



Chapter # 13

Halogens



- 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).
- These are very reactive non-metals. These have quite similar chemical properties.
- First four elements are the common elements of the halogen family
- The last two astatine (At) and tennessine (Ts) are very rare and radioactive elements.
- Halogens exist as separate diatomic molecules in all phases (gas, liquid or solid).
- Fluorine (F_2) and chlorine (Cl_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 vapor.
- The colors of halogens (X_2) darken gradually from chlorine to iodine. This is due to changes in the absorption of light. The light absorption depends upon electron transitions within the molecules of halogens.

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.

Although chlorine is poisonous but small amount is essential to human health and life in the form of chloride.

Table: Atomic and Physical properties of the common halogens.

Element	Flourine	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	$2s^2 2p^5$	$2s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$
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 vaporisation /kJ / mol ⁻¹	+3.3	+10.2	+15	+30
Solubility/g per 100g of water at 20°C	reacts readily with water	0.59 (reacts slightly)	3.6	0.018



VOLATILITY OF CHLORINE, BROMINE AND IODINE

- Chlorine is a gas. So, it is very volatile at room temperature. It disperses quickly in the air.
- Bromine is a liquid. So, it is less volatile than chlorine but more volatile than iodine. It evaporates readily giving toxic fumes at room temperature.
- Iodine is a solid. So, it is least volatile. At room temperature, it shows lower volatility than chlorine and bromine.

Short Question

Volatility decreases from chlorine to iodine

- Generally, volatility decreases from chlorine to iodine. It is because down the group molecular mass and size of outer shell increases. Thus, strength of intermolecular forces (London dispersion forces) increases down the group in the periodic table.

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

TREND IN VOLATILITY OF THE HALOGENS

- Halogens are non-polar. In these instantaneous dipole-induced forces (id-id or London dispersion forces) are significant. These forces play role in determining the volatility of halogens.
- The id-id forces depend on molecular size, shape and polarizability.
- Larger the size, higher the polarizability, stronger the id-id forces and thus lower the volatility.
- In halogens, atomic size increases down the group. Thus, polarizability increases and id-id forces also increases. Hence, volatility of halogens decreases and boiling points increases down the group.

Generally

- ✓ Substances with weak id-id forces, smaller and less polarizable molecule have lower boiling points and higher volatility.
- ✓ Substances with stronger id-id forces, bigger and more polarizable molecule 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.

Short Question

Physical state of halogens changes down the group

- 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 because its size is bigger and so 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.

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



Quick Check 13.1

a) Which halogen elements are radioactive?

Astatine (${}_{85}\text{At}$) and tennessine (${}_{117}\text{Ts}$) are radioactive halogen elements.

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

Fluorine (F_2) and chlorine (Cl_2) are pale yellow and greenish yellow gases respectively.

Bromine (Br_2) is a volatile liquid of reddish-brown colour.

Iodine (I_2) is shiny greyish black solid

The colors of halogens (X_2) darken gradually from chlorine to iodine. This is due to changes in the absorption of light. The light absorption depends upon electron transitions within the molecules of halogens.

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

Halogens are non-polar. In these instantaneous dipole-induced forces (id-id or London dispersion forces) are significant. These forces depend upon molecular size. Greater the molecular size, stronger the forces.

Chlorine is smaller in size so it has weaker id-id forces. Thus, it is more volatile than bromine and iodine.

The size of these halogens is in the order $\text{Cl} < \text{Br} < \text{I}$. Thus, volatility order is: $\text{Cl} > \text{Br} > \text{I}$



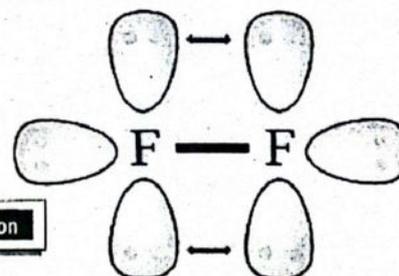
THE BOND STRENGTH OF HALOGEN MOLECULES

- In halogens, bond strength decreases down the group.

Short Question

It is because atomic size increases down the group. Thus, bonds become longer and weaker down the group. Hence, in group 17, the bond energy of halogens decreases gradually from chlorine to iodine.

However, fluorine is an exception.



- Fluorine has weakest bond strength than other halogens.

Short Question

It is because fluorine atoms are very small. So, the lone pairs on the fluorine atoms are close to each other and has significant electron-electron repulsions. This weakens the bond although fluorine has high electronegativity.

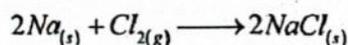
Table: Bond energies of halogen molecules

Halogen Molecules	Bond Energy (kJ/mol)
F_2	156
Cl_2	243
Br_2	193
I_2	151

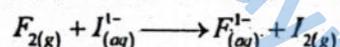
RELATIVE REACTIVITIES OF THE HALOGENS AS OXIDIZING AGENTS

- All the free halogens act as oxidizing agents.
- They react with metals and most of non-metals.
- They form ionic compounds with metals. The halogens gain electrons and are converted to negative halide ions.

