SELF-ASSESSMENT Chapter # 12

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) The oxidation State of S in $S_2O_3^{-2}$ is:

A. +1 B. +2 C. +3 D. +4

(ii) Despite being the most abundant gas in the Earth's atmosphere, nitrogen does not readily participate in combustion reactions because:

A. It is denser than oxygen.
B. It has a high specific heat capacity.
C. Breaking the N≡N bond requires a large amount of energy.
D. It is a noble gas.

(iii) The shape of ammonium (ion) is:

A. pyramidal B. triangular planar C. tetrahedral D. linear

(iv) Nitrification is the process by which:

A. Atmospheric nitrogen is converted into ammonia.
B. Nitrate is converted into nitrogen gas.
C. Ammonia is converted into nitrite and then nitrate.
D. Organic nitrogen is converted into ammonia.

(v) The most stable species in an acidic environment is:

A. SO_4^{2-} B. SO_2 C. H_2S D. S

(vi) Sulphur trioxide (SO_3) is not directly dissolved in water to produce sulphuric acid in the Contact Process because this reaction is:

A. Too slow.
B. Reversible and would result in a low yield.
C. Highly exothermic and produces a mist of sulphuric acid.
D. Requires very high pressures.

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) If magnesium ribbon is ignited and placed in a jar containing N_2O, it continues to burn brightly. Explain this observation with reason.
(ii) Why N_2 gas is used in food packaging?
(iii) Write down the reduction and oxidation reactions that occur in the catalytic converter in the vehicle exhausts.
(iv) What is the basic principle of catalytic converter? Describe the role of catalyst in the catalytic converter.
(v) Give the reaction of S with NaOH.
(vi) Write down self-ionization equation of sulphuric acid and its ionization in water.

Q.3 Extensive Questions. **(2 × 4 = 8)**

(a) Discuss sulphuric acid as an oxidizing agent and a dehydrating agent with three reactions for each.
(b) How oxides of nitrogen (NO_x) cause the formation of photochemical smog and PAN? Give its mechanism.

Chapter 13 HALOGENS

Student Learning Outcomes

After studying this chapter, students will be able to:

- Describe the colours and the trends in volatility of chlorine, bromine, and iodine. **(Understanding)**
- Describe the trend in bond strength of halogen molecules. **(Understanding)**
- Interpret the volatility of the elements in terms of instantaneous dipole-induced dipole forces. **(Understanding)**
- Describe the relative reactivity of halogen elements as oxidizing agents. **(Understanding)**
- Describe the reactions of elements with hydrogen and explain their relative reactivity in these reactions. **(Understanding)**
- Describe the relative thermal stabilities of hydrogen halides and explain these in terms of bond strength. **(Understanding)**
- Describe the relative reactivity of halide ions as reducing agents. **(Understanding)**
- Explain the reactions of halide ions with aqueous silver nitrate and concentrated sulphuric acid. **(Understanding)**
- Describe the reactions of halides with aqueous silver ions followed by aqueous ammonia. **(Understanding)**
- Interpret the reaction of Chlorine with cold and hot aqueous sodium hydroxide as disproportion reactions. **(Understanding)**
- Explain the use of chlorine in water purification, including the production of the active species HOCl and ClO^- which kill bacteria. **(Understanding)**

Elements present in Group 17 or VIIA of the periodic table are termed as halogens.

- It includes fluorine (F), chlorine (Cℓ), bromine (Br), iodine (I), astatine (At) and tennessine (Ts).
- The halogen elements form a group of very reactive non-metals and are quite similar to each other in their chemical properties.
- First four elements are the common elements of the halogen family but last two astatine (At) and tennessine (Ts) are very rare and radioactive elements.

Physical States of Halogens

- Halogens exist as diatomic molecules (X_2 = F_2, $C\ell_2$, Br_2, I_2) in all phases (gas, liquid or solid).
- **Fluorine (F_2) and chlorine ($C\ell_2$)** are gases of pale yellow and greenish yellow colours respectively at room temperature and pressure.
- **Bromine (Br_2)** is a volatile liquid of reddish-brown colour at room temperature. It has corrosive and toxic fumes.
- **Iodine (I_2)** is shiny greyish black solid at room temperature. It sublimes directly from solid to a violet vapour. The colors of halogens (X_2) darken progressively from chlorine to iodine.

Rock Your Mind!

1. Why I_2 is solid while F_2 is gas?

Rock Your Mind!

2. Which halogen occurs naturally in a positive oxidation state?
(A) Fluorine (F) (B) Chlorine (Cℓ)
(C) Bromine (Br) (D) Iodine (I)

Reason:

The trends of colour changes from chlorine to iodine is due to changes in the absorption of light as a result of electron transitions within the molecules of respective halogens.

Figure: The greenish yellow chlorine (left), orange bromine (middle) and purple iodine (right)

Did You Know?

The name halogen comes from the Greek words "halos", meaning "salt", and "gen", meaning "to make." The first halogen to be isolated and recognized as an element was chlorine. Despite the fact that chlorine is poisonous, small amount is essential to human health and life in the form of chloride.

Table: Atomic and Physical properties of the common halogens.

Element	Fluorine	Chlorine	Bromine	Iodine
Proton number	9	17	35	53
Electron shell structure	2, 7	2, 8, 7	2, 8, 18, 7	2, 8, 18, 18, 7
Outer shell electron configuration	$2s^2 2p^5$	$3s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$
Relative atomic mass	19.0	35.5	79.9	126.9
Physical state at of 20°C	gas	gas	liquid	solid
Colour	pale yellow	pale green	red-brown	dark gray
Melting point/°C	−220	−101	−7	113
Boiling point/°C	−188	−35	59	183
Enthalpy change of vaporization/kJ mol^{-1}	+3.3	+10.2	+15	+30
Solubility /g per 100 g of water at 20°C	reacts readily with water	0.59 (reacts slightly)	3.6	0.018

VOLATILITY OF CHLORINE, BROMINE AND IODINE

- **Chlorine:**
  Chlorine being a liquid is very volatile at room temperature and it disperses quickly in the air.
- **Bromine:**
  Bromine being a liquid is less volatile than chlorine but more volatile than iodine. It evaporates readily releasing toxic fumes at room temperature. Iodine is the least volatile among the three. At room temperature, its solid states show lower volatility as compared to chlorine and bromine. Generally, volatility decreases from chlorine to iodine. This trend is due to the increasing molecular mass, increase in size of outer shell and stronger intermolecular forces (London dispersion forces) as we move down the group in the periodic table.

Rock Your Mind!

3. Which of the following halogens is solid at room temperature?
A) F_2 B) Cl_2
C) Br_2 D) I_2

Interesting Information!

Bromine liquid evaporates easily at room temperatures emitting an orange vapour. Bromine has a very strong and bad odour. It gets its name from the Greek word "bromos" which means "stench."

TREND IN VOLATILITY OF THE HALOGENS

Halogens are non-polar and instantaneous dipole-induced forces play a significant role in determining the volatility of halogens.

