



WEIRD CHEMIST

Group 17 Elements — The Halogens

Chapter: p-Block Elements

DPP-10

TOPIC 1 Introduction

(a) Elements, Nature & Occurrence

SKILL: Analytical Ability

Q1. The passage states that halogens show far greater similarity amongst themselves than the elements of most other groups. Which of the following best explains why this exceptional similarity exists? [JEE]

- (1) Because all halogens are gases at room temperature, and gaseous elements always behave similarly
- (2) Because all halogens share the same ns^2np^5 valence configuration — just one electron short of the next noble gas — so they share the same fundamental chemical drive (gaining one electron) and differ only in the size and energy of the orbital involved, producing strong and regular gradation rather than dramatic differences
- (3) Because halogens were all discovered at the same time and were classified together by convention rather than genuine chemical similarity
- (4) Because halogens are all diatomic molecules, and all diatomic elements always show greater group similarity than polyatomic ones

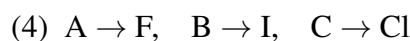
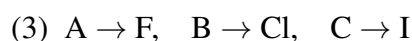
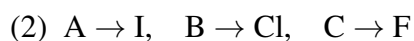
SKILL: Conceptual Clarity

Q2. The word ‘halogen’ has Greek origins. Which of the following correctly gives its meaning, and connects it to the chemistry of these elements? [NEET]

- | | |
|--|---|
| (1) “Fire maker” — because halogens react violently and exothermically with metals | (3) “Salt eater” — because halogens dissolve readily in sea water, which is salty |
| (2) “Colour bearer” — because all halogens are intensely coloured in their elemental state | (4) “Salt producer” — from Greek <i>halo</i> (salt) and <i>genes</i> (born), reflecting that halogens readily combine with metals to form salts |

SKILL: Application Skills

Q3. A chemist analyses three samples: Sample A is fluorspar (CaF_2); Sample B is carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$); Sample C is dried seaweed known to contain up to 0.5% iodine. Which option correctly matches each sample to the halogen most directly obtainable from it? [NEET]

**SKILL: Diagram-Based Visual Literacy**

Q4. The table below lists key occurrence facts for Group 17 elements. Based on this data, which statement is correctly supported? [JEE]

Element	Key natural sources
F	Fluorspar (CaF_2), cryolite (Na_3AlF_6), fluoroapatite ($3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$); soil, bones, teeth
Cl	Sea water (mainly NaCl , 2.5% by mass); carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in dried-up sea deposits
Br	Sea water (as bromides, along with Cl and I)
I	Seaweeds (up to 0.5%); Chile saltpetre (up to 0.2% NaIO_3)
At	Radioactive; no stable mineral sources

- (1) Fluorine occurs mainly in mineral ores while chlorine is found chiefly as dissolved salts in sea water and dry deposits; iodine's chief natural sources are seaweeds and Chile saltpetre
- (2) Fluorine is the most abundant halogen dissolved in sea water
- (3) Iodine is present in sea water in concentrations comparable to those of chlorine
- (4) Chlorine and bromine are both found mainly in seaweeds rather than in sea water

SKILL: Time Management and Strategic Thinking

Q5. Consider the following statements about Group 17 elements and select the option with the correct combination of true statements: [JEE]

- I. Astatine is a radioactive element.
- II. Halogens show less similarity amongst themselves than elements of most other groups.
- III. Fluorine and chlorine are fairly abundant, while bromine and iodine are present in smaller quantities.
- IV. Sea water is mainly a sodium chloride solution present at about 2.5% by mass.

- (1) I, II and III only (2) I, III and IV only (3) II, III and IV only (4) I, II, III and IV

TOPIC 2 Atomic Properties

(a)–(d) Electronic Configuration, Atomic Radii, Ionisation Enthalpy & Electron Gain Enthalpy

SKILL: Analytical Ability

Q6. The electron gain enthalpy of fluorine (-333 kJ mol^{-1}) is *less* negative than that of chlorine (-349 kJ mol^{-1}), even though fluorine sits higher in the group and generally has stronger nuclear-electron attraction. Which of the following correctly resolves this anomaly? [JEE]

- (1) Fluorine has a much higher ionisation enthalpy than chlorine, and ionisation enthalpy and electron gain enthalpy always move in opposite directions, so a higher IE automatically makes EGE less negative
- (2) Fluorine's $2p$ orbitals are very small and compact; when an incoming electron tries to enter this already electron-dense space, strong interelectronic repulsions in the congested $2p$ subshell reduce the net attraction experienced, making fluorine's electron gain enthalpy less negative than chlorine's
- (3) The general rule states that electron gain enthalpy always becomes less negative going up a group, so fluorine having the least negative value is simply the expected trend, not an anomaly
- (4) Fluorine and chlorine are both gases, and gaseous halogens always have identical electron gain enthalpies regardless of their position in the group