Exercise Q 4: Long Q



- The oxidizing power of halogens decreases down the group. The order of decreasing power as an oxidizing agent is $F_2 > Cl_2 > Br_2 > I_2$.
- The reactivity of halogens is directly related to gain electron and form halide ions (F, Cl, Br and I).
- Fluorine has the highest ability to gain an electron and form fluoride ion. So, the oxidizing power of F_2 is the highest and that of I_2 is the lowest.
- Fluorine molecule can oxidize and displace all the halide ions from their solutions (Cl-, Br- and I-) to free halogens.



Short Question

Fluorine can displace all halides ions from their solution. Why?

- Similarly, 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 measured by standard electrode potential (E°) values.
- The standard electrode potential $E^\circ(X_2 / X^-)$ for halogens become less positive from fluorine to iodine.
- This shows the decreasing oxidizing power.
- Fluorine is the most reactive halogen. It is the most powerful oxidizing agent.

Factors affecting oxidizing power

The oxidizing power of halogens depends upon various factors,

- i) energy of dissociation
- ii) electron affinity of atoms
- iii) hydration energies of ions
- iv) 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.

Short Question

What factors affect the oxidizing power of halogens?

Halogens Molecule (X_2)	Standard reduction potential, $E^\circ(V)$
F_2	+2.87
Cl_2	+1.36
Br_2	+1.07
I_2	+0.54

Quick Check 13.2

a) The F-F bond is weaker than Cl-Cl bond although fluorine is the most electronegative element, Explain.

It is because fluorine atoms are very small. So, the lone pairs on the fluorine atoms are close to each other and has significant electron-electron repulsions. This weakens the bond although fluorine has high electronegativity. Thus, F-F bond is weaker than Cl-Cl bond.



b) Is the reaction between $\text{NaCl}_{(aq)}$ and F_2 gas possible?

i) Give reason whether yes or no.

Yes, the reaction between $\text{NaCl}_{(aq)}$ and F_2 gas is possible

Fluorine has the highest ability to gain an electron and form fluoride ion. So, the oxidizing power of F_2 is the highest. Fluorine molecule can oxidize and displace all the halide ions from their solutions (Cl^- , Br^- and I^-) to free halogens.

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



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

The standard electrode potential $E^\circ (X_2 / X^-)$ for halogens become less positive from fluorine to iodine.

This shows the decreasing oxidizing power.

Fluorine is the most reactive halogen. It is the most powerful oxidizing agent.

ADDITIONAL MCQs

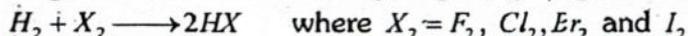
(Answers on Page 428)

- Which group in the periodic table contains the halogens?
(A) Group 15 (B) Group 16 (C) Group 17 (D) Group 18
- Which of the following halogens is a liquid at room temperature?
(A) Chlorine (B) Bromine (C) Fluorine (D) Iodine
- Which halogen is a shiny greyish-black solid that sublimes to violet vapor?
(A) Fluorine (B) Chlorine (C) Bromine (D) Iodine
- What causes the color of halogens to darken from chlorine to iodine?
(A) Increase in molecular polarity (B) Decrease in density
(C) Change in electron transitions (D) Decrease in atomic size
- Why is iodine less volatile than chlorine?
(A) Lower boiling point (B) Stronger London dispersion forces
(C) Weaker bond energy (D) Lower molecular mass
- Which of the following halogens molecule has the weakest bond strength?
(A) Chlorine (B) Iodine (C) Fluorine (D) Bromine
- What is the correct order of oxidizing power among halogens?
(A) $\text{I}_2 > \text{Br}_2 > \text{Cl}_2 > \text{F}_2$ (B) $\text{Cl}_2 > \text{F}_2 > \text{Br}_2 > \text{I}_2$ (C) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (D) $\text{Br}_2 > \text{I}_2 > \text{F}_2 > \text{Cl}_2$
- Why does fluorine have weaker bond strength than chlorine?
(A) High electronegativity (B) High polarizability
(C) Electron-electron repulsions (D) Weak nuclear attraction
- Which halogen can oxidize all the other halide ions?
(A) Chlorine (B) Bromine (C) Iodine (D) Fluorine
- What does the term "halogen" literally mean?
(A) Salt remover (B) Salt producer (C) Metal binder (D) Acid former
- Which of the following factors does NOT directly affect the oxidizing power of halogens?
(A) Hydration energy (B) Atomic number (C) Electron affinity (D) Dissociation energy



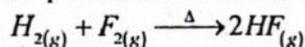
REACTION WITH HYDROGEN

- When halogen elements react with hydrogen, hydrogen halides are produced.



- Hydrogen halides are colourless gases. These dissolve in water to form hydrohalic acid.
- The reactivity order of halogens with hydrogen decreases as $F_2 > Cl_2 > Br_2 > I_2$

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



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

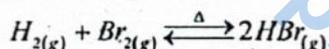
Short Question
How does fluorine react with hydrogen?