- **Factors:**
  - The forces depend on factors like molecular size, shape and polarizability, with stronger forces leading to lower volatility and higher boiling points.
  - Substances with weak id-id forces, smaller and less polarizable molecule have lower boiling points and higher volatility.
  - Larger, more polarizable molecules with stronger London dispersion forces have higher boiling points and lower volatility.
  - Volatility is inversely related to the boiling point of a substance.
  - A more volatile substance will have a lower boiling point.
  - Stronger intermolecular forces require more energy to separate the molecules from the liquid phase to the gaseous phase. A summary is given in Table.

Table: Effect of London forces on physical properties

Size	Polarizability	Instantaneous dipole-induced dipole forces	Boiling Point	Volatility
Small	Small	Weak	Lower	Higher
Large	High	Strong	Higher	Lower

- The first two halogens, i.e., fluorine (colourless or very light green) and chlorine (greenish yellow) are gases due to weaker id-id forces. Bromine is a liquid as its size is bigger and it possesses stronger intermolecular forces than fluorine and chlorine. Iodine has the strongest forces among the group, so it is in solid state at room temperature.

QUICK CHECK 13.1

a) **Which halogens elements are radioactive?**

Ans. Astatine (At) and Tennessine (Ts) are radioactive halogens.
- Astatine is the only naturally occurring radioactive halogen, but it's extremely rare.
- Tennessine is artificially produced and is also radioactive.

b) **What is the reason behind the different colours of halogens?**

Ans. The different colours of halogens are due to:
- Electron transitions between energy levels.
- As we go down the group, the energy gap between molecular orbitals decreases, allowing absorption of longer wavelengths of visible light.

Example:
- **Fluorine** – pale yellow (absorbs violet light)
- **Chlorine** – yellow-green
- **Bromine** – reddish-brown
- **Iodine** – violet

c) **Why chlorine is more volatile than bromine and iodine?**

Ans. Chlorine is more volatile because:
- It has weaker intermolecular forces (London dispersion forces) due to its smaller molecular size and lower molar mass.
- Volatility decreases down the group as the halogen molecules get larger and heavier, increasing the strength of dispersion forces.

So, Cl_2 (gas) > Br_2 (liquid) > I_2 (solid) in terms of volatility.

THE BOND STRENGTH OF HALOGEN MOLECULES

Bond strength in halogens decreases as we move down the group from chlorine to iodine.

➤ **Reason:**
This is due to the increase in the atomic size down the group which results in longer bond lengths and weaker bonds. Moving from top to bottom in group 17, the bond energy of halogens decreases gradually from chlorine to iodine.

➤ **Exceptional Behaviour of Fluorine:**
Fluorine is an exception in this group. In the case of fluorine, the bond strength is relatively weak because fluorine atoms are very small. Due to the small size, there is significant electron-electron repulsion between the lone pairs on the fluorine atoms, which weakens the bond despite the high electronegativity of fluorine. The bond energy of halogens is listed in Table.

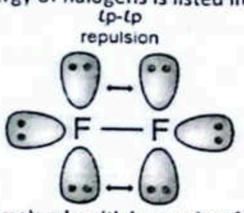


Figure: F_2 molecule with lone pairs of electrons

Table: Bond energies of halogen molecules

Halogen Molecule	Bond Energy (kJ mol^{-1})
F_2	156
$C\ell_2$	243
Br_2	193
I_2	151

RELATIVE REACTIVITIES OF THE HALOGENS AS OXIDIZING AGENTS

(Exercise LO.4)

Q. Discuss the relative reactivity of the halogen elements as oxidizing agents. Arrange $F_2, C\ell_2, Br_2, I_2$ in increasing order of the oxidizing power.

- All the free halogens act as oxidizing agents when they react with metals and most of non-metals.
- On forming ionic compounds with metals, the halogens gain electrons and are converted to negative halide ions.

$$2Na_{(s)} + C\ell_{2(g)} \longrightarrow 2NaC\ell_{(s)}$$

- The oxidizing power of halogens decreases down the group. Fluorine has the highest oxidizing power and iodine the least.
- The order of decreasing power as an oxidizing agent is:

$$F_2 > C\ell_2 > Br_2 > I_2$$

> **Rock Your Mind!**
> 4. $C\ell_2$ cannot oxidize:
> A) F^- B) Br^-
> C) I^- D) Na-metal

- The reactivity of halogens is directly related to their ability to acquire an electron and form halide ions ($F^-, C\ell^-, Br^-$ and I^-) when they react with other elements.
- Fluorine has the highest tendency to acquire an electron and form fluoride.
- Fluorine molecule can oxidize and displace all the halide ions from their solutions ($C\ell^-, Br^-$ and I^-) to free halogens.

$$F_{2(g)} + C\ell^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + C\ell_{2(g)}$$
$$F_{2(g)} + Br^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + Br_{2(g)}$$
$$F_{2(g)} + I^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + I_{2(g)}$$

- Chlorine can oxidize and displace Br^- and I^-. Bromine can oxidize and displace I^-. Iodine cannot oxidize any halide ion.
- The oxidizing power of halogens can be related to standard electrode potential (E°) values. Fluorine is the most reactive halogen and the most powerful oxidizing agent. The standard electrode potential $E^\circ(X_2/X^-)$ for halogens shown in Table become less positive from fluorine to iodine.

Table: Standard electrode potential $E^\circ(X_2/X^-)$

Halogen Molecule (X_2)	Standard Reduction Potential, E°(V)
F_2	+2.87
$C\ell_2$	+1.36
Br_2	+1.07
I_2	+0.54

- This shows the decreasing oxidizing power.

➤ **Factors affecting Oxidizing Power of Halogen:**

- The oxidizing power of halogens depends upon various factors, i.e., energy of dissociation, electron affinity of atoms, hydration energies of ions, and heats of vaporization (for Br_2 and I_2). A halogen having low energy of dissociation, high electron affinity and higher hydration energy of its ions, will have a high oxidizing power.

QUICK CHECK 13.2

a) The F – F bond is weaker than $C\ell - C\ell$ bond although fluorine is the most electronegative element, Explain.

Ans. Yes, despite fluorine being the most electronegative:
- The F–F bond is weaker due to strong repulsion between the lone pairs of electrons on the small fluorine atoms.
- The small atomic radius of fluorine causes the non-bonding electrons to be closer, increasing electron–electron repulsion.
- In contrast, $C\ell$–$C\ell$ has a larger bond length, reducing repulsion and making the bond stronger.

b) Is the reaction between $NaC\ell_{aq}$ and F_2 gas possible?

i) Give reason whether yes or no.

Ans. Reason:
Yes, the reaction is **possible**.
- Fluorine is more reactive and has a higher oxidizing power than chlorine.
- Therefore, fluorine can displace chlorine from sodium chloride solution.

ii) If yes, write the equation for this reaction.

Ans. Reaction Equation:

$$F_{2(g)} + 2NaC\ell_{(aq)} \longrightarrow 2NaF_{(aq)} + C\ell_{2(g)}$$

c) What is the relationship between the oxidizing power of halogens and their standard reduction potential values?

Ans.
- The oxidizing power of a halogen is directly related to its standard reduction potential (E°).
- A higher E° value means the halogen is a stronger oxidizing agent (more likely to gain electrons).