SKILL: Conceptual Clarity

Q7. Halogens have the most negative electron gain enthalpies among all elements in their respective periods. Which of the following correctly identifies the root cause? [NEET]

- (1) Because halogens have the highest atomic masses in their respective periods
- (2) Because their small atomic size means electrons are located far from the nucleus, reducing repulsion
- (3) Because halogens already have completely filled orbitals, so they accommodate extra electrons without any disruption to their existing configuration
- (4) Because their ns^2np^5 configuration is just one electron short of the stable noble gas configuration, giving them an exceptionally strong drive to gain one more electron and complete the octet

SKILL: Application Skills

Q8. The ionisation enthalpies of the halogens are: F = 1680, Cl = 1256, Br = 1142 and I = 1008 kJ mol^{-1} . Between which consecutive pair is the *largest* drop in ionisation enthalpy observed? [NEET]

- | | | | |
|-----------------------------|------------------------------|-----------------------------|--|
| (1) Br to I
(drop = 134) | (2) Cl to Br
(drop = 114) | (3) F to Cl
(drop = 424) | (4) Each consecutive
drop is roughly
equal |
|-----------------------------|------------------------------|-----------------------------|--|

SKILL: Diagram-Based Visual Literacy

Q9. The table below lists covalent radius and ionic radius (X^-) for four halogens. Based on this data, which statement is correctly supported? [JEE]

Property	F	Cl	Br	I
Covalent radius / pm	64	99	114	133
Ionic radius X^- / pm	133	184	196	220

- (1) For every halogen listed, the ionic radius (X^-) is substantially larger than the covalent radius, and both sets of radii increase regularly from F to I
- (2) The ionic radius is smaller than the covalent radius in all cases, since gaining an extra electron compresses the electron cloud inward
- (3) Fluorine's covalent radius is larger than chlorine's, because fluorine is at the top of the group
- (4) The covalent and ionic radii follow opposite trends down the group – as covalent radius increases, ionic radius decreases

SKILL: Time Management and Strategic Thinking

Q10. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. Halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge.
- II. The ionisation enthalpy of fluorine (1680 kJ mol^{-1}) is higher than that of chlorine (1256 kJ mol^{-1}).
- III. Chlorine has a more negative electron gain enthalpy than fluorine because of strong interelectronic repulsions in fluorine's small, compact $2p$ orbitals.
- IV. Electronegativity of halogens increases from fluorine to iodine going down the group.

- (1) I, II, III and IV
- (2) I, III and IV only
- (3) II and IV only
- (4) I, II and III only

TOPIC 3 Physical Properties

(a)–(f) Physical State, Boiling / Melting Point, Colour, Solubility & Bond Dissociation Enthalpy

SKILL: Analytical Ability

Q11. F_2 has a *smaller* bond dissociation enthalpy than Cl_2 , even though fluorine is a smaller atom and generally expected to form stronger bonds. From chlorine onwards the expected order holds: $Cl-Cl > Br-Br > I-I$. Which of the following correctly explains why F_2 is an exception? [JEE]

- (1) Fluorine is a gas at room temperature, and gaseous molecules always have weaker bonds than halogens that are liquid or solid
- (2) Fluorine's high electronegativity means it always forms weaker bonds with itself than with other elements
- (3) The lone pairs on the two fluorine atoms in F_2 are extremely close together because of fluorine's small size; the resulting strong electron–electron repulsion between these lone pairs weakens the

F–F bond, giving it a smaller dissociation enthalpy than Cl_2

- (4) F_2 actually has a larger bond dissociation enthalpy than Cl_2 ; the data only appears anomalous because of a measurement error

SKILL: Conceptual Clarity

Q12. All halogens are coloured. Which of the following correctly identifies the reason for their colour and correctly pairs at least two halogens with their actual colours? [NEET]

- (1) Halogens absorb radiation in the visible region, exciting outer electrons to higher energy levels; different quanta absorbed by different halogens produce different colours — F_2 is yellow and Cl_2 is greenish yellow
- (2) Halogens emit radiation in the visible region rather than absorbing it; the emitted light gives each its colour — F_2 is violet and I_2 is yellow
- (3) All halogens display the same greenish-yellow colour since they share the same valence shell configuration ns^2np^5
- (4) Halogens are coloured because they are all toxic; toxicity causes the colouration by reacting with the observer's eye

