pale yellow ppt insoluble in the acid.

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

(ii) Lead (II) Nitrate solution, then warm.

With Cl^{-}, a white ppt soluble in worming and repplates on cooling.

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

With iodide ions, a yellow ppt soluble on warming and reprecipitates on cooling.

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

No. 8 In moving from one element to another down the group VII, a full energy level is added while a proton is added to the nucleus. Both nuclear charge and screening effect increase down the group but increase in screening effect outweighs increase in nuclear charge because of addition of a whole energy level. Effective nuclear charge decreases down the group. Ability to attract bond electrons towards the atom decreases down the group and therefore electronegativity decreases down the group VII elements.