Order of oxidizing power (strongest to weakest):

$$F_2 > C\ell_2 > Br_2 > I_2$$

Corresponding E° values (approx.):
- **F_2:** + 2.87 V
- **$C\ell_2$:** +1.36 V
- **Br_2:** +1.07 V
- **I_2:** +0.54 V

REACTIONS OF THE HALOGENS WITH HYDROGEN

➤ **Hydrogen Halides:**

- When halogen elements react with hydrogen, they produce hydrogen halides.

$$H_2 + X_2 \longrightarrow 2HX \qquad \text{Where } X_2 = F_2, C\ell_2, Br_2 \text{ and } I_2$$

- Hydrogen halides are colourless gases that dissolve in water to form hydrohalic acid. When we move down the group from fluorine to iodine, the reactivity of halogens with hydrogen decreases.

$$F_2 > C\ell_2 > Br_2 > I_2$$

- At low temperature and in the dark, fluorine reacts explosively with hydrogen.

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

- When this gas is dissolved in water, it forms hydrofluoric acid.

> **Rack Your Mind!**
> 5. Maximum bond energy is of:
> A) HF B) HBr
> C) HCℓ D) HI

- In the presence of UV light or a spark, chlorine reacts readily with hydrogen and produces colourless HCℓ gas which forms hydrochloric acid in water.

$$H_{2(g)} + C\ell_{2(g)} \xrightarrow{h\nu} 2HC\ell_{(g)}$$

- Hydrogen bromide (HBr) gas is produced when bromine reacts with the hydrogen upon heating. HBr gas is less reactive than HCℓ and HF. It forms a strong hydrobromic acid in water. This is an exothermic reaction.

$$H_{2(g)} + Br_{2(g)} \xrightarrow{\Delta} 2HBr_{(g)}$$

- At high temperature and in presence of a catalyst, iodine reacts with hydrogen to form hydrogen iodide (HI) gas, which forms hydroiodic acid in water.

$$H_{2(g)} + I_{2(g)} \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} 2HI_{(g)}$$

- This is a reversible reaction and occurs very slowly.

RELATIVE THERMAL STABILITIES OF HYDROGEN HALIDES IN TERMS OF THEIR BOND STRENGTH

(Exercise LQ1)

Q. Describe and explain the relative thermal stabilities of the halogen hydrides in terms of bonds strength.

- As we move down the halogen group from fluorine to iodine, the thermal stabilities of hydrogen halides (H-X) decrease due to decrease in bond dissociation energies as given in Table 13.5. The order of thermal stability of HX is as follows:

$$HF > HC\ell > HBr > HI$$

- Bond strength between the hydrogen and the halogen atom in the H – X molecule explain this trend.
- Hydrogen fluoride (HF) is the most thermally stable hydrogen halide. Due to the high electronegativity of fluorine and its small atomic radius, a strong overlap of orbitals produces a very strong H – F bond.
- The bond dissociation energy of H – F (569 kJ/mol) is the highest among the hydrogen halides.

> **Rack Your Mind!**
> 6. Which of the following hydrogen halides is the most thermally stable?
> A) HF B) HCℓ
> C) HBr D) HI

- Hydrogen chloride (HCl) is less thermally stable than hydrogen fluoride but more stable than other hydrogen halides.
- Due to the larger atomic radius of chlorine than fluorine H – Cℓ bond is weaker than H – F bond. Its bond dissociation energy is less than that of H – F.

- Its bond dissociation energy is 431 kJ/mol. Hydrogen bromide (H – Br) bond is weaker than H – F and H – Cℓ due to the larger atomic radius of bromine. There is a reduced overlapping of orbitals. Its bond dissociation energy is 366 kJ/mol.
- Among the common hydrogen halides, hydrogen iodide (HI) is the least thermally stable. Atomic radius of iodine is very large leading to poor orbital overlap due to which hydrogen iodide bond is the weakest among H – F, HCℓ and HBr.
- The bond dissociation energy of hydrogen iodide is 299 kJ/mol.

Table: Bond dissociation energy of H – X bonds

Hydrogen halide (HX)	Bond dissociation energy (kJ mol^{-1})
H – F	569
H – Cℓ	431
H – Br	366
H – I	299

QUICK CHECK 13.3

a) The reaction between H_2 and F_2 is explosive but that between H_2 and I_2 is slow and reversible. Explain why.

Ans.

- The H–F bond is very strong and releases a large amount of energy when formed, making the reaction with F_2 highly exothermic and explosive.
- The activation energy for the $H_2 + F_2$ reaction is also very low.
- In contrast, the H–I bond is weaker, the reaction is less exothermic, and it has a higher activation energy, making it slow and reversible.

b) Refer to Table 13.4 and 13.5 to predict which of the following reactions would be more exothermic. Explain your answer.

$$H_{2(g)} + C\ell_{2(g)} \longrightarrow 2HC\ell_{(g)} \text{ and } H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$$

Ans. **Reaction 1 is more exothermic.**

Reason:

- The H–Cℓ bond is stronger than the H–Br bond.
- More energy is released when forming strong H–Cℓ bonds compared to H–Br.
- Also, $C\ell_2$ has a weaker bond than Br_2, requiring less energy to break.
- So, overall energy change is more negative (exothermic) for the HCℓ reaction.

c) How thermal stability of hydrogen halides is related to their bond dissociation energies?

Ans.

- Thermal stability of hydrogen halides increases with higher bond dissociation energy.
- Stronger H–X bonds (higher bond energy) are harder to break, so the compound is more stable under heat.

Trend:

$$HF > HC\ell > HBr > HI$$

This trend corresponds to decreasing bond dissociation energy and thermal stability.

d) HF is the most thermally stable hydrogen halide. Give reasons.

Ans.

- The H–F bond has the highest bond dissociation energy among hydrogen halides.
- Fluorine is small and highly electronegative, forming a strong, short bond with hydrogen.
- This makes HF harder to decompose on heating → most thermally stable.

RELATIVE REACTIVITY OF HALIDE IONS AS REDUCING AGENTS

Q1. Discuss the reducing power of halide ions with relevant reactions. Also explain the factors affecting it.

- The reducing ability of halide ions increases as we move down the group from fluorine to iodine.
- This trend is mostly due to the decreasing electronegativity and increasing atomic radius down the group. This result in lower charge density and greater ease of electron donation.
- Fluoride ion is the weakest reducing agent while iodide is the strongest reducing agent among the halides.
- The order of decreasing power as a reducing agent is $I^- > Br^- > Cl^- > F^-$.
  The following is an explanation of this trend in terms of their properties.
- The high electronegativity of fluorine and the strong bond between the fluorine atom and its extra electron make it difficult for fluoride ion (F^-) to donate electrons. The small size of fluoride ion results in a high charge density, further stabilizing the fluoride ion and reducing its tendency to lose an electron.
- Chloride ion (Cl^-) is a stronger reducing agent than fluoride but still weaker than bromide and iodide. This is due to its larger size and lower electronegativity.
- Bromide (Br^-) is a stronger reducing agent than chloride. Bromine is less electronegative than chlorine. Bromide ion (Br^-) has a larger ionic radius and lower charge density due to which it easily loses an electron and act as a reducing agent.
- Iodide (I^-) is much stronger reducing agent than both chloride and bromide. Electronegativity of iodine is much lower than chlorine and bromine. Iodide ion (I^-) is large in size. This results in a lower charge density and a tendency to donate an electron by the iodide ion, making it strong reducing agent.