SKILL: Application Skills

Q13. A student adds small quantities of F_2 , Cl_2 , Br_2 and I_2 to separate beakers containing water, and then to separate beakers containing carbon tetrachloride (CCl_4). Which of the following correctly describes the observations? [NEET]

- (1) All four halogens dissolve freely in water and none dissolves in CCl_4
- (2) All four halogens are insoluble in water but dissolve readily in CCl_4
- (3) F_2 dissolves in CCl_4 to give a coloured solution; Br_2 and I_2 react vigorously with water
- (4) F_2 and Cl_2 react with water; Br_2 and I_2 are only sparingly soluble in water but dissolve in CCl_4 to give coloured solutions

SKILL: Diagram-Based Visual Literacy

Q14. The table below gives the physical state at room temperature and boiling point for Group 17 elements. Based on this data, which statement is correctly supported? [JEE]

Element	Physical state (298 K)	Boiling point / K
F_2	Gas	85
Cl_2	Gas	239
Br_2	Liquid	332
I_2	Solid	457

- (1) The physical states appear random with no trend down the group and boiling points decrease from F_2 to I_2

- (2) Physical state changes from gas $\rightarrow$ liquid $\rightarrow$ solid down the group and boiling points steadily increase, consistent with increasing atomic number and stronger intermolecular forces
- (3) Br_2 is a solid and I_2 is a liquid at room temperature, and all four boiling points are below 300 K
- (4) All halogens are gases at room temperature since they are all non-metallic elements

SKILL: Time Management and Strategic Thinking

Q15. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. The melting and boiling points of halogens steadily increase with atomic number.
- II. F_2 has a larger bond dissociation enthalpy than Cl_2 because fluorine is the lightest halogen.
- III. Bromine and iodine are only sparingly soluble in water but are soluble in organic solvents such as carbon tetrachloride and chloroform.
- IV. The colour of halogens arises from absorption of radiation in the visible region, which excites outer electrons to higher energy levels.

- (1) I, II, III and IV (2) II and IV only (3) I, III and IV only (4) I and II only

TOPIC 4 Chemical Properties

(a) Oxidation States, Oxidising Behaviour & Reaction with Water

SKILL: Analytical Ability

Q16. F_2 oxidises Cl^- , Br^- and I^- ions; Cl_2 oxidises Br^- and I^- but not F^- ; Br_2 oxidises only I^- . Which of the following best captures the underlying principle governing these displacement reactions? [JEE]

- (1) Any halogen can only oxidise fluoride ions, since fluorine is the most electronegative element and therefore always involved
- (2) A halogen can only oxidise the halide ion that is immediately above it in the group — never any other halide
- (3) A stronger oxidising halogen can oxidise the halide ions of weaker oxidising halogens (those of higher atomic number), because its greater tendency to gain electrons allows it to displace the less electron-hungry halogen from its salt
- (4) All halogens can oxidise all other halide ions, since they all belong to the same group and have the same oxidising strength

SKILL: Conceptual Clarity

Q17. Fluorine exhibits only the -1 oxidation state, whereas chlorine, bromine and iodine show -1 , $+1$, $+3$, $+5$ and $+7$ as well. Which of the following correctly explains why fluorine is restricted to -1 ? [NEET]

- (1) Fluorine's valence shell has no d orbitals; it cannot expand its octet beyond four electron pairs, and being the most electronegative element it never loses electrons to a more electronegative partner — so positive oxidation states are simply inaccessible to it
- (2) Fluorine has too many electrons in its valence shell, making it impossible to remove any of them under any conditions
- (3) Fluorine is a gas at room temperature, and gaseous non-metals can never exhibit positive oxidation states regardless of their electronic configuration
- (4) Fluorine has exactly the same ground-state configuration as chlorine, so they should always exhibit the same oxidation states

SKILL: Application Skills

Q18. Three halogens X , Y and Z are added separately to water. X is a vigorous enough oxidising agent to oxidise water itself, producing O_2 gas. Y reacts with water more gently to form a mixture of its hydrohalic acid (HY) and a hypohalous acid (HOY). Z 's reaction with water is non-spontaneous; in fact, Z 's halide ion can be oxidised by dissolved O_2 in acidic medium—exactly the reverse of what X does. Identify X , Y and Z . [NEET]

- (1) $X = Cl_2$, $Y = Br_2$, $Z = I_2$
- (2) $X = Br_2$, $Y = Cl_2$, $Z = F_2$
- (3) $X = I_2$, $Y = Cl_2$, $Z = F_2$
- (4) $X = F_2$, $Y = Cl_2$ or Br_2 , $Z = I_2$

SKILL: Diagram-Based Visual Literacy

Q19. The table below links the orbital excitation state of halogens (other than fluorine) to the number of unpaired electrons and the oxidation state that becomes accessible. Based on this table, which statement is correctly supported? [JEE]