- In the presence of UV light or a spark, chlorine reacts readily with hydrogen. A colourless gas is produced which is dissolved in water to form hydrochloric acid.

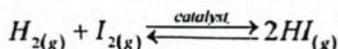


Short Question
How does chlorine react with hydrogen?

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



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

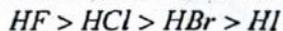


Short Question
How does iodine react with hydrogen?

- This is a reversible reaction and occurs very slowly.

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

- The thermal stabilities of hydrogen halides (H-X) decrease down the group.
- It is due to decrease in bond dissociation energies.



Exercise Q 3: Long Q

- Hydrogen fluoride (HF) is the most thermally stable hydrogen halide.**

It is due to the high electronegativity and small atomic radius of fluorine. Thus, a strong overlap of orbitals produces a very strong H-F bond. The bond dissociation energy of H-F is the highest among the hydrogen halides. Its bond dissociation energy is 569 kJ/mol.

Short Question

- HCl is less thermally stable than HF but more stable than other HBr and HI.**

It is because chlorine has less electronegativity and larger atomic radius than fluorine. Thus, overlap of orbitals is comparatively weaker. Hence, H-Cl bond is weaker than H-F bond. Its bond dissociation energy is 431 kJ/mol.

Short Question

- Hydrogen bromide (H-Br) bond is weaker than H-F and H-Cl**

It is due to the larger atomic radius of bromine. Thus, there is a reduced overlapping of orbitals. Its bond dissociation energy is 366 kJ/mol.

Short Question



• **Hydrogen iodide HI is the least thermally stable.**

It is because 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.

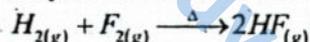
Table: The Bond dissociation energy of H-X bonds

Hydrogen Halide (HX)	Bond Dissociation energy (kJmol ⁻¹)
H-F	569
H-Cl	431
H-Br	366
H-I	299

Quick Check 13.3

- a) **The reaction between H₂ and F₂ is explosive but that between H₂ and I₂ is slow and reversible. Explain why.**

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



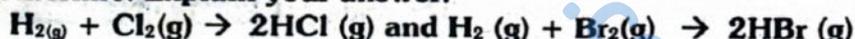
It is because, F₂ has very low bond dissociation energy. So, it reacts explosively. The bond between HF is very strong so it is not broken easily. Thus, the reaction is not reversible.

The reaction of H₂ and I₂ is slow because I-I bond has relatively higher bond dissociation energy.

The HI formed has very low bond dissociation energy. Thus, it dissociates into H₂ and I₂ and reaction becomes reversible.

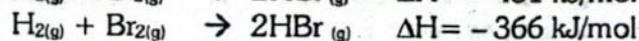
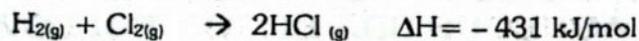


- b) **Refer to Table 13.4 and 13.5 to predict which of the following reactions would be more exothermic. Explain your answer.**



The bond dissociation energies of HCl and HBr are 431 and 366 kJ/mol respectively.

Hence, when these compounds are formed then same amount of energy will be released. So,



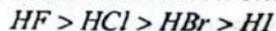
Thus, formation of HCl is more exothermic

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

The thermal stabilities of hydrogen halides (H-X) decrease down the group.

It is due to decrease in bond dissociation energies.

Hence, bond dissociation energy and stability order is:



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

It is due to the high electronegativity and small atomic radius of fluorine. Thus, a strong overlap of orbitals produces a very strong H-F bond. The bond dissociation energy of H-F is the highest among the hydrogen halides. Its bond dissociation energy is 569 kJ/mol

THE RELATIVE REACTIVITY OF HALIDE IONS AS REDUCING AGENTS

The reducing ability of halide ions increases as we move down the group from fluorine to iodine.

- It is because, electronegativity decreases and atomic radius increases down the group. This results in lower charge density and greater ease of electron donation.
- Fluoride ion is the weakest reducing agent while iodide is much stronger reducing agent.
- The order of decreasing power as a reducing agent is $I^- > Br^- > Cl^- > F^-$.

Exercise Q 6: Long Q

Reducing Strength of fluoride ion (F^-)

- The high electronegativity of fluorine and the strong bond and extra electrons make it difficult for fluoride ion (F^-) to donate electrons. The small size of fluoride ion results in a high charge density. This further stabilizes the fluoride ion. Thus it reduces its tendency to lose an electron.

Reducing Strength of Chloride ion (Cl^-)

- Chloride ion (Cl^-) is a stronger reducing agent than fluoride ion but weaker than bromide and iodide.
- Chlorine is less electronegative than fluorine so it is easier for chloride ion (Cl^-) to donate electrons.
- Chloride ion is less stable than fluoride ion due to its larger ionic radius. This decreases the charge density. Thus, Chloride ion acts as a reducing agent.