REACTIONS OF HALIDES WITH AQUEOUS SILVER ION FOLLOWED BY AQUEOUS AMMONIA

Reactions of Halides with Aqueous Silver Ion (Silver Nitrate Test for Halide Ions)

Insoluble silver halides (AgX) are formed when halide ions react with aqueous silver nitrate ($AgNO_3$). These reactions are used in qualitative analysis to identify halides ions. The general reaction is given below:

$$X^-_{(aq)} + Ag^+_{(aq)} \longrightarrow AgX_{(s)}$$

> **Rack Your Mind!**
> 7. Why AgF does not form precipitates with water while other silver halides form?

- **AgF:** No reaction is visible when silver ions and fluoride ions are mixed in the aqueous medium. As silver fluoride is soluble in water, **Fluoride (F^-) does not form precipitate as silver fluoride.**
- **AgCl:** When silver ions and chloride ions are mixed in the aqueous medium a white precipitate of silver chloride forms, which is soluble in dilute ammonia.

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

- **AgBr:** On mixing of aqueous silver ions with aqueous Bromide ions, a cream-coloured precipitate of silver bromide forms. This precipitate of silver bromide is sparingly soluble in concentrated ammonia.

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

- **AgI:** A yellow precipitate of silver iodide forms on mixing aqueous silver ion with aqueous halide solution. The product AgI is insoluble in ammonia.

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

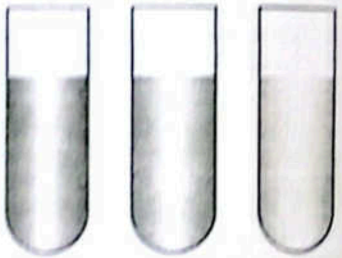


Figure: Colours of the silver halide precipitates: silver chloride (left), silver bromide (middle), and silver iodide (right)

This type of reactions is used to identify halide ions and is called silver nitrate test.

Reaction of Silver Halides (AgX) with Aqueous Ammonia

Addition of aqueous ammonia tests the solubility of initially formed silver halide precipitates.

AgF is soluble in water so it does not form precipitate, so ammonia has no effect. Silver chloride dissolves in dilute ammonia to form diamminesilver (I) complex. The white precipitate of AgCl dissolves in dilute ammonia forming a colourless solution.

$$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + Cl^-_{(aq)}$$

The cream coloured precipitate of AgBr dissolves in concentrated ammonia, forming a colourless solution.

$$AgBr_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + Br^-_{(aq)}$$

The yellow precipitate of silver iodide (AgI) does not dissolve in both dilute and concentrated ammonia, so there is no change in the presence of ammonia.

The below sequence of reactions in Table provides a systematic way to differentiate between halide ions using their solubility with aqueous silver ions and ammonia.

QUICK CHECK 13.4

a) F^- is a weaker reducing agent than Cl^-. Explain why.

Ans.
- A reducing agent donates electrons (gets oxidized).
- To be a good reducing agent, the halide ion must easily lose electrons to form the halogen.

Reason F^- is weaker:
- F^- has a very strong bond with its electron due to its small size and high electronegativity.
- It is less willing to give up electrons.
- Therefore, F^- is a poor reducing agent, Cl^- is better at losing electrons (i.e., stronger reducing agent).

b) What is the cause of the different solubilities of silver halides in ammonia?

Ans.
- Solubility in ammonia depends on the ability of the silver halide to form a complex ion with ammonia: $[Ag(NH_3)_2]^+$
- AgCl and AgBr form this complex and dissolve in ammonia (AgCl is more soluble than AgBr).
- AgI is insoluble because it forms a very insoluble salt and does not readily form a complex with ammonia.

Trend of solubility in NH_3:

$$AgCl > AgBr > AgI$$

c) Write down the equation for the reaction of KI with Ag^+ followed by NH_3. What would you observe at the completion of this reaction?

Ans. Step 1: Reaction with silver nitrate (Ag^+):

$$KI_{(aq)} + AgNO_{3(aq)} \longrightarrow AgI_{(s)} + KNO_{3(aq)}$$

- A yellow precipitate of AgI forms.

Step 2: Addition of NH_3 (aqueous ammonia):
- AgI does not dissolve in ammonia.

$$AgI_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+ + I^-$$

Observation:
- Yellow precipitate remains unchanged on adding ammonia.

Table: Action of Ag^+ followed by Ammonia on Silver Halides

Halide ion	Action of aq. Ag^+ ion	Action of Aqueous Ammonia
Fluoride ion (F^-)	No precipitate	No reaction with aq. NH_3
Chloride ion (Cl^-)	White precipitate (AgCl)	Soluble in dil. aq. NH_3
Bromide ion (Br^-)	Cream colour precipitate (AgBr)	Soluble in conc. aq. NH_3
Iodide ion (I^-)	Pale yellow precipitate(AgI)	Insoluble in aq. NH_3

REACTIONS OF HALIDES (X^-) WITH CONCENTRATED SULFURIC ACID

The reactions of different halide ions with concentrated sulfuric acid are different from one another. The nature of the product and nature of reaction changes down the group from fluoride to iodide.
Fumes of hydrogen fluoride gas are produced when concentrated sulfuric acid reacts with NaF. HF is a weak reducing agent, therefore, it does not react with H_2SO_4 further.

$$NaF_{(s)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HF_{(g)}$$

When concentrated sulfuric acid reacts with sodium chloride, fumes of hydrogen chloride gas are produced.

$$NaC\ell_{(s)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HC\ell_{(g)}$$

In case of Br^{1-} ion, steamy fumes of hydrogen bromide (HBr) gas and brown fumes of bromine (Br_2) are produced along with the smell of sulfur dioxide (SO_2). It is a redox reaction. Hydrogen bromide acts as a reducing agent by reducing sulfuric acid to sulfur dioxide and is self-oxidized to bromine.

$$NaBr + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HBr_{(g)}$$

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

When concentrated sulfuric acid reacts with sodium iodide, fumes of hydrogen iodide gas, purple fumes of solid iodine I_2 and smell of H_2S gas produced. HI acts as a strong reducing agent. It reduces H_2SO_4 to H_2S and is itself oxidized to I_2.

$$NaI_{(aq)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HI_{(g)}$$

$$8HI_{(s)} + H_2SO_{4(\ell)} \longrightarrow 4I_{2(s)} + H_2S_{(g)} + 4H_2O_{(\ell)}$$

The trend of increasing reducing power of the halide ions (X^-) from fluoride to iodide, leads to more complex reactions with concentrated sulfuric acid.

REACTIONS OF CHLORINE WITH COLD AND HOT AQUEOUS SODIUM HYDROXIDE

Disproportionation Reaction:

Those reactions in which a single element undergoes both oxidation and reduction simultaneously are known as disproportionation reactions. When chlorine reacts with cold and hot aqueous sodium hydroxide (NaOH), it undergoes disproportion and form different products according to the temperature of the reaction.

> **Rock Your Mind!**
> 8. Give chemical reaction of NaOH and Cl_2 in hot state at 70°C.

