Chem Factsheet

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How to Answer Questions on Halogens

This Factsheet gives guidance on answering questions on Group 7. The answers given are "best" answers but, in some cases, other answers will gain equal / partial credit. Common mistakes are also indicated so they can be avoided.

Before starting this Factsheet make sure you know about oxidation numbers and the definitions of oxidation and reduction.

The following summaries provide the basis for answering questions related to group 7 chemistry. Be sure to check that each summary point corresponds to your specification.

1. Atom / outer e's / halide ion / molecule	F / $2s^22p^5$ / F^- / F_2	Cl / $3s^23p^5$ / Cl^- / Cl_2	Br / $4s^24p^5$ / Br^- / Br_2	I / $5s^25p^5$ / I^- / I_2
2. Element's appearance at room temp.	Pale yellow gas	Green gas	Dark red-brown liquid	black, shiny, **solid**
3. Appearance in aqueous solution	(Reacts)	Very, very pale green	Orange to yellow	Yellowish-brown
4. Appearance in organic solvent	N/A	N/A	Orange	Purple
5. Structure and bonding	Single covalent bond → non-polar, diatomic molecules → Van der Waals forces strong enough to form *liquid* Br_2 and *crystalline* I_2 *as the molecules get larger.*			

Trends in Physical Properties that occur on moving down Group 7

6. **Electronegativity** - ***decreases***. The covalent bond's electron pair is *further from* and *more shielded* from the attracting nucleus as the atoms get larger. These two factors outweigh the increase in nuclear charge → attraction for the electron pair decreases → electronegativity decreases.

7. **Boiling point** - ***increases***. Diatomic molecules increase in size as the halogen atoms increase in size → number of electrons increase → molecules become more polarisable → van der Waals forces get stronger → more heat energy needed to overcome these forces.

Trends in Chemical Properties that occur on moving down Group 7

8. **Halogens as Oxidising Agents**. - ***decrease in oxidising power***. Atomic radius and shielding both increase → nuclear attraction for electrons decreases → e- is less readily gained by the outer shell → less oxidising. Note – distance and shielding outweigh the increase in nuclear charge. Thus Cl_2 will oxidise aqueous solutions of bromide ions and iodide ions to the respective elements. See 3 for observations.

e.g. $2NaBr(aq) + Cl_2(aq) \rightarrow 2NaCl(aq) + Br_2(aq)$

or $2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$ ——— (A)

e.g. $2NaI(aq) + Cl_2(aq) \rightarrow 2NaCl(aq) + I_2(aq)$

or $2I^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$ ——— (B)

Also, Br_2 will oxidise an aqueous solution of iodide ions to produce a solution of I_2. See 3 for observations.

e.g. $2NaI(aq) + Br_2(aq) \rightarrow 2NaBr(aq) + I_2(aq)$

or $2I^-(aq) + Br_2(aq) \rightarrow 2Br^-(aq) + I_2(aq)$ ——— (C)

These reactions are called '***displacement reactions***' - more reactive halogen displaces a less reactive halogen. They are also ***redox reactions***.

e.g. Half-equation: $\frac{1}{2}Br_2 + e^- \rightarrow Br^-$ (reduction)

and half-equation: $I^- \rightarrow \frac{1}{2}I_2 + e^-$ (oxidation).

9. **The Halide Ions as Reducing Agents**. - ***Increase in reducing power***. The size of the ion and shielding both increase → nuclear attraction for electrons decreases → electron is more readily lost from outer shell. Note – distance and shielding outweigh the increase in nuclear charge.

(a) Reduction of Halogens by Halide Ions in Aqueous Solution. (see 8) When a halogen oxidises a halide ion, the halide ion *reduces* the halogen. A more powerful oxidising agent (a halogen, e.g. Cl_2) is associated with a less powerful reducing agent (the corresponding halide, e.g. Cl^-). A halogen will oxidise the halide of a halogen *below* it in Group 7.

(b) Reactions of Solid Halides (e.g. NaX(s)) with Concentrated Sulphuric Acid.

NaCl(s), NaBr(s) and NaI(s) all react with conc. H_2SO_4 → HCl(g), HBr(g) and HI(g) respectively → (faint) white fumes seen → *acid-base* reactions → acid donates a proton to the base (X^-).

$NaX(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HX(g)$ ——— (A)

Note: The Ox. No. of S remains at +6 → no reduction of H_2SO_4 has occurred.

(i) HCl - no further reaction – HCl is too weak a reducing agent to reduce H_2SO_4.

(ii) HBr - reduces the H_2SO_4 (S = + 6) to SO_2 (S = +4), a gas with a pungent smell. HBr (Br = -1) is oxidised to Br_2 (Br = 0), an orange liquid or red vapour. The half-equations and equations can be written using either H_2SO_4 or SO_4^{2-} and HBr or Br^-.