Orbital state	Unpaired e^-	Oxidation state accessible
Ground state	1	-1 or +1
First excited state	3	+3
Second excited state	5	+5
Third excited state	7	+7

- (1) Fluorine can reach the third excited state to show a +7 oxidation state just like iodine
- (2) The maximum oxidation state of Cl, Br and I is +7, achieved in the third excited state; this is possible because they have accessible d orbitals — fluorine cannot reach this state since its $n = 2$ valence shell has no d orbitals
- (3) Only the ground-state configuration determines a halogen's oxidation state; excited states have no relevance to bonding
- (4) All halogens including fluorine can access all oxidation states shown in the table, since they all share the same ns^2np^5 configuration

SKILL: Time Management and Strategic Thinking

Q20. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. Fluorine is the strongest oxidising agent among all the halogens.
- II. Chlorine can oxidise bromide and iodide ions in aqueous solution or in the solid phase.
- III. Iodine reacts spontaneously with water to form HI and HOI.
- IV. In combination with oxygen or fluorine, chlorine and bromine can also exhibit +4 and +6 oxidation states in their oxides and oxoacids.

- (1) I, II and IV only (2) I, II, III and IV (3) II and III only (4) I, III and IV only

(b) Reactivity towards Hydrogen

SKILL: Analytical Ability

Q21. The acidic strength order $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ seems counterintuitive — fluorine is the most electronegative element, so HF might be expected to be the strongest acid. Which of the following correctly resolves this apparent contradiction? [JEE]

- (1) HF is the weakest acid because fluorine is so electronegative that it never permits the release of H^+ under any circumstances
- (2) HF is the weakest acid because its melting point (190 K) is higher than that of HCl (159 K), and compounds with higher melting points are always weaker acids
- (3) HF is weakest because the H–F bond is too short and weak compared to other hydrogen halides, making it reluctant to ionise
- (4) The H–F bond has the highest dissociation enthalpy (574 kJ mol^{-1}) and is the shortest; it is very difficult to break, so very little H^+ is released in water. As bond dissociation enthalpy decreases from HF to HI, the bond becomes progressively easier to break and acidity increases — making HI the strongest acid

SKILL: Conceptual Clarity

Q22. From Table 7.9, the boiling points of the hydrogen halides are: $\text{HF} = 293 \text{ K}$, $\text{HCl} = 189 \text{ K}$, $\text{HBr} = 206 \text{ K}$, $\text{HI} = 238 \text{ K}$. While HCl, HBr and HI show a steady increase, HF is anomalously high at 293 K — even higher than HI. Which of the following correctly explains this? [NEET]

- (1) All fluorine compounds have anomalously high boiling points simply because fluorine is the first element in Group 17
- (2) HF molecules are strongly associated in the liquid state through extensive intermolecular hydrogen bonding, made possible by fluorine's extreme electronegativity and very small size; much more energy is required to break these associations, which causes the exceptionally high boiling point
- (3) HF has the shortest bond length (91.7 pm), and the shorter the H–X bond, the higher the boiling point of the hydrogen halide
- (4) HF is a gas at room temperature just like HCl, so both should have similar, low boiling points, which makes the data in the table incorrect

SKILL: Application Skills

Q23. The bond lengths and bond dissociation enthalpies of the hydrogen halides from Table 7.9 are listed below. Based on this data, which statement is correctly supported? [NEET]

Property	HF	HCl	HBr	HI
Bond length (H–X) / pm	91.7	127.4	141.4	160.9
$\Delta_{diss}H^\circ$ / kJ mol ^{–1}	574	432	363	295

- (1) Bond dissociation enthalpy increases as bond length increases, meaning longer H–X bonds are stronger and harder to break
- (2) All four hydrogen halides have the same bond dissociation enthalpy since they all contain one hydrogen atom and one halogen atom
- (3) As the H–X bond length increases from HF to HI, the bond dissociation enthalpy decreases — consistent with longer bonds being weaker and easier to break, explaining the decrease in stability down the group
- (4) HF has the longest bond length and therefore the highest bond dissociation enthalpy — these two quantities always increase together

SKILL: Diagram-Based Visual Literacy

Q24. The table below gives the pK_a values for the four hydrogen halides. A more negative pK_a means a stronger acid. Based on this data, which statement is correctly supported? [JEE]

Compound	HF	HCl	HBr	HI
pK_a	3.2	–7.0	–9.5	–10.0

- (1) Acidic strength increases from HF to HI; HF with $pK_a = 3.2$ is the weakest acid and HI with $pK_a = -10.0$ is the strongest, consistent with the decreasing H–X bond dissociation enthalpy down the group
- (2) HF is the strongest acid because it has the highest (most positive) pK_a value
- (3) All four hydrogen halides are equally strong acids since they all dissociate in water to release H^+ ions
- (4) HCl is the strongest acid in the series because its pK_a is the most negative among all four

SKILL: Time Management and Strategic Thinking

Q25. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. All halogens react with hydrogen, but the affinity for hydrogen decreases from fluorine to iodine.
- II. The acidic strength of hydrohalic acids follows the order $HF < HCl < HBr < HI$.