➲ Reaction with Cold Aqueous Sodium Hydroxide

Chlorine undergoes disproportion when it reacts with cold aqueous sodium hydroxide (NaOH) forming sodium chloride (NaCℓ) and sodium chlorate (I) (NaClO).

$$C\ell_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaC\ell_{(aq)} + NaC\ell O_{(aq)} + H_2O_{(\ell)}$$

Oxidation states of chlorine in the above reaction are given below:

Chlorine in $C\ell_2$	=	0
Chlorine in NaCℓ	=	−1
Chlorine in NaCℓO	=	+1

> **KEEP IN MIND**
> Sodium chlorate (I) was previously called sodium hypochlorite.

Chlorine in $C\ell_2$ is oxidized from 0 to +1 in NaOCℓ. Chlorine in $C\ell_2$ is reduced from 0 to 1 in NaCℓ.
The above reaction shows the simultaneous oxidation and reduction of chlorine and is example of disproportionation reaction.

➲ Reaction with Hot Aqueous Sodium Hydroxide

When chlorine reacts with hot aqueous sodium hydroxide (NaOH), it forms sodium chloride (NaCℓ) and sodium chlorate (V) ($NaC\ell O_3$). It is another example of disproportionation reaction.

$$3C\ell_{2(g)} + 6NaOH_{(aq)} \longrightarrow NaC\ell_{(aq)} + NaC\ell O_{3(aq)} + 3H_2O_{(\ell)}$$

Chlorine in $C\ell_2 = 0$
Chlorine in $NaC\ell = -1$
Chlorine in $NaC\ell O_3 = +5$

Chlorine is oxidized from 0 to +5 in $NaC\ell O_3$. Chlorine is reduced from 0 to −1 in NaCℓ This disproportionation reaction shows how the temperature of the reaction influences the products formed, demonstrating the versatility of chlorine in undergoing redox reactions.

☑ QUICK CHECK 13.5

a) How would KI react with conc. H_2SO_4. What does this reaction indicate about the reducing power of iodide?

Ans. When potassium iodide (KI) reacts with concentrated sulfuric acid (H_2SO_4), it shows strong reducing behavior:

Reaction:

$$2KI + H_2SO_4 \longrightarrow 2HI + KH_2SO_4$$

Then, HI reduces H_2SO_4:

$$8HI + H_2SO_4 \longrightarrow H_2S + 4I_2 + 4H_2O$$

Observation:
- Purple iodine vapor (I_2) appears
- Rotten egg smell of hydrogen sulfide (H_2S) may be detected

Conclusion:
- Iodide (I^-) is a very strong reducing agent
- It reduces sulfur in H_2SO_4 from +6 to −2 (H_2S)

b) Show that the reaction of $C\ell_2$ with cold and hot aqueous KOH is a disproportionation reaction.

Ans. A disproportionation reaction is where the same element is both oxidized and reduced.

Cold KOH (Cl_2 in cold, dilute alkali):

$$C\ell_2 + 2KOH \longrightarrow KC\ell + KC\ell O + H_2O$$

- Chlorine (0) ⟶ $C\ell^-$ (−1) ⟶ reduced
- Chlorine (0) ⟶ $C\ell O^-$ (+1) ⟶ oxidized

Disproportionation

Hot KOH ($C\ell_2$ in hot, concentrated alkali):

$$3C\ell_2 + 6KOH \rightarrow 5KC\ell + KC\ell O_3 + 3H_2O$$

- $C\ell_2$ (0) ⟶ $C\ell^-$ (−1) ⟶ reduced
- $C\ell_2$ (0) ⟶ $C\ell O_3^-$ (+5) ⟶ oxidized

c) HI acts as strong reducing agent. Explain it with chemical reactions.

Ans. HI (hydroiodic acid) is a strong reducing agent because iodide ions (I^-) easily donate electrons.

Examples:
1. **Reduction of Fe^{3+} to Fe^{2+}:** $Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$
2. **Reduction of H_2SO_4 to H_2S (as in part a):** $8HI + H_2SO_4 \longrightarrow H2S + 4I_2 + 4H_2O$
3. **Reduction of MnO_4^- to Mn^{2+}:** $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

Conclusion:
- HI reduces a variety of substances.
- Its strong reducing power is due to the ease of oxidation of I^- to I_2.

USE OF CHLORINE IN WATER PURIFICATION

Chlorine gas is very poisonous. However, in small quantities, they are harmless to humans but poisonous to the bacteria which cause diseases. Due to its strong disinfectant properties, chlorine is widely used at the treatment plants for water purification. The process involves adding chlorine to water, where it forms active species that kill bacteria and other pathogens. Water in the swimming pools is also chlorinated with slightly higher concentrations of chorine because there is likely to be a higher concentration of bacteria in the water. The primary active species are chloric (I) acid or hypochlorous acid (HOCl) and the chlorate (I) or hypochlorite ions (OCl^-). Chlorination is a relatively inexpensive method of water disinfections.

➲ Chlorine Addition to Water

When chlorine gas (Cl_2) is added to water, it undergoes hydrolysis to form a mixture of hydrochloric acid (HCl) and chloric (I) acid (HClO).

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

> **Rack Your Mind!**
> 9. Discuss harmful effects of chlorinated water.

Chloric (I) acid (HOCl) is a weak acid and partially dissociate in water to form hydrogen ions (H^+) and chlorate (I) ion (OCl^-).

➲ Disinfection Activity

HOCl and OCl^- are effective disinfectants, but HOCl is more effective due to its neutral charge. The neutral charge of HOCl allows to penetrate the cell walls of micro-organisms easily. Essential cellular components such as proteins and lipids are oxidized by HOCl and OCl^-, which disrupt the cell function leading to cell death. HOCl and OCl can oxidize and inactivate enzymes that are crucial for survival and replication of bacteria.

> **Interesting Information!**
> Nucleic acids (DNA and RNA) can be oxidized by HOCl and OCl^- and thus preventing bacteria from replicating and vital cellular functions.

➲ Factors Affecting Disinfection

> **Rack Your Mind!**
> 10. Which one is frequently used to disinfect water?
> A) Sodium chloride B) Hydrochloric acid
> C) Chlorine D) Sodium hydroxide

➢ pH

- At pH around 6 – 7.5, HOCl predominates and makes the disinfection process more effective.
- At higher pH (above 7.5), OCl^- predominates, its less effective but still provides disinfection.

➢ Chorine Dose

The higher the amount of chlorine, the more effective the disinfection. Sufficient chlorine must be added to get enough HOCl and OCl^- to kill bacteria.

➢ Contact Time

Contact time of water with chlorine must be long enough, to allow the disinfectants to penetrate and kill bacteria, viruses and protozoa.

QUICK CHECK 13.6

a) Why HOCl is more effective disinfectant than OCl^- to kill bacteria in water?

Ans.
- HOCl (hypochlorous acid) is more effective because:
- It is neutral and penetrates bacterial cell walls more easily than the negatively charged OCl^- (hypochlorite ion).
- Once inside the cell, HOCl can disrupt vital cell processes and oxidize cell components.

Conclusion:
HOCl is 80–100 times more effective than OCl^- in killing microorganisms.