Reduction : $H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

Oxidation : $2HBr \rightarrow Br_2 + 2H^+ + 2e^-$

$\therefore H_2SO_4 + 2HBr \rightarrow Br_2 + SO_2 + 2H_2O$ ——— (A)

Or, Reduction: $SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

Oxidation: $2Br^- - 2e^- \rightarrow Br_2$

$\therefore SO_4^{2-} + 4H^+ + 2Br^- \rightarrow Br_2 + SO_2 + 2H_2O$ — (A)

(iii) HI = strongest reductant → reduces H_2SO_4 further than SO_2 → S (S= 0), a yellow solid, and finally H_2S (S = -2), a gas with an odour of bad eggs are both formed. The HI (I = -1) is oxidised to I_2 (I = 0), a black solid or purple vapour.

Reduction : $H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

Oxidation : $2HI \rightarrow I_2 + 2H^+ + 2e^-$

$\therefore H_2SO_4 + 2H^+ + 2I^- \rightarrow I_2 + SO_2 + 2H_2O$

and $H_2SO_4 + 6H^+ + 6e^- \rightarrow S + 4H_2O$

$\therefore H_2SO_4 + 6HI \rightarrow 3I_2 + S + 4H_2O$

and $H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$

$\therefore H_2SO_4 + 8HI \rightarrow 4I_2 + H_2S + 4H_2O$

10. **Using Silver Nitrate Solution [$AgNO_3$(aq)] to Identify Halide Ions in Aqueous Solution**.

Aqueous halide ion solutions (except F^-) form *different coloured precipitates* with $AgNO_3$(aq) → different halide ions can be identified - except Cl^- since, like silver chloride, silver carbonate is also white and insoluble in water.

For $Na_2CO_{3(aq)}$ Observations – colourless solutions mix → *white ppt.*

$Na_2CO_{3(aq)} + 2AgNO_{3(aq)} \rightarrow Ag_2CO_{3(s)} + 2NaNO_{3(aq)}$

or $2Ag^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow Ag_2CO_{3(s)}$ ______ (A)

For $NaF_{(aq)}$ Observations – solutions mix and remain colourless / no reaction. (AgF is soluble in water.)

For $NaCl_{(aq)}$ Observations – colourless solutions mix → *white ppt.*

$NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$

or $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ ______ (B)

For $NaBr_{(aq)}$ Observations – colourless solutions mix → *cream ppt.*

$NaBr_{(aq)} + AgNO_{3(aq)} \rightarrow AgBr_{(s)} + NaNO_{3(aq)}$

or $Ag^+_{(aq)} + Br^-_{(aq)} \rightarrow AgBr_{(s)}$ ______ (C)

For $NaI_{(aq)}$ Observations – colourless solutions mix → *yellow ppt.*

$NaI_{(aq)} + AgNO_{3(aq)} \rightarrow AgI_{(s)} + NaNO_{3(aq)}$

or $Ag^+_{(aq)} + I^-_{(aq)} \rightarrow AgI_{(s)}$ ______ (D)

Aq. solutions of chloride ions (Cl^-) and carbonate ions (CO_3^{2-}) are distinguished by *acidification* with *dilute nitric acid before adding the silver nitrate.* If there are carbonate ions in solution *fizzing* will occur due to carbon dioxide being evolved as the acid and carbonate react.

This removes carbonate ions → any white ppt when $AgNO_3$ added can be attributed to Cl^-.

$Na_2CO_{3(aq)} + 2HNO_{3(aq)} \rightarrow 2NaNO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}$

or $2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)}$

Trend in Solubility of the Silver Halides in Ammonia (NH_3)

s***olubility decreases***. Dilute ammonia: only AgCl dissolves → colourless solution. Conc. ammonia: only AgCl and AgBr are soluble - colourless solutions are formed.

Testing for Halide Ions in Solution.

(1) *Acidify* with dilute nitric acid.
(2) Add a few drops of *silver nitrate* solution.
(3) If precipitates form add *dilute ammonia*.
(4) If precipitates form but don't dissolve in dil. ammonia, add *conc. ammonia*.

11. **Uses of Chlorine and Chlorate (I).**

(a) Chlorine is added to water supplies to kill bacteria and hence help to prevent water-born diseases (e.g. typhoid and cholera). The benefits to health outweigh chlorine's toxic effects and the possible risks from formation of chlorinated hydrocarbons which are health hazard. Cl_2(g) - slightly soluble in cold water → dynamic equilibrium → pale green (Cl_2 molecules) soln.

$Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HClO(aq)$ ____ (A)

HClO is a weak acid, chloric(I) acid. Cl_2 (Ox. No. = 0) is both reduced to Cl^- (Ox. No. = -1) and oxidised to HClO (Ox. No. Cl = +1) → chlorine is simultaneously oxidised and reduced → called 'disproportionation'. If chlorine water is heated or left in sunlight, bubbles of colourless gas are seen:

$Cl_2(aq) + H_2O(l) \rightarrow 2H^+(aq) + 2Cl^-(aq) + \frac{1}{2}O_2(g)$ ——— (B)

(b) Cl_2 *disproportionates* with a cold, dilute solution of sodium hydroxide → a mixture of two salts;

$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$ ——— (C)

This solution is used as a bleach, disinfectant, steriliser - chlorate(I) ion kills bacteria If hot conc. NaOH is used, sodium chlorate(V) is formed not sodium chlorate(I):

$Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

Some general points:(G.P.)

(a) There is not need to write out the question as part of the answer.

(b) Since chemical formula and equations are often required, learn the formulae of the ions.
e.g. Ag^+ and NO_3^- ∴ $AgNO_3$; Na^+ and ClO^- ∴ NaClO ; Na^+ and CO_3^{2-} ∴ Na_2CO_3.

(c) Only answer the question – don't give explanations if they are not asked for.

(d) When a white precipitate is the expected observation, "white suspension" / "white solid" are both acceptable alternatives but ***not*** "white solution","cloudy precipitate","milky precipitate", just "white" or just "precipitate".

(e) When "fizzing" / "effervescence" / "bubbles" is the expected observation, *do not* write carbon dioxide / CO_2 / colourless gas etc – these are interpretations, not observations!

(f) If an observation is required and no reaction occurs *don't answer* "nothing", "none", "no observation" etc. "No change" or "no visible reaction" are acceptable.

(g) If no reaction occurs there is *no equation.*

(h) Take care over the choice of, for example Br_2, Br and Br^-, as the answer to a question. It is often safer to use the *name* rather than the formula but again take care that for example, bromine and bromide, are not confused.

(i) Do not give two answers to a question requiring only one. If either answer is wrong then no mark is gained.

(j) In an observation requiring "colour" the initial colour as well as the final colour should be given.

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Practice Questions

To help, the *key words / phrases* in each question have been highlighted. Identifying these key words / phrases is essential and can give a very good guide to the distribution of the marks.

1. (a) (i) **State** and **explain** the trend in electronegativity of the elements down Group VII. (3 marks)
   (ii) **State** and **explain** the trend in boiling point of the elements down Group VII. (3 marks)
   (b) (i) **State** the trend in reducing ability of the halide ions down Group VII. (1 mark)
   (ii) **Give an example** of a reagent which could be used to show that bromide ions are stronger reducing agents than chloride ions. (2 marks)
   (c) Aqueous solutions of chloride and bromide ions can be distinguished by the addition of silver nitrate solution followed by dilute aqueous ammonia. For each ion, **state** what observation would be seen. (4 marks)
   (d) **Write an equation** for the reaction between cold, dilute aqueous sodium hydroxide and chlorine. **Give two uses** of the resulting solution. (3 marks)

2. (a) **State** the trend in the reducing ability of the halide ions from fluoride to iodide. (1 mark)
   (b) **State** what you would observe when potassium iodide solution reacts with an aqueous solution of bromine. **Write an equation** for the reaction. **State** the role of bromine in the reaction. (3 marks)
   (c) **Give a reagent** which could be used to distinguish between separate solutions of sodium bromide and sodium iodide. **State** what would be observed when this reagent is added to each of the separate solutions of sodium bromide and sodium iodide. **Write an equation** for one of the reactions. **Identify a reagent** which could be added to the mixtures from the first test to confirm the identity of the halide ions. **State** what would be observed in each case. (7 marks)

3. (a) **Explain**, in terms of electrons, what is meant by "*reduction*" and "*reducing agent*". (2 marks)
   (b) Iodide ions can reduce conc. sulphuric acid to three different products.
   (i) **Name** the three reduction products and give the oxidation state of sulfur in each of these products.
   (ii) **Describe** how observations of the reaction between solid sodium iodide and concentrated sulphuric acid can be used to indicate the presence of any two of these reduction products.
   (iii) **Write half-equations** to show how two of these products are formed by reduction of sulphuric acid. (10 marks)
   (c) **Write an equation** for the reaction that occurs when chlorine is added to cold water.
   State whether or not the water is oxidised and **explain** your answer. (3 marks)

4. Aqueous bromide ions can be detected by using either chlorine or aqueous silver nitrate solution.
   (a) (i) **State** what is observed when chlorine is added to an aqueous solution containing bromide ions. **Write an ionic equation** for the reaction which occurs.
   (ii) **Identify** one halide ion, other than chloride, which will not react with chlorine. **Explain** why a reaction does not take place. (4 marks)
   (b) (i) **State** what is observed when aqueous silver nitrate is added to an aqueous solution containing bromide ions. **Write an ionic equation** for the reaction which occurs.
   (ii) **What is observed** when an excess of conc. aqueous ammonia is added to the products formed in part b) i). (3 marks)
   (c) Chlorine and bromine both reacts with cold aqueous sodium hydroxide in a similar way.
   Write an equation for the reaction of bromine with cold aqueous sodium hydroxide. (2 marks)