Reducing Strength of Bromide ion (Br^-)

- 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. Thus, it easily loses an electron and acts as a reducing agent.

Reducing Strength of Iodide ion (I^-)

- 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. Thus it has high tendency to donate an electron. Hence, it is strong reducing agent.

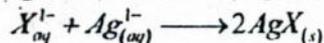
Short Question

Iodide ion is the strongest reducing agent among halide ions. Why?

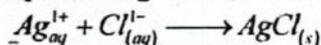
REACTIONS OF HALIDES WITH AQUEOUS SILVER ION FOLLOWED BY AQUEOUS AMMONIA

Reactions of halides with aqueous silver ion

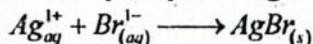
- When halide ions react with aqueous silver nitrate ($AgNO_3$), insoluble silver halides (AgX) are formed.
- These reactions are used in qualitative analysis to identify halide ions.
- The general reaction is given below:



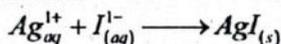
- No visible reaction occurs when silver ions and fluoride ions are mixed in the aqueous medium.
- Silver fluoride is soluble in water. Thus, Fluoride (F^-) does not form precipitate as silver fluoride.
- On mixing of aqueous silver ions with aqueous chloride ions, a white precipitate of silver chloride forms. The precipitates $AgCl$ are soluble in dilute ammonia.



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



- On mixing of aqueous silver ions with aqueous iodide ions, a yellow precipitate of silver iodide forms. The precipitates AgI is insoluble in ammonia.



- These reactions is used to identify halide ions and is called silver nitrate test.**
- Silver nitrate aqueous solution followed by aqueous ammonia solution can be used as a test for halide ions.**

Short Question

Why yellow ppt. are formed when AgNO₃ is added to aq. iodide ions?

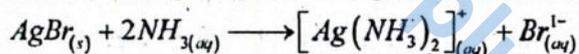
Reaction of silver halides (AgX) with aqueous ammonia

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.
- AgCl dissolves in dilute ammonia to form diamminesilver(1) complex. The white precipitate of AgCl dissolves in dilute ammonia forming a colourless solution.



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



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

Short Question

Why AgCl ppt. dissolve in ammonia solution?

Table: Action of Ag⁺ followed by ammonia on silver halides

Halide ion	Action of aq. Ag ⁺ ion	Action of ammonia
Fluoride ion (F ⁻)	No precipitate with	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

Quick Check 13.4

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

The reducing ability of halide ions increases 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.

Hence, F⁻ ion is a weaker reducing agent than Cl⁻



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

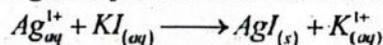
The different solubilities of silver halides in ammonia are due to:

- The difference in lattice energies of AgX,
- The solubility product (K_{sp}),
- And the stability of the [Ag(NH₃)₂]⁺ complex ion.

These factors together make AgCl dissolve easily, AgBr dissolve a little, and AgI remain insoluble in ammonia.

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?

On mixing of aqueous silver ions with aqueous KI, a yellow precipitate of silver iodide forms.



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

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

- The reactions of halide ions with concentrated sulfuric acid are different from each other.
- The nature of the product and nature of reaction changes down the group from fluoride to iodide.

• Reaction with fluoride

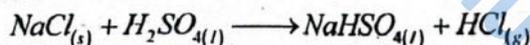
Fumes of hydrogen fluoride gas are produced when concentrated sulfuric acid reacts with NaF. No redox reaction occurs. HF is not a strong reducing agent.



• Reaction with chloride

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

Hydrogen chloride is not a strong reducing agent. No redox reaction occurs.



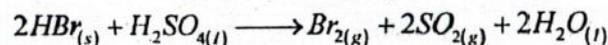
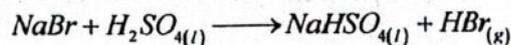
Short Question

The reaction of chloride with sulfuric acid is not a redox reaction. Justify?

• Reaction with bromide

In case of Br^- 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 and reduces sulfuric acid to sulfur dioxide. It is self-oxidized to bromine.



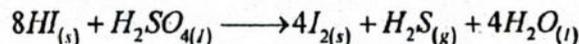
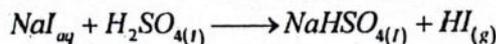
Short Question

The reaction of bromide with sulfuric acid is a redox reaction. Justify?

• Reaction with iodide

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 itself is oxidized to I_2 .



- The reducing power of halides ions increases from fluoride to iodide. Thus, bromides and iodides give more complex reactions with concentrated sulfuric acid.