(b) What are the factors that affect disinfection of bacteria in water?

Ans. Key factors include:

1. **pH of water**
   - Lower pH favors HOCl formation, which is more effective.
   - At higher pH, more OCl^- is formed (less effective).
2. **Temperature**
   - Higher temperatures generally increase the rate of disinfection.
3. **Contact time**
   - Longer exposure allows more time for disinfection.
4. **Concentration of disinfectant**
   - More chlorine or HOCl increases effectiveness.
5. **Presence of organic matter**
   - Organic compounds can consume chlorine, reducing its availability for disinfection.

(c) What are the primary active species in the chlorination of water? Give equation that shows their production.

Ans. The primary active species are:
- Hypochlorous acid (HOCl)
- Hypochlorite ion (OCl^-)

These are produced when chlorine reacts with water:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

Then, depending on the pH:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

Summary:
- HOCl is the main active disinfectant at low to neutral pH.
- OCl^- predominates at higher pH, but is less effective.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	S.Q	All the halogens exist as non-polar diatomic molecules and their molecules are held together by London dispersion force. The physical state of a molecular substance depends upon the strength of these forces. Fluorine at the top to group VII A has small size and low polarizability, therefore the intermolecular forces between F_2 molecules are weak and it exist as a gas. Iodine at the bottom of group VIIA has relatively large size, high polarizability, and there are very strong forces of attraction between I_2 molecules. Hence it exists as a solid at room temperature.
2.	D	Iodine show positive oxidation states of +1, +3, +5 and +7 e.g. In HIO_3, its oxidation state = +5 HIO_4, its oxidation state = +7
3.	D	Iodine is a solid halogen because as we move down the group, strength of van der waals forces increases and Iodine is at the bottom having strongest intermolecular force.
4.	A	Chlorine cannot oxidize F^- (Fluoride ion) to F^2 between Fluorine is more electronegative.
5.	A	HF has the maximum bond energy because the bond between hydrogen and fluorine is the shortest and strongest due to flurine's high electronegativity and small atomic size.
6.	A	Thermal stability decreases down the group due to increasing bond length and decreasing bond dissociation energy. HF has the strongest H–X bond, making it the most stable.
7.	S.Q	AgF is highly soluble in water. All other silver fluorides are form precipitates i.e. insoluble in water.

8.	S.Q	Sodium hypochlorite which is produced in cold state in the above reaction decomposes forming sodium chloride and sodium chlorate **at 70°C.** $3NaClO_{(aq)} \longrightarrow 2NaCl_{(aq)} + NaClO_{3(aq)}$
9.	S.Q	Chlorinated water has also some harmful effects which are discussed below. **1.** Hypochlorous acid or chlorine of water reacts with dissolved ammonia to form chloramines NH_2Cl, $NHCl_2$ and especially NCl_3 (nitrogen trichloride). NCl_3 is a powerful eye irritant. $NH_3 + 3HOCl \longrightarrow NCl_3 + 3H_2O$ The alkaline pH can prevent the formation of chloramines. **2.** If phenol is present in water then chlorinated phenols are formed which have offensive odour and taste and are toxic.
10.	C	Chlorine reacts with water to form hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) which are powerful oxidizing agents that destory microorganisms.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. Which halogen molecule has the strongest bond?
a) F_2 b) Br_2 c) I_2 d) Cl_2

II. The volatility of the halogens (Group 17) generally as you move down the group (from Fluorine to Iodine).
a) Increases b) Decreases c) Remains the same d) Fluctuates unpredictably

III. Which one of the following halogen molecules has strongest oxidizing power?
a) Br_2 b) F_2 c) I_2 d) Cl_2

IV. The decreasing thermal stability of the halogens down the group is primarily due to the:
a) Increasing electronegativity of the atoms.
b) Decreasing bond length between the halogen atoms.
c) Increasing atomic radius, leading to a weaker covalent bond.
d) Increasing strength of van der Waals forces

V. Which one of the following halides has strongest reducing power?
a) F^- b) Cl^- b) Br^- d) I^-

VI. Which statement about the reaction between halogens and hydrogen is correct?
a) Iodine reacts most vigorously with hydrogen
b) Chlorine and hydrogen explode in darkness
c) Fluorine combines explosively with hydrogen even in cold and dark conditions
d) Bromine and hydrogen do not react at all

VII. How does the acidic strength of hydrogen halides change as you move down the group?
a) It remains constant. b) It decreases from HF to HI.
c) It increases from HF to HI. d) It fluctuates erratically

VIII. Why is fluorine the most reactive halogen?
a) Bond length in the halogen molecule b) Bond strength in the halogen molecule
c) Electronegativity of the halogen d) Number of electrons in the halogen molecule

IX. When aqueous silver nitrate is added to a solution containing bromide ions, a cream precipitate forms. What is the solubility of this precipitate in ammonia solution?
a) Soluble in dilute ammonia solution. b) Partially soluble in dilute ammonia solution.
c) Insoluble in dilute ammonia solution. d) Soluble only upon heating with ammonia.

X. Concentrated sulfuric acid is added to solid sodium chloride. What is the initial observation?
a) Reddish-brown fumes are evolved.
b) A purple vapor is evolved.
c) Steamy white fumes of hydrogen chloride are evolved.
d) A black solid is formed.

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	I_2	• Bond strength increases down Group 17 due to greater orbital overlap (larger atomic size). • Iodine (I_2) has the strongest bond (bond energy: $F_2 < Cl_2 < Br_2 < I_2$).
II.	b	Decreases	• Volatility decreases down the group as van der Waals forces increase with larger atomic size (F_2 gas → I_2 solid).
III.	b	F_2	• Fluorine (F_2) is the strongest oxidizer due to its highest electronegativity and weak F–F bond (easily breaks to oxidize others).
IV.	c	Increasing atomic radius, leading to a weaker covalent bond	• Larger atomic size reduces orbital overlap, weakening the X-X bond (e.g., $F_2 > Cl_2 > Br_2 > I_2$ stability).
V.	b	It decreases from HF to HI	• HF has strong hydrogen bonding, while HI has weak dipole forces. Boiling points: HF > HI > HBr > HCl.
VI.	c	Electronegativity of the halogen	• Fluorine is most reactive due to its highest electronegativity (attracts electrons aggressively) and low bond energy (F–F bond weak).
VII.	c	It increases from HF to HI	• **Acidic strength order:** HI > HBr > HCl > HF. • Reason: Bond strength decreases down the group (HF has the strongest H–F bond due to high electronegativity and small size of F), making HX dissociation easier.
VIII.	b	Bond strength in the halogen molecule	• Fluorine (F_2) is the most reactive halogen because its weak F–F bond (due to lone pair repulsions in small atoms) is easily broken, facilitating reactions.
IX.	b	Partially soluble in dilute ammonia solution	• **Cream Precipitate:** AgBr (silver bromide). • **Solubility:** AgBr is partially soluble in dilute NH_3 (unlike AgCl, which dissolves completely, and AgI, which is insoluble).
X.	c	Steamy white fumes of hydrogen chloride are evolved	• **Reaction:** $NaCl_{(s)} + H_2SO_4 \rightarrow NaHSO_4 + HCl_{(g)}\uparrow$ • **Observation:** Steamy white fumes of HCl gas (due to HCl reacting with moisture in air).