III. The stability of hydrogen halides increases down the group because the bond dissociation enthalpy increases from HF to HI.

IV. Hydrogen halides dissolve in water to form hydrohalic acids.

- (1) I, II, III and IV (2) I, II and IV only (3) II, III and IV only (4) I and III only

(c) Reactivity towards Oxygen — Halogen Oxides

SKILL: Analytical Ability

Q26. Fluorine's compounds with oxygen (OF_2 and O_2F_2) are described in NCERT as "oxygen fluorides" rather than "fluorine oxides." Which of the following best explains why this naming convention is used? [JEE]

- (1) Oxygen is always written and named before fluorine in binary compounds as a matter of periodic table convention
- (2) Fluorine is less electronegative than oxygen in these compounds, so oxygen takes the negative oxidation state and fluorine takes a positive one, just as in a normal oxide
- (3) Fluorine is a metal in these compounds while oxygen behaves as a non-metal, and the metal element is always named last
- (4) Since fluorine is more electronegative than oxygen, it takes the negative oxidation state (-1) and oxygen is forced into a positive oxidation state — making these compounds correctly described as derivatives of oxygen (with a positive oxidation state) combined with fluoride, i.e. oxygen fluorides

SKILL: Conceptual Clarity

Q27. Which of the following correctly matches each halogen oxide to its specific industrial or analytical application mentioned in the passage? [NEET]

- (1) I_2O_5 is used as a bleaching agent for paper pulp; ClO_2 is used in the estimation of carbon monoxide
- (2) Cl_2O_7 is used in water treatment; I_2O_4 is used as an oxidising agent for carbon monoxide estimation
- (3) ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment; I_2O_5 is used as a very good oxidising agent in the estimation of carbon monoxide
- (4) O_2F_2 is used in water treatment; Br_2O is used as the primary bleaching agent for paper pulp

SKILL: Application Skills

Q28. O_2F_2 is one of fluorine's two oxides and is described as a strong fluorinating agent. It is used to oxidise plutonium to PuF_6 in the processing of spent nuclear fuel. Which of the following correctly identifies the dual chemical role that makes O_2F_2 suitable for this specific purpose? [JEE]

- (1) O_2F_2 acts as a reducing agent, donating electrons to plutonium and simultaneously removing fluorine from the spent fuel
- (2) O_2F_2 acts as an acid, reacting with basic plutonium compounds to form soluble products that are washed out of the spent fuel

- (3) O_2F_2 acts as a bleaching agent, removing coloured impurities from the spent fuel without changing the oxidation state of plutonium
- (4) O_2F_2 acts as both a fluorinating agent (attaching fluorine atoms to plutonium) and an oxidising agent (raising plutonium to its +6 state) to form volatile PuF_6 , which can then be separated from the spent fuel

SKILL: Diagram-Based Visual Literacy

Q29. The table below summarises key properties of the oxides of each Group 17 element. Based on this table, which statement is correctly supported? [JEE]

Element	Key oxides	Stability & notable feature
F	OF_2 , O_2F_2	Only OF_2 stable at 298 K; strong fluorinating agents
Cl	Cl_2O , ClO_2 , Cl_2O_6 , Cl_2O_7	Reactive, tend to explode; ClO_2 used for bleaching
Br	Br_2O , BrO_2 , BrO_3	Least stable; exist only at low temperatures (middle row anomaly)
I	I_2O_4 , I_2O_5 , I_2O_7	Insoluble solids; decompose on heating; I_2O_5 used for CO estimation

- (1) Iodine oxides are the most explosive and reactive, while chlorine oxides are the most thermally stable among all the halogen oxides
- (2) Bromine oxides are more stable than iodine oxides because bromine sits between chlorine and iodine in the group
- (3) The general stability order of halogen oxides is $\text{I} > \text{Cl} > \text{Br}$; bromine oxides are uniquely the least stable (a middle row anomaly) and exist only at low temperatures
- (4) Fluorine forms the most stable and numerous oxides among all Group 17 elements, since it is the most electronegative

SKILL: Time Management and Strategic Thinking

Q30. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. Fluorine's oxides (OF_2 and O_2F_2) are called "oxygen fluorides" because fluorine, being more electronegative than oxygen, takes the negative oxidation state in these compounds.
- II. The general stability order of halogen oxides is $\text{I} > \text{Cl} > \text{Br}$.
- III. Chlorine oxides are insoluble solids, and ClO_2 is used in the estimation of carbon monoxide.
- IV. I_2O_5 is a powerful oxidising agent used in the estimation of carbon monoxide.