12. What is the product when halogens react with hydrogen?
(A) Hydrogen oxides (B) Hydrogen halides (C) Halogen acids (D) Hydroxides
13. Which hydrogen halide is formed explosively at room temperature and in the dark?
(A) HCl (B) HBr (C) HI (D) HF
14. Which hydrogen halide is least thermally stable?
(A) HF (B) HCl (C) HBr (D) HI
15. What is the correct order of thermal stability of hydrogen halides?
(A) HI > HBr > HCl > HF (B) HF > HCl > HBr > HI
(C) HBr > HCl > HI > HF (D) HCl > HF > HBr > HI
16. Which halide ion is the strongest reducing agent?
(A) F⁻ (B) Cl⁻ (C) Br⁻ (D) I⁻
17. Which halide forms a white precipitate with silver nitrate that dissolves in dilute ammonia?
(A) Cl⁻ (B) Br⁻ (C) I⁻ (D) F⁻
18. Which silver halide precipitate is yellow and insoluble in ammonia?
(A) AgCl (B) AgBr (C) AgI (D) AgF
19. What is observed when NaBr reacts with concentrated sulfuric acid?
(A) Only HBr fumes (B) No reaction (C) HBr and brown Br₂ fumes (D) Only SO₂ is released
20. What happens when silver nitrate is added to a solution containing fluoride ions?
(A) White precipitate forms (B) Yellow precipitate forms (C) No visible reaction (D) Gas is released
21. Which of the following halide ions reacts with concentrated sulfuric acid to produce purple iodine vapors?
(A) F⁻ (B) Cl⁻ (C) Br⁻ (D) I⁻

Exercise Q 5: Long Q

REACTIONS OF CHLORINE WITH COLD AND HOT AQUEOUS SODIUM HYDROXIDE

The reactions in which a single element undergoes both oxidation and reduction simultaneously are known as disproportionation reactions.

A disproportionation reaction is one in which a particular molecule, atom or ion is simultaneously oxidized and reduced.

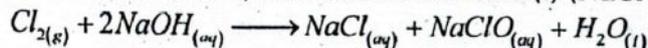
Short Question

What is a disproportionation reaction? Give an example

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.

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).



Oxidation states of chlorine in the above reaction are:

Chlorine in Cl₂ = 0

Chlorine in NaCl = -1

Chlorine in NaClO = +1

Thus,

Chlorine in Cl₂ is oxidized from 0 to +1 in NaOCl.

Chlorine in Cl₂ is reduced from 0 to -1 in NaCl.

The above reaction shows the simultaneous oxidation and reduction of chlorine. It is an 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 (NaClO_3).



Chlorine in $\text{Cl}_2 = 0$

Chlorine in NaCl = -1

Chlorine in $\text{NaClO}_3 = +5$

Thus,

Chlorine is oxidized from 0 to +5 in NaClO_3 .

Chlorine is reduced from 0 to -1 in NaCl

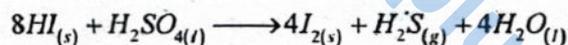
The above reaction shows the simultaneous oxidation and reduction of chlorine. It is an example of disproportionation reaction.

This disproportionation reaction shows that the temperature of the reaction influences the products formed. This shows 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?

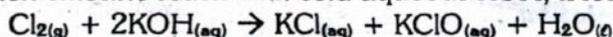
When concentrated sulfuric acid reacts with KI, fumes of hydrogen iodide gas, purple fumes of solid iodine I_2 and smell of H_2S gas produced. HI acts as a strong reducing agent. It reduces H_2SO_4 to H_2S and itself is oxidized to I_2 .



b) Show that the reaction of Cl_2 with cold and hot aqueous KOH is a disproportionation reaction.

Reaction with cold aqueous potassium hydroxide

When chlorine reacts with cold aqueous KOH, it forms KCl and KClO.



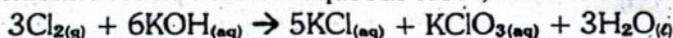
Chlorine in Cl_2 is oxidized from 0 to +1 in KClO.

Chlorine in Cl_2 is reduced from 0 to -1 in KCl.

This shows the simultaneous oxidation and reduction of chlorine. So it is a disproportionation reaction.

Reaction with hot aqueous potassium hydroxide

When chlorine reacts with hot aqueous KOH, it forms KCl and KClO_3 .



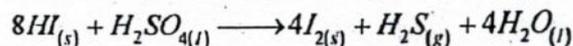
Chlorine is oxidized from 0 to +5 in KClO_3 .

Chlorine is reduced from 0 to -1 in KCl.

This shows the simultaneous oxidation and reduction of chlorine. So it is a disproportionation reaction.

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

HI acts as a strong reducing agent. It reduces H_2SO_4 to H_2S and itself is oxidized to I_2 .

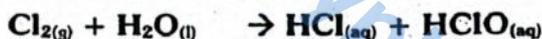


USE OF CHLORINE IN WATER PURIFICATION

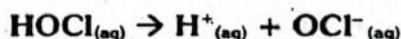
- Chlorine gas is very poisonous. It is harmless to human being when used in very small quantities. However it is still poisonous to the bacteria which cause diseases.
- Due to its strong disinfectant properties, chlorine is widely used at the treatment plants for water purification.
- The process involves adding chlorine to water. In water it forms active species that kill bacteria and other pathogens.
- Water in the swimming pools is also chlorinated with slightly higher concentrations of chlorine because there is likely to be a higher concentration of bacteria in the water.
- The primary active species for disinfection 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 (Cl₂) is added to water, it undergoes hydrolysis to form a mixture of hydrochloric acid (HCl) and chloric (I) (HClO).