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Which halogen is the least reactive, which is the most reactive? Give reason.

Ans.
- **Most reactive halogen:** Fluorine (F_2)
- **Least reactive halogen:** Iodine (I_2)

Reason:

As we go down Group 17 in the periodic table

- Atomic size increases.
- Electronegativity decreases.
- Bond energy decreases.

This makes fluorine the most reactive because it attracts electrons strongly. Iodine is the least reactive because its larger atoms hold electrons less tightly.

b. The ionic equation for a reaction is: $Br_2 + 2I^- \longrightarrow Br^- + I_2$

Explain which species is oxidized in this reaction. Why?

Ans. The given reaction is a redox (displacement) reaction:

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

Observations:

Oxidation: $I^- \longrightarrow I_2 + 2e^-$ (Iodide is oxidized, losing electrons).

Reduction: $Br_2 + 2e^- \longrightarrow 2Br^-$

Displacement:

- Br_2 (stronger oxidant) displaces I^- from its compound, confirming the trend:
- Br_2 is more reactive than I_2 in the halogen reactivity series.

In short:

- Spontaneous reaction (Br_2 has higher reduction potential than I_2).
- Net ionic form (spectator ions omitted).

Species is oxidized in this Reaction:

- Iodide ion (I^-) is oxidized.
- It loses electrons and forms iodine (I_2).
- Oxidation means loss of electrons.

So, iodide is oxidized and bromine is reduced.

c. What is role of London dispersion forces in the trend of volatility of halogens?

Ans. Role of London dispersion forces in the trend of volatility of Halogens:

- London dispersion forces are weak forces between molecules.
- As you move down the group, atoms become larger, so dispersion forces become stronger.
- Stronger forces mean lower volatility (less easily turned to gas).

This is the reason that fluorine (gas) is most volatile and iodine (solid) is least volatile.

d. How does the reactivity of halogens with hydrogen vary?

Ans. Reactivity **decreases down the group:**

- Fluorine reacts explosively with hydrogen.
- Chlorine reacts quickly in light.
- Bromine reacts slowly.
- Iodine reacts very slowly and incompletely.

This is due to decreasing bond strength and oxidizing power down the group.

e. Which halogen is used as an antiseptic? How does it work?

Ans. Halogen is used as an Antiseptic:

- Iodine is used as an antiseptic.
- It kills bacteria by oxidizing their cell contents.
- Often used in the form of tincture of iodine (iodine + alcohol).

f. What is the colour change when chlorine displaces bromine?

Ans. Chlorine displaces bromine from a solution of potassium bromide:

$$Cl_2 + 2KBr \rightarrow 2KCl + Br_2$$

Observation:

- Colourless solution turns reddish-brown due to the formation of bromine.

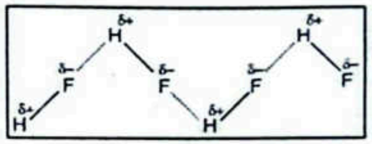
g. How the halogen acids are ionized in water?

Ans. Halogen acids ionize in water and form Halide ions and hydronium ions (H_3O^+).

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
$$HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$$
$$HI + H_2O \rightleftharpoons H_3O^+ + I^-$$

h. Why HF is weaker acid than HCl?

Ans. HF is a weaker acid than HCl (Acidic strength ∝ Ionization)



A substance which has a tendency to give proton (H^+) in an aqueous solution is called acid. The strength of an acid is directly proportional to its proton (H^+) releasing power.

HF has weak acidic properties in aqueous solution to incomplete dissociation of HF molecule in water. In HF, strong hydrogen bonding is present and partially positive hydrogen is entrapped between two strong electronegative fluorine atoms. Moreover, HF has a strong polar covalent bound with high bond energy (566 kJ/mol). So, Hydrogen ions (H^+) are not released easily.

As a result it becomes difficult for proton (H^+) to be ionized (released) resulting in lower concentration of hydrogen ions compared to stronger acids like HCl in water making HF a weaker acid.

On the other hand in HCl dipole-dipole interaction is present which is weaker than hydrogen bonding. Therefore proton (H^+) releasing power of HCl is more which makes it strong acid.

$$\cdots \overset{\delta+}{H} - \overset{\delta-}{Cl} \cdots \overset{\delta+}{H} - \overset{\delta-}{Cl} \cdots \overset{\delta+}{H} - \overset{\delta-}{Cl} \cdots$$

Therefore, it is not easy for HF to release H^+ as compared to HCl. It makes HF weaker acid than HCl.

i. Describe a simple chemical test that could be used to distinguish between aqueous solutions of potassium bromide and potassium iodide. Include the reagents and expected observations.

Ans. Reagents:

- Chlorine water
- Organic solvent (like carbon tetrachloride or hexane)

Procedure & Observation:

- Add chlorine water to both solutions.
- Then shake with organic solvent.

Solution	Observation	Conclusion
KBr	Reddish-brown layer	Br_2 formed
KI	Purple/violet layer	I_2 formed

j. Explain the chemical principles behind the use of chlorine as a disinfectant in water purification. Include relevant chemical equations in your explanation.

Ans. Chlorine kills bacteria by forming hypochlorous acid (HOCl):

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

HOCl is a strong oxidizing agent. It penetrates and destroys bacterial cells.

k. Describe one significant disadvantage associated with the use of chlorine in water purification.

Ans. Disadvantage:

- Chlorine reacts with organic matter in water to form harmful by-products called trihalomethanes (THMs).
- These can be carcinogenic (cancer-causing).

l. What is disproportionation reaction? Give an example.

Ans. A disproportionation reaction is when one element is both oxidized and reduced in the same reaction.

Example:

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$$

Chlorine goes from 0 to −1 (reduced) and 0 to +1 (oxidized).

m. Chlorine gas reacts differently with sodium hydroxide solution depending on the temperature and concentration.

Ans. Yes. It forms different products with **cold and hot** NaOH.

n. Write balanced chemical equations for the reaction of chlorine (Cl_2) with:

i) Cold, dilute sodium hydroxide (NaOH).

ii) Hot, concentrated sodium hydroxide (NaOH).

Ans. i) Cold, dilute NaOH: $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$

ii) Hot, concentrated NaOH: $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

o. For each reaction in question 1), identify the oxidation states of chlorine in the reactant (Cl_2) and in each of the chlorine-containing products. Use these oxidation states to explain why both reactions are classified as disproportionation reactions.

Ans. Cold reaction:

- $Cl_2(0) \longrightarrow Cl^-$ (−1) = reduction
- $Cl_2(0) \longrightarrow ClO^-$ (+1) = oxidation

Hot reaction:

- $Cl_2(0) \longrightarrow Cl^-$ (−1) = reduction
- Cl_2 (0) $\longrightarrow ClO_3^-$ (+5) = oxidation
- In both reactions, chlorine is oxidized and reduced — a disproportionation reaction.

DESCRIPTIVE QUESTIONS

Q.3 Describe and explain the relative thermal stabilities of the halogen hydrides in terms of bonds strength.

