#### 1.Title

Reactions of solid halides

# 2.Aim

The purpose of this experiment is to study the effect of an oxidizing acid [concentrated sulphuric(VI) acid] and a non-oxidizing acid [concentrated phosphoric(V) acid] on three solid potassium halides, namely potassium chloride, potassium bromide and potassium iodide..

### 3. Results & Calculations

Table 1

Halide ion	Action of conc.	Product(s)	Confirmatory
	$H_2SO_4(1)$ &		test of
	$MnO_2$		product(s)
C1 <sup>-</sup>		$Cl_2$	A yelllow
			colour is
			observed
			when adding
			hexane
Br		$Br_2$	A red colour
	Steamy fumes		is observed
	are formed		when adding
			hexane
I		$I_2$	A violet
			colour is
			observed
			when adding
			hexane

Table 2

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Halide ion	Action of conc. $H_2SO_4(1)$	Product(s)	Confirmatory test of product(s)

Cl	<ul> <li>Steamy fumes are formed</li> <li>No green gas is evolved even on heating</li> </ul>	HC1	<ul> <li>Dense white fumes are formed with aqueous ammonia</li> <li>It turns blue litmus paper red but not bleached</li> </ul>
Br	<ul><li>Steamy fumes are formed</li><li>A pungent smell is</li></ul>	HBr	White fumes are formed with aqueous ammonia
	<ul><li>detected</li><li>A brown gas is evolved on warming</li></ul>	$SO_2$	<ul> <li>It turns orange dichromate(VI) solution green</li> </ul>
		$\mathrm{Br}_2$	A red colour is observed when adding hexane
Γ	Steamy violet fumes are formed	HI	White fumes are formed with aqueous ammonia
	<ul> <li>A bad egg smell is detected</li> </ul>	$H_2S$	It turns lead(II) ethanoate paper black
		$I_2$	A violet colour is observed when adding hexane

Table 3

Halide ion	Action of conc. H <sub>3</sub> PO <sub>4</sub> (1)	Product(s)	Confirmatory test of product(s)
C1 <sup>-</sup>	Steamy fumes are formed	HC1	White fumes are formed with
Br	on warming