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



Short Question

How HOCl or OCl⁻ disinfect water?

Disinfection Activity

- HOCl and OCl⁻ are effective disinfectants. HOCl is more effective due to its neutral charge.
- The neutral charge of HOCl allows to penetrate the cell walls of micro-organisms easily.
- HOCl and OCl⁻ disinfect water by oxidizing
 - ✓ Essential cellular components e.g. proteins and lipids. This disrupt the cell function and cause cell death.
 - ✓ Inactivate enzymes that are crucial for survival and replication of bacteria.
 - ✓ Nucleic acids (DNA and RNA) thus preventing bacteria from replicating and vital cellular functions.

Factors affecting disinfection

1. pH

- i). At pH around 6-7.5, HOCl predominates, It makes the disinfection process more effective.
- ii). At higher pH (above 7.5), OCl⁻ predominates. It is less effective but still provides disinfection.

Short Question

How pH and chlorine dose affect the disinfection process by chlorine?

2. Chlorine 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.

3. Contact time

Contact time of water with chlorine must be long enough 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?

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. Thus, it disrupt the cell function leading to cell death.



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

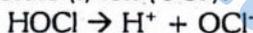
The factors which affect disinfection of water by chlorine are:
pH, Chlorine dose and Contact time

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

When chlorine gas (Cl₂) is added to water, it undergoes hydrolysis to form a mixture of hydrochloric acid (HCl) and chloric (I) (HOCl).



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



ADDITIONAL MCQs

(Answers on Page 428)

22. What type of reaction occurs when chlorine reacts with cold aqueous sodium hydroxide?

(A) Neutralization (B) Displacement (C) Disproportionation (D) Combination

23. In the reaction of chlorine with cold NaOH, chlorine is oxidized to which product?

(A) NaCl (B) NaClO (C) NaClO₂ (D) Cl₂

24. When chlorine reacts with hot aqueous sodium hydroxide, what is the oxidation state of chlorine in sodium chlorate (NaClO₃)?

(A) -1 (B) 0 (C) +1 (D) +5

25. Which species formed during chlorination is more effective at killing bacteria?

(A) Cl₂ (B) HCl (C) HOCl (D) OCl⁻

26. At what pH is the disinfection activity of chlorine most effective?

(A) Below 5 (B) Around 6-7.5 (C) 8-9 (D) Above 10

27. Which factor does NOT directly affect chlorine's disinfection ability?

(A) pH (B) Contact time (C) Sunlight (D) Chlorine dose

ANSWERS TO ADDITIONAL MCQs

Q#	Ans														
1	C	2	B	3	D	4	C	5	B	6	C	7	C	8	C
9	D	10	B	11	B	12	B	13	D	14	D	15	B	16	D
17	A	18	C	19	C	20	C	21	D	22	C	23	B	24	D
25	C	26	B	27	C										



Exercise

Q1 MULTIPLE CHOICE QUESTIONS

- 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^- c) 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.

ANSWERS TO MULTIPLE CHOICE QUESTIONS

No.	Ans	EXPLANATION
I.	D	F_2 has very low bond energy due to small size and high electronegativity. After that the bond energy decreases down the group in the order $Cl_2 > Br_2 > I_2$. Hence, Cl_2 has the strongest bond.
II.	B	It is because down the group atomic size increases, so polarizability increases. The forces becomes stronger, thus volatility decreases.
III.	B	F_2 has highest reduction potential. Thus, it is the best oxidizing agent among halogens
IV.	C	Down the group atomic size increases, so the bond length increases. Hence, bond becomes weaker down the group and stability decreases. F_2 is exception. It has lowest bond energy among halogens due to small size and high electronegativity.



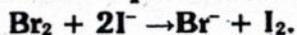
V.	D	I ⁻ ion is the strongest reducing agent. It is because, it can give electrons relatively easy due to bigger size and less electronegativity of iodine.
VI.	C	Fluorine is the most reactive among halogens. So, it combine explosively with hydrogen.
VII.	C	Down the group atomic size increases and electronegativity of halogens decreases. Thus, the bond strength of HX decreases in the order HF > HCl > HBr > HI. Thus, HI readily donates proton hence it is the strongest acid.
VIII.	B	F ₂ has very low bond energy due to small size and high electronegativity. Hence, due to low bond dissociation energy, it is the most reactive among halogens.
IX.	B	Silver nitrate reacts with bromide ions to give AgBr which is partially soluble in ammonia solution.
X.	C	Steamy white fumes of HCl are evolved. $2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$

Q2 SHORT QUESTIONS

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

The reactivity of halogens is directly related to gain electron and form halide ions (F⁻, Cl⁻, Br⁻ and I⁻). Fluorine has the highest ability to gain an electron and form fluoride ion. Also, F-F bond is weakest bond than other halogens. So, F₂ is most reactive. Iodine has the least ability to gain an electron and form iodide ion so I₂ is the least reactive.

b. The ionic equation for a reaction is:



Explain which species is oxidized in this reaction. Why?