Ans. See Page No. (450)

Q.4 Discuss the relative reactivity of the halogen elements as oxidizing agents. Arrange F_2, Cl_2, Br_2, I_2 in increasing order of the oxidizing power.

Ans. See Page No. (448)

Q.5 Discuss the reducing power of halide ions with relevant reactions. Also explain the factors affecting it.

Ans. See Page No. (452)

ADDITIONAL SLOs BASED MCQs

1. **Which halogen has greenish yellow colour?**
   A. F_2 B. Cl_2 C. Br_2 D. I_2
2. **Which halogen exist in liquid state?**
   A. F_2 B. Cl_2 C. Br_2 D. I_2
3. **Which of the following is a strongest reducing agent?**
   A. F^- B. Br^- C. Cl^- D. I^-
4. **Oxidizing power of which halogen is highest?**
   A. F_2 B. Cl_2 C. Br_2 D. I_2
5. **Which is strongest acid?**
   A. HF B. HCl C. HBr D. HI
6. **Highest electron affinity is shown by?**
   A. F B. I C. Br D. Cl
7. **Which is the strongest reducing agent?**
   A. HF B. HCl C. HI D. HBr
8. **Substance boiling at higher temperature among following is?**
   A. HI B. HF C. HCl D. HBr
9. **Group VII-A elements are generally called:**
   A. halogens B. noble gases C. inert gases D. metalloids
10. **The radioactive element in halogen group is:**
    A. radon B. radium C. astatine D. bromine

Answer Key with Explanations

Sr.#	Ans.	Explanations
1.	B	Chlorine (Cl_2) is a greenish-yellow gas.
2.	C	Bromine (Br_2) is the only halogen that exists as a liquid at room temperature.
3.	D	Iodide (I^-) is the strongest reducing agent among the halide ions due to its larger size and lower ionization energy, making it easier to donate electrons.
4.	A	Fluorine (F_2) has the highest oxidizing power among the halogens due to its high electronegativity and small atomic size.
5.	D	Hydroiodic acid (HI) is the strongest acid among the hydrohalic acids due to the weak bond between hydrogen and iodine, which makes it easier to dissociate in water.
6.	D	Electron affinity, of halogens is F (−322kJmol^{-1}), Cl (−349 kJ mol^{-1}), Br (−325 kJ mol^{-1}) and I (−295 kJ mol^{-1})
7.	C	HF, HCl, HBr and HI act as reducing agents in the following order: HF < HCl < HBr < HI
8.	B	The boiling points of hydrogen halides are as follow: HF = 19.5°C, HCl = −85.0°C, HBr = −66.7°C, HI = −35.3°C
9.	A	Group VIIA elements are called the halogens from Greek **hals, "salt"** and gennan, **"to form or generate"**, because they are literally the salt formers.
10.	C	**Astatine** is a rare halogen. It is radioactive and its most stable isotope has a half life of 8.3 hrs.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 The reducing power of halide ions decreases in the order: $I^- > Br^- > Cl^- > F^-$. Give reason.

Ans. Iodide is the best reducing agent due to its large size and low electronegativity, making electron loss easier. Fluoride, being small and highly electronegative, holds its electrons tightly and resists oxidation. As size increases and electronegativity decreases, the tendency to donate electrons (reducing power) increases.

Q.2 The thermal stability of hydrogen halides decrease down the group. Why?

Ans. The thermal stability of hydrogen halides decreases in the order: **HF > HCl > HBr > HI**.
This is because the **H–X bond strength decreases down the group**.
HF has the strongest bond due to the small size of fluorine, making it more stable to heat.
As the size of halogen increases from F to I, the H–X bond becomes weaker and easier to break on heating.

Q.3 Bond strength in halogens decreases as we move down the group from chlorine to iodine. WHY?

Ans. Bond strength in halogens decreases as we move down the group from chlorine to iodine. This is due to the increase in the atomic size down the group which results in longer bond lengths and weaker bonds. Moving from top to bottom in group 17, the bond energy of halogens decreases gradually from chlorine to iodine.

Q.4 The thermal stability of hydrogen halides decrease down the group. Why?

Ans. Halogens are non-polar and instantaneous dipole-induced forces play a significant role in determining the volatility of halogens. The forces depend on factors like molecular size, shape and polarizability, with stronger forces leading to lower volatility and higher boiling points. The first two halogens, i.e., fluorine (colourless or very light green) and chlorine (greenish yellow) are gases due to weaker id-id forces. Bromine is a liquid as its size is bigger and it possesses stronger intermolecular forces than fluorine and chlorine. Iodine has the strongest forces among the group, so it is in solid state at room temperature.

Q.5 The reactivity of halogens with hydrogen decreases down the group. Why?

Ans. The reactivity of halogens with hydrogen decreases down the group: $F_2 > Cl_2 > Br_2 > I_2$.
This is because **bond dissociation energy of H–X decreases** and **halogens become less electronegative** down the group.
Fluorine forms a strong H–F bond and is highly reactive due to its small size and high electronegativity.
As we move down, halogens form weaker H–X bonds and react less readily with hydrogen.

Q.6 What is disproportionation reaction?

Ans. Those reactions in which a single element undergoes both oxidation and reduction simultaneously are known as disproportionation reactions. When chlorine reacts with cold and hot aqueous sodium hydroxide (NaOH), it undergoes disproportion and form different products according to the temperature of the reaction.

Q.7 The thermal stability of hydrogen halides decrease down the group. Why?

Ans. Chlorine undergoes disproportion when it reacts with cold aqueous sodium hydroxide (NaOH) forming sodium chloride (NaCl) and sodium chlorate (I) (NaClO).

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

Oxidation states of chlorine in the above reaction are given below:

Chlorine in Cl_2 = 0
Chlorine in NaCl = –1
Chlorine in NaClO = +1

Q.8 what happens when chlorine react with water?

Ans. When chlorine gas (Cl_2) is added to water, it undergoes hydrolysis to form a mixture of hydrochloric acid (HCl) and chloric (I) acid (HClO).

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

Chloric (I) acid (HOCl) is a weak acid and partially dissociate in water to form hydrogen ions (H^+) and chlorate (I) ion (OCl^-).

Q.9 How do pH and chlorine dose affect the disinfection?

Ans. **pH:**
At pH around 6-7.5, HOCl predominates and makes the disinfection process more effective.
At higher pH (above 7.5), OCl^- predominates, it is less effective but still provides disinfection.
Chorine Dose:
The higher the amount of chlorine, the more effective the disinfection. Sufficient chlorine must be added to get enough HOCl and OCl^- to kill bacteria.
Contact Time:
Contact time of water with chlorine must be long enough, to allow the disinfectants to penetrate and kill bacteria, viruses and protozoa.

Q.10 Write reaction of halides with conc. sulphuric acid.

Ans. Halides react differently with concentrated sulphuric acid (H_2SO_4) depending on their nature:

Fluoride (F^-) and Chloride (Cl^-):
Act as acids only — produce HF or HCl gas.
Example:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$

Bromide (Br^-) and Iodide (I^-):
Act as reducing agents — reduce H_2SO_4 and are oxidized to Br_2 or I_2.
Example:

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$
$$8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O$$

Trend: Reducing ability increases from $Cl^- < Br^- < I^-$.