Reactions of the halides

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The halides are the ions of the halogens with a –1 oxidation number eg Fluoride F^- Chloride Cl^-, Bromide Br^-, Iodide I^-.

Reactions of Halides in Solution

Reaction with Silver Nitrate

The reactions of halide ions with silver nitrate.

Method

The test solution is made acidic with **nitric acid,** and then **Silver nitrate solution** is added dropwise:

The role of nitric acid is to react with any carbonates present to prevent formation of the precipitate Ag_2CO_3. This would mask the desired observations

e.g. $2\ HNO_3 + Na_2CO_3 \rightarrow 2\ NaNO_3 + H_2O + CO_2$

Observations

Fluorides produce no precipitate

Chlorides produce a white precipitate

Bromides produce a cream precipitate

Iodides produce a pale yellow precipitate

AgCl AgBr AgI

key

Equations for the reactions of halide ions with silver nitrate.

Full equation for reactions

$AgNO_3$ (aq) + NaCl (aq) → AgCl (s) + $NaNO_3$ (aq)

$AgNO_3$ (aq) + NaBr (aq) → AgBr (s) + $NaNO_3$ (aq)

$AgNO_3$ (aq) + NaI (aq) → AgI (s) + $NaNO_3$ (aq)

Normally we write ionic equations for these reactions

ionic equation for reactions

$Ag^+(aq) + Cl^-(aq)$ → AgCl(s) (White precipitate)

$Ag^+(aq) + Br^-(aq)$ → AgBr(s) (Cream precipitate)

$Ag^+(aq) + I^-(aq)$ → AgI(s) (Yellow precipitate)

key

Effect Of Light on Silver Halides

The precipitates (except AgI) darken in light forming silver. This reaction is used in photography to form the dark bits on photographic film

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Addition of Ammonia to Silver Halides

The precipitates can be reacted with ammonia solution (to help differentiate between them if the colours look similar):

	AgCl	AgBr	AgI
Addition of aqueous ammonia	Dissolves	Does not dissolve	Does not dissolve
Addition of concentrated ammonia	Dissolves	Dissolves	Does not dissolve

The solubility of the silver halides in ammonia decreases in the order: AgF > AgCl > AgBr > AgI

key

Equations for reactions with ammonia

Silver chloride dissolves in **dilute ammonia (**to form a complex ion)

$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

Colourless solution

Silver bromide only dissolves in **concentrated ammonia** to form a complex ion

$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Br^-(aq)$

Colourless solution

Silver iodide does not react with ammonia – it is too insoluble.

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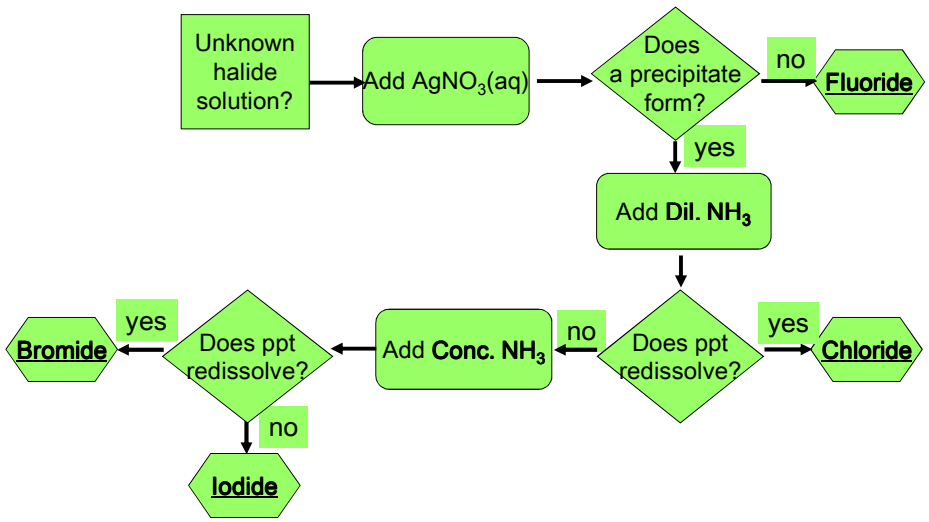
Testing for Halides



Reactions of Solid Halides

Reaction of Halides with Concentrated Sulphuric Acid

The reaction of solid halides with concentrated sulphuric acid.

Fluorides:

* $NaF(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HF(g)$

sodium hydrogen sulphate

Observations: White steamy fumes of HF are evolved.

Chlorides:

* $NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$

sodium hydrogen sulphate

Observations: White steamy fumes of HCl are evolved.

Type of reaction: acid base reaction (not redox)

The **F^- and Cl^-** ion are not **strong enough reducing agents** to reduce the S in H_2SO_4. No redox reactions occur

key

Bromides with conc H_2SO_4:

Br^- ions are stronger reducing agents than Cl^- and F^- and after the initial acid-base reaction reduce the Sulphur in H_2SO_4 from +6 to + 4 in SO_2

$NaBr(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HBr(g)$

acid -base

$2HBr(g) + H_2SO_4(l) \rightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$

redox

Observations for reaction:

White steamy fumes of HBr are evolved.