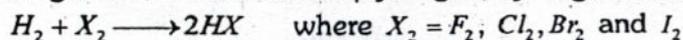
In this reaction, the oxidation state of iodine changes from -1 in I⁻ to zero in I₂. So, iodine has lost electrons. Hence, it is oxidized by Br₂.

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

Halogens are non-polar. In these instantaneous dipole-induced forces (id-id or London dispersion forces) are significant. The id-id forces depend on molecular size, shape and polarizability. Greater the size, higher the polarizability, stronger the id-id forces and thus lower the volatility. In halogens, atomic size increases down the group. Thus, polarizability increases and id-id forces also increases. Hence, volatility of halogens decreases down the group.

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

When halogen elements react with hydrogen, hydrogen halides are produced.



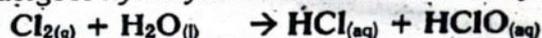
The reactivity order of halogens with hydrogen decreases as $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

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

I₂ is used as antiseptic. Iodine acts by penetrating microbial cell walls and disrupting proteins and nucleic acids. It oxidizes cellular components leading to cell death.

Cl₂ is also antiseptic. However, it is generally used for disinfection of water.

Cl₂ undergoes hydrolysis to form a mixture of hydrochloric acid (HCl) and chloric (I) (HOCl).

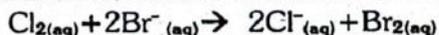


HOCl partially dissociate in water to form hydrogen ions (H⁺) and OCl⁻ ions.

- HOCl and OCl⁻ disinfect water by oxidizing cellular components leading to cell death.

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

When chlorine (Cl_2) is added to a solution containing bromide ions (Br^-), it displaces bromine (Br_2) because chlorine is more reactive and better oxidizing agent.

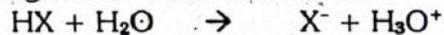


Before reaction, the solution is colourless because only bromide ions are present.

After reaction, bromine (Br_2) is formed. Thus, the solution turns reddish-brown due to formation of Br_2 .

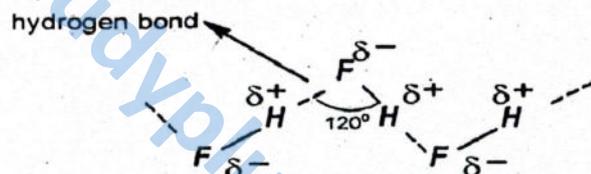
g. How the halogen acids are ionized in water?

Halogen acid ionize in water as:



h. Why HF is weaker acid than HCl?

In HF, molecules are H-bonded in a zigzag manner. Thus, H is entrapped between two F atoms as shown in the fig. Hence, HF cannot easily donate its H^+ ions easily, so it is a weaker acid.

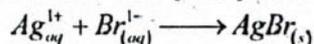


i. Describe a simple chemical test that could be used to distinguish between aqueous solutions of potassium bromide and potassium iodide. Include the reagents and expected observations.

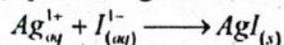
When halide ions react with aqueous silver nitrate (AgNO_3), Insoluble silver halides (AgX) are formed

These reactions are used in qualitative analysis to identify halides ions.

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

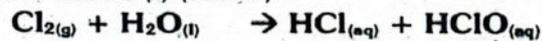


- On mixing of aqueous silver ions with aqueous iodide ions, a yellow precipitate of silver iodide forms. The precipitates AgI is insoluble in ammonia.



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

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



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



HOCl and OCl^- disinfect water by oxidizing

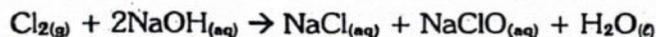
- ✓ Essential cellular components e.g. proteins and lipids. This disrupt the cell function and cause cell death.
- ✓ Inactivate enzymes that are crucial for survival and replication of bacteria.
- ✓ Nucleic acids (DNA and RNA) thus preventing bacteria from replicating and vital cellular functions.

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

- Chlorine gas is harmless to human being in small quantities, but still poisonous to the bacteria. Thus, due to its strong disinfectant properties, chlorine is widely used for water purification
- Chlorination is a relatively inexpensive method of water disinfections

l. What is disproportionation reaction? Give an example.

Chlorine undergoes disproportionation when it reacts with cold aqueous KOH forming KCl and KClO.



- Chlorine in Cl_2 is oxidized from 0 to +1 in NaClO.
- Chlorine in Cl_2 is reduced from 0 to -1 in NaCl.

This shows the simultaneous oxidation and reduction of chlorine. So it is a disproportionation reaction.

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

Chlorine undergoes disproportionation when it reacts with cold aqueous KOH forming KCl and KClO.



When chlorine reacts with hot aqueous NaOH, it forms NaCl and NaClO_3 .

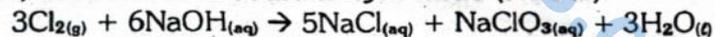


n. Write balanced chemical equations for the reaction of chlorine (Cl_2) with:

i. Cold, dilute sodium hydroxide (NaOH).



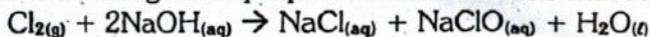
ii. Hot, concentrated sodium hydroxide (NaOH).



o. For each reaction in question l), 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.

Reaction with cold aqueous sodium hydroxide

Chlorine undergoes disproportionation when it reacts with cold aqueous KOH forming KCl and KClO.



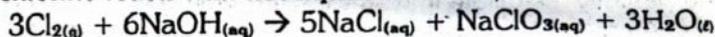
Chlorine in Cl_2 is oxidized from 0 to +1 in NaClO.

Chlorine in Cl_2 is reduced from 0 to -1 in NaCl.

This shows the simultaneous oxidation and reduction of chlorine. So it is a disproportionation reaction.

Reaction with hot concentrated potassium hydroxide

When chlorine reacts with hot aqueous NaOH, it forms NaCl and NaClO_3 .



Chlorine is oxidized from 0 to +5 in NaClO_3 .

Chlorine is reduced from 0 to -1 in NaCl.

This shows the simultaneous oxidation and reduction of chlorine. So it is a disproportionation reaction.

DESCRIPTIVE QUESTIONS

- Q.3** Describe and explain the relative thermal stabilities of the halogen hydrides in terms of bonds strength.
Page 420
- 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.
Page 418
- Q.5** Describe the reactions that occur when chlorine is bubbled through
(i) Cold and (ii) Hot, aqueous sodium hydroxide (NaOH).
Page 425-426
- Q.6** Discuss the reducing power of halide ions with relevant reactions. Also explain the factors affecting it.
Page 422

Tests MCQs

1. Which of the following element is not present in halogens? **MDCAT 2019**
(A) I (B) Cl (C) Fe (D) F
2. The strongest acid is: **MCAT 2010**
(A) HF (B) HBr (C) HCl (D) HI

ANSWERS															
Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	C	2	D												



Test Your Skills

OBJECTIVE: Time: 10 Minutes: Marks: 08

Q1. Choose the correct answer and encircle it.

- Which of the following hydrogen halide is the weaker acid in solution?
(A) HF (B) HBr (C) HI (D) HCl
- Which one of halogens is a liquid at room temperature?
(A) F₂ (B) Cl₂ (C) Br₂ (D) I₂
- When chlorine is reacted with NaOH at high temperature, the products formed are:
(A) NaCl + NaClO (B) NaCl + NaClO₃
(C) NaClO + NaClO₃ (D) NaCl + NaClO₄
- Hydrogen bond is the strongest between the molecules of:
(A) HCl (B) HF (C) HBr (D) HI
- Oxidation state of chlorine in HClO₄ is
(A) +7 (B) -7 (C) +1 (D) -1
- Which species are active in chlorine water for disinfection
(A) HOCl (B) OCl⁻ (C) both A and B (D) Cl₂
- Which of the following is the strongest reducing agent?
(A) HF (B) HBr (C) HI (D) HCl
- Which is most reactive?
(A) F₂ (B) Br₂ (C) I₂ (D) Cl₂

Fill in the correct option					Write Correct option here
1.	(A)	(B)	(C)	(D)	
2.	(A)	(B)	(C)	(D)	
3.	(A)	(B)	(C)	(D)	
4.	(A)	(B)	(C)	(D)	
5.	(A)	(B)	(C)	(D)	
6.	(A)	(B)	(C)	(D)	
7.	(A)	(B)	(C)	(D)	
8.	(A)	(B)	(C)	(D)	

SUBJECTIVE: Time: 60 minutes Marks: 32

Section - I

Q2. Answer the following short questions.

(2 × 12 = 24)

- What are disproportionation reactions? Explain your answer with an example.
- Halogens are strong oxidizing agents. Why?
- Why colours of halogens are different?
- Give reason why fluorine is a gas, iodine is solid?
- Why HF is weaker acid than HCl
- Name the factors on which oxidizing power of halogens depend?
- The reaction of NaBr with H₂SO₄ is a redox reaction. Justify
- HOCl is better than OCl⁻ ion to disinfect water?
- The volatility of halogens decreases down the group. Why?
- Differentiate between NaCl and NaI by a chemical test
- How does fluorine react with hydrogen?
- What are halogens? Why they are called so?
- What is the colour change when chlorine displaces bromide?
- How halogen acids ionize in water?

Section - II

(8 × 1 = 08)

- Q3. (a) What are disproportionation reactions? Explain your answer with an example.
(b) Explain the process of water disinfection by chlorination

(04)
(04)

ANSWERS TO MCQs: TEST YOUR SKILLS-I

Q#	Ans														
1	A	2	C	3	B	4	B	5	A	6	C	7	C	8	A