- (1) I, II and IV only (2) I, II, III and IV (3) II and III only (4) I, III and IV only

(d) Reactivity towards Metals — Metal Halides

SKILL: Analytical Ability

Q31. SnCl_4 , PbCl_4 , SbCl_5 and UF_6 are all described as more covalent than SnCl_2 , PbCl_2 , SbCl_3 and UF_4 respectively. What underlying principle links all these comparisons? [JEE]

- (1) Compounds with more atoms are always more covalent; since the higher-oxidation-state halides contain more halogen atoms, they are automatically more covalent
- (2) A metal in a higher oxidation state has a smaller size and a greater positive charge, giving it a higher charge density; this greater charge density polarises the electron cloud of the halide ion more strongly, increasing covalent character — a direct consequence of Fajans' rules
- (3) Higher-oxidation-state halides have higher melting points, and all compounds with high melting points are more covalent than those with low melting points
- (4) The number of lone pairs on the halide ion determines covalent character; since higher-oxidation-state halides have fewer lone pairs, they are more covalent

SKILL: Conceptual Clarity

Q32. The ionic character of metal halides (where M is a monovalent metal) decreases in the order $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$. Which of the following correctly explains why iodides are the least ionic and fluorides the most ionic? [NEET]

- (1) As the halide ion gets larger from F^- to I^- , its electron cloud becomes more diffuse and more easily distorted (polarised) by the metal cation; this greater polarisation of I^- increases covalent character, making iodides the most covalent — conversely, the small, compact F^- ion resists polarisation, keeping the M–F bond predominantly ionic
- (2) Fluorine is the most electronegative halogen, and all fluorine compounds are always the most covalent for this reason
- (3) All four types of metal halides are equally ionic since they each contain exactly one metal cation bonded to a halide anion
- (4) Iodides are most ionic because iodine is the heaviest halogen and heavy halogens always form ionic compounds

SKILL: Application Skills

Q33. A student is given four pairs of compounds and asked to identify which compound in each pair is more covalent. Which pair is correctly identified? [NEET]

- (1) UF_4 is more covalent than UF_6 because uranium has fewer bonds in UF_4
- (2) MgF_2 is more covalent than MgI_2 because fluorine has the highest electronegativity among the halogens

- (3) PbCl_2 is more covalent than PbCl_4 because lead has a lower oxidation state in PbCl_2 , which makes the bond weaker
- (4) PbCl_4 is more covalent than PbCl_2 because the higher +4 oxidation state of lead gives it a greater charge density, leading to stronger polarisation of the Cl^- ions and hence greater covalent character

SKILL: Diagram-Based Visual Literacy

Q34. The table below compares the bonding character of three pairs of metal halides that differ only in the oxidation state of the metal. Based on this data, which statement is correctly supported? [JEE]

Metal	Lower OS halide	Higher OS halide	More covalent
Sn	SnCl_2 (+2)	SnCl_4 (+4)	SnCl_4
Pb	PbCl_2 (+2)	PbCl_4 (+4)	PbCl_4
Sb	SbCl_3 (+3)	SbCl_5 (+5)	SbCl_5

- (1) Higher oxidation state halides are more ionic, not more covalent, because a greater charge on the metal makes the bond more electrostatic
- (2) In all three pairs, the compound in the higher oxidation state is more covalent because the higher metal charge density polarises the anion more strongly, increasing covalent character
- (3) Lower oxidation state halides are more covalent because fewer bonds means each bond has more electron density
- (4) All three pairs show equal covalent character since the same halogen (chlorine) is present in all six compounds

SKILL: Time Management and Strategic Thinking

Q35. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. Halogens react with metals to form metal halides.
- II. The ionic character of metal halides decreases in the order $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$ (where M is a monovalent metal).
- III. Metal halides in higher oxidation states are more covalent than those in lower oxidation states.
- IV. SnCl_2 is more covalent than SnCl_4 because tin has a lower oxidation state in SnCl_2 .

- (1) I, II, III and IV (2) I, III and IV only (3) I, II and III only (4) II and IV only

(e) Reactivity towards other Halogens & NCERT In-Text Questions (7.16, 7.26–7.28)

SKILL: Analytical Ability

Q36. Interhalogens form as XX' , XX'_3 , XX'_5 and XX'_7 , where X is the larger halogen and X' is the smaller. In IF_7 for example, iodine occupies the central position, not fluorine. Which of the following best explains why the larger halogen is always the central atom? [JEE]

- (1) Iodine is heavier than fluorine, and the heavier atom always occupies the central position in any binary halogen compound
- (2) Fluorine is gaseous while iodine is solid, and solid elements cannot bond to more than one gaseous atom at the periphery
- (3) The larger halogen has the greater atomic size and available d orbitals in its valence shell, allowing it to accommodate multiple smaller halogen atoms around it and expand its octet as needed; the smaller halogen lacks these d orbitals and cannot act as the central atom in an expanded-octet species
- (4) The central position is determined by electronegativity: the least electronegative halogen is always placed at the centre regardless of size or orbital availability

SKILL: Conceptual Clarity

Q37. [NCERT Example 7.16] Fluorine exhibits only -1 oxidation state whereas other halogens also exhibit $+1$, $+3$, $+5$ and $+7$ states. Which of the following correctly and completely explains this difference? [NCERT]

- (1) Fluorine has only 9 protons, and a higher proton count is required to sustain positive oxidation states
- (2) Fluorine is the most electronegative element and therefore never loses electrons to show a positive oxidation state; additionally, its valence shell ($n = 2$) has no d orbitals and it cannot expand its octet — both factors together confine it strictly to -1
- (3) Fluorine has too few electrons in its outer shell; since it cannot gain more than one electron it is restricted to -1
- (4) Fluorine atoms are too small to bond in positive oxidation states; size alone is the limiting factor

SKILL: Application Skills

Q38. [NCERT Intext 7.26] When comparing the oxidising power of F_2 and Cl_2 using bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, which of the following correctly accounts for all three parameters? [NCERT]

- (1) F_2 wins on all three parameters — its bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy are all individually more favourable, making it the stronger oxidiser
- (2) Cl_2 is the stronger oxidising agent when all three parameters are considered, since chlorine's electron gain enthalpy (-349 kJ mol^{-1}) is more negative than fluorine's (-333 kJ mol^{-1})
- (3) The three parameters cancel each other out exactly, making F_2 and Cl_2 equal in oxidising power
- (4) F_2 wins overall despite its electron gain enthalpy being *less* negative than Cl_2 's; this is more than compensated by F_2 's lower bond dissociation enthalpy (easier to dissociate) and the far greater hydration enthalpy of F^- compared to Cl^- , making the overall thermodynamic driving force for oxidation by F_2 greater

SKILL: Diagram-Based Visual Literacy

Q39. [NCERT Intext 7.26] The table below shows the three thermodynamic parameters used to

compare the oxidising power of F_2 and Cl_2 . Based on this data, which statement is correctly supported? [NCERT]

Parameter	F_2/F^-	Cl_2/Cl^-	Favours F_2 as stronger oxidiser?
Bond dissociation enthalpy	Lower	Higher	Yes — F_2 easier to break
Electron gain enthalpy	-333 kJ mol^{-1}	-349 kJ mol^{-1}	No — Cl favoured here
Hydration enthalpy of X^-	Much more negative	Less negative	Yes — F^- hydrates far better

- (1) Two of the three parameters (bond dissociation enthalpy and hydration enthalpy) favour F_2 as the stronger oxidiser; only electron gain enthalpy favours Cl_2 — the net combined effect still makes F_2 the stronger oxidising agent
- (2) All three parameters individually favour F_2 over Cl_2 as the stronger oxidising agent
- (3) Since the electron gain enthalpy parameter favours Cl_2 , Cl_2 must overall be the stronger oxidising agent
- (4) The hydration enthalpy of the halide ion is irrelevant when comparing oxidising power in solution; only bond dissociation enthalpy and electron gain enthalpy matter

SKILL: Time Management and Strategic Thinking

Q40. Consider the following statements (based on NCERT Intext 7.27 and 7.28) and select the correct combination of true statements: [NCERT]

- I. Interhalogens form in the types XX' , XX'_3 , XX'_5 and XX'_7 , where X is the larger halogen and X' is the smaller.
- II. Fluorine exhibits only -1 oxidation state because it is the most electronegative element and has no d orbitals in its valence shell.
- III. The stronger oxidising power of F_2 compared to Cl_2 is mainly because chlorine's electron gain enthalpy is less negative than fluorine's.
- IV. Sea water is a major natural source of chloride, bromide and iodide ions for the corresponding halogens.

- (1) I, II, III and IV (2) II and III only (3) I, II and IV only (4) I, III and IV only

TOPIC 5 Anomalous Behaviour of Fluorine

Small Size, Highest Electronegativity, Low F–F BDE & Absence of d Orbitals

SKILL: Analytical Ability

Q41. The passage states that most reactions of fluorine are exothermic. Which of the following best explains why fluorine releases so much energy in its reactions with other elements? [JEE]

- (1) Fluorine is a diatomic gas, and diatomic molecules always release more heat on reaction than liquid or solid elements do
- (2) The bond that fluorine forms with virtually any other element is characteristically small in size and very strong; the large amount of energy released when this compact, strong bond forms more than compensates for the energy needed to break F_2 , making nearly all fluorine reactions exothermic
- (3) Fluorine's electron gain enthalpy is highly negative, making every single reaction with F_2 both spontaneous and exothermic regardless of the other reactant
- (4) Fluorine atoms are so electronegative that they absorb heat from the surroundings, which is then re-released as the product forms, making the net process exothermic

SKILL: Conceptual Clarity

Q42. Fluorine's anomalous properties can be grouped into those that are **higher** than expected from group trends and those that are **lower**. Which of the following correctly classifies these properties? [NEET]

- (1) Higher than expected: ionic radius, boiling point, electron gain enthalpy;
Lower than expected: ionisation enthalpy, electronegativity
- (2) Higher than expected: bond dissociation enthalpy, m.p., b.p.;
Lower than expected: electronegativity, electrode potential
- (3) Higher than expected: ionisation enthalpy, electronegativity, boiling point;
Lower than expected: ionic radius, bond dissociation enthalpy
- (4) Higher than expected: ionisation enthalpy, electronegativity, electrode potentials;
Lower than expected: ionic and covalent radii, m.p., b.p., bond dissociation enthalpy, electron gain enthalpy

SKILL: Application Skills

Q43. Fluorine forms only **one** oxoacid while chlorine, bromine and iodine each form several. Using what you know about fluorine's electronic structure, which of the following best explains this difference? [NEET]

- (1) Since fluorine cannot exhibit positive oxidation states (due to its highest electronegativity and absence of d orbitals in its valence shell), it cannot form the variety of oxoacids that other halogens form — those oxoacids require the halogen to be in positive oxidation states (+1, +3, +5, +7) bonded to oxygen
- (2) Fluorine cannot dissolve in water, so it is simply unable to form any water-based acid at all
- (3) Fluorine's low boiling point means it escapes as a gas before it can react with oxygen to form oxoacids
- (4) Fluorine forms multiple oxoacids just like the other halogens; the passage is incorrect on this point

SKILL: Diagram-Based Visual Literacy

Q44. The table below summarises the anomalous properties of fluorine, comparing each to the trend expected from the other halogens. Based on this, which statement is correctly supported? [JEE]

Property	Expected trend	F anomaly (Higher/Lower?)
Ionisation enthalpy	Decreases down group	Higher than expected
Electronegativity	Decreases down group	Higher than expected
Electrode potential	Decreases down group	Higher than expected
Ionic & covalent radii	Increase down group	Lower (smaller) than expected
M.p. and B.p.	Increase from Cl to I	Lower than expected
Bond dissociation enthalpy	Decreases from Cl	Lower than Cl ₂ (anomaly)
Electron gain enthalpy	More negative up group	Less negative than Cl

- (1) Fluorine's anomalous behaviour is consistent: all its properties are higher than expected from group trends in Group 17
- (2) Fluorine's bond dissociation enthalpy is higher than chlorine's, confirming its status as the strongest single-halogen bond
- (3) The table confirms that some properties (ionisation enthalpy, electronegativity, electrode potential) are anomalously high while others (radii, m.p., b.p., bond dissociation enthalpy, electron gain enthalpy) are anomalously low — all attributable to fluorine's small size, highest electronegativity, and absence of *d* orbitals
- (4) Fluorine's anomalous behaviour is limited to physical properties only; its chemical properties (electron gain enthalpy, electrode potential) follow the expected group trend

SKILL: Time Management and Strategic Thinking

Q45. Consider the following statements about the anomalous behaviour of fluorine and select the correct combination of true statements: [JEE]

- The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F–F bond dissociation enthalpy, and non-availability of *d* orbitals in its valence shell.
- Most reactions of fluorine are exothermic because the bond formed by fluorine with other elements is small and strong, releasing large amounts of energy.
- Hydrogen fluoride is a gas at room temperature, just like all other hydrogen halides.
- Fluorine forms only one oxoacid while other halogens form many oxoacids.

- (1) I, II, III and IV (2) I, II and IV only (3) II, III and IV only (4) I, III and IV only

— Answers & solutions are provided separately. —