Red/brown fumes of Bromine are evolved

colourless, acidic gas **SO_2**

key

Iodides with conc H_2SO_4

I^- ions are the strongest halide reducing agents. They can reduce the Sulphur in H_2SO_4 from +6 to + 4 in SO_2, to 0 in S and -2 in H_2S.

There are four possible reactions with iodides

$NaI(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HI(g)$ *(not redox)*

$2HI(g) + H_2SO_4(l) \rightarrow I_2(s) + SO_2(g) + 2H_2O(l)$

$6HI(g) + H_2SO_4 \rightarrow 3I_2 + S + 4H_2O$

$8HI(g) + H_2SO_4(l) \rightarrow 4I_2(s) + H_2S(s) + 4H_2O(l)$

Observations:
White **steamy fumes** of HI are evolved.
Black solid and **purple fumes** of Iodine are also evolved
A **colourless**, acidic **gas** SO_2
A **yellow solid** of Sulphur
H_2S (Hydrogen Sulphide), a **gas** with a **bad egg smell**,

key

Summary of reducing power of halides

- A reducing agent donates electrons
- The reducing power of the halides increases down group 7
- They have a greater tendency to donate electrons
- This is because as the ions get bigger it is easier for the outer electrons to be given away as the pull from the nucleus on them becomes smaller

Producing the redox equations for these reactions using half equations

Let us produce this equation using half equations

$2HBr(g) + H_2SO_4(l) \rightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$

Write a half equation for the change Br^- to Br_2

$2\ Br^- \rightarrow Br_2 + 2e^-$

Write a half equation for the change H_2SO_4 to SO_2

First add electrons to balance change in oxidation numbers

$H_2SO_4 + 2\ e^- \rightarrow SO_2$

+6 +4

Next add water followed by H^+ ions to balance O's and then H's

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

key

Then combine the reduction half equation with the oxidation half equation cancelling out electrons to give the full redox equation

$2\ Br^- \rightarrow Br_2 + 2e^-$

+

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

$H_2SO_4 + 2\ H^+ + 2\ Br^- \rightarrow Br_2 + SO_2 + 2\ H_2O$

Remember the order of the strength of the **halides** as **reducing agents**

$F^- < Cl^- < Br^- < I^-$

Increasing strength

key

Iodide reactions

Combine the Iodide half reaction with the three different reductions half equations for H_2SO_4

$2\ I^- \rightarrow I_2 + 2e^-$

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

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

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

You should be able to write these reduction half equations from just being given the Sulphur containing substances

e.g. Write the half equation for the reduction of H_2SO_4 to H_2S

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Laboratory Tests for gases produced

Test for Hydrogen halides

If tested with conc ammonia gas lots of white smoke is seen due to following reaction

$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

The white smoke is ammonium chloride

$HBr(g) + NH_3(g) \rightarrow NH_4Br(s)$

$HI(g) + NH_3(g) \rightarrow NH_4I(s)$

SO_2 turns filter paper soaked **in potassium dichromate from orange to green**.

H_2S (Hydrogen Sulphide), a colourless, toxic, pungent gas, is also given off which turns **lead ethanoate paper black**.

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The reaction of halide salts with concentrated phosphoric acid.

$$NaCl(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HCl(g)$$
$$NaBr(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HBr(g)$$
$$NaI(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HI(g)$$

Observations: White steamy fumes of the Hydrogen Halides are evolved. As above, if tested with ammonia gas lots of white smoke is given off.

Role of $H_3PO_4(l)$: it only acts as an acid (proton donor), and not as an oxidising agent.

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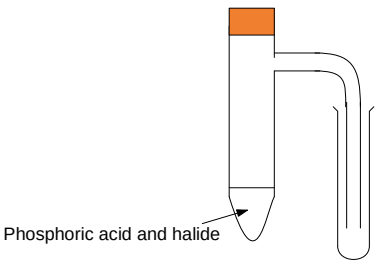
- Phosphoric acid is not an oxidising agent and so does not oxidise HBr and HI.
- These reactions are more suitable than the ones with concentrated sulphuric acid to make HCl, HBr, and HI because there are no extra redox reactions taking place.

This is the apparatus used to make the hydrogen halide using phosphoric acid.

Notice the downward delivery which is used because the hydrogen halides are more dense than air (Learn)



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The reactions of the hydrogen halides

a) All the hydrogen halides react readily with ammonia to give the **white smoke** of ammonium chloride

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

b) **Thermal stability of halides:** Hydrogen Iodide will decompose if a hot nichrome wire is plunged into it. Purple vapour of Iodine will be seen.

$$2\,HI(g) \rightarrow H_2(g) + I_2(g)$$

A very hot wire would also decompose Hydrogen Bromide

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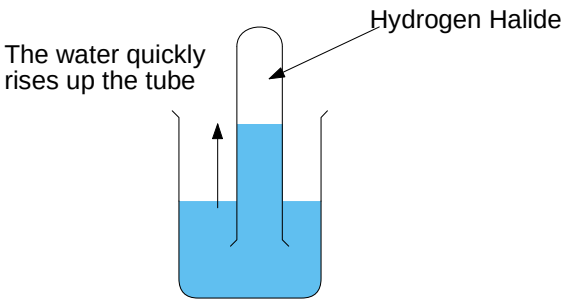
c) **Solubility in water :** The hydrogen halides are all soluble in water. They dissolve to form acidic solutions.



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