5. (a) **State**, in terms of electrons, what happens to an oxidising agent when it reacts. (1 mark)
   (b) When concentrated sulphuric acid is added to solid potassium bromide, two products are SO_2 and Br_2.
   (i) **Write a half-equation** to show how SO_2 is formed from sulphuric acid. (1 mark)
   (ii) **Write a half-equation** to show how Br_2 is formed from Br^- ions. (1 mark)
   (iii) Hence **write an overall equation** for the reaction of Br^- ions with sulphuric acid. (1 mark)
   (iv) **State** the role of Br^- ions in this reaction. (1 mark)
   (c) (i) **Identify** a halide ion that does not produce SO_2 when the solid sodium halide reacts with conc. sulphuric acid. (1 mark)
   (ii) **Write an equation** for the reaction of conc. sulphuric acid with the halide ion that you identified in part c) i). (1 mark)
   (iii) **State** the role of sulphuric acid in this reaction. (1 mark)

Answers

1. (a) (i) See 6 ✓✓✓. (ii) See 7 ✓✓✓.
   (b) (i) See 9. ✓ (ii) e.g. conc. H_2SO_4. ✓
   (c) $Br^-_{(aq)}$: cream ppte, ✓ insoluble in dil. NH_3. ✓
   $Cl^-_{(aq)}$: white ppte, ✓ soluble in NH_3. ✓
   (d) See 11 b). ✓✓ ✓

2. (a) Increase ✓.
   (b) Yellow-orange solution turns to a brown solution. ✓
   (See G.P. j). Equation: See 8(C) ✓.
   Role: Br_2 is an oxidising agent ✓.
   (c) Add silver nitrate solution ✓. See 10(C) and (D) ✓✓.
   Reagent: add conc. ammonia ✓. AgBr dissolves ✓ forming a colourless solution. ✓. AgI is insoluble. ✓.

   or (c) Using Cl_2. Equation. See 8 (A) and (B).
   Reagent: Organic solvent. See 4.
   or (c) Using Br_2. Equation. See 8 (C).
   Reagent: Organic solvent. See 4.

<u>Note</u>: When answering these longer questions, don't think a "discussion" or "mini essay" is needed. See the Q as having to state 7 answers – see ✓'s. Also see G.P. (a).

3. (a) Reduction is gain of electrons. ✓
   A reducing agent loses electrons. ✓
   (b) (i) Sulphur dioxide ✓ S +4 ✓; Sulphur ✓ S = 0 ✓;
   Hydrogen sulphide ✓ S = -2✓.
   (ii) SO_2 has a pungent smell. ✓ Sulphur is a yellow solid ✓ H_2S smells of bad eggs ✓ (Any 2)
   (iii) See 9 (b) (iii) ✓ ✓
   (c) See 11 equation (A) ✓ Water is not oxidised ✓ The oxidation states of O (-2) and H (+1) don't change ✓ (Notice ox. State *values* need to be stated.)

4. (a) (i) Yellow / brown solution forms ✓. $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$✓
   (ii) Fluoride ion ✓. F^- is a weaker reducing agent than Cl^- ✓ <u>or</u> Cl_2 is a weaker oxidising agent than F_2 ✓ <u>or</u> Cl_2 is less reactive than F_2 ✓.

<u>Note</u>: When making a comparison *both species* are needed. Don't just say e.g. F^- is a weaker reductant.)

   (b) (i) Cream precipitate ✓. $Ag^+ + Br^- \rightarrow AgBr$. ✓ (ii) Ppte dissolves forming a colourless solution. ✓
   (c) $2NaOH + Br_2 \rightarrow NaBr + NaBrO + H_2O$ ✓✓.

5. (a) Gains electrons ✓.
   (b) (i) $H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$ ✓
   <u>or</u> $SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$ ✓
   (ii) $2Br^- \rightarrow Br_2 + 2e^-$ ✓.
   (iii) See 9 b) ii) (A) ✓. {A correct equation can be with NaBr.}
   (iv) Reducing agent ✓.
   (c) (i) Cl^- / chloride (ion) or F^- fluoride (ion) ✓. (See G.P. h).
   (ii) $Cl^- + H_2SO_4 \rightarrow HSO_4^- + HCl$ ✓
   <u>or</u> $F^- + H_2SO_4 \rightarrow HSO_4^- + HF$ ✓ <u>or</u> see 9 b) (A) ✓.
   (<u>Note</u>. Ion + molecule = Ion + molecule with charges as well as atoms balanced)
   (iii) An acid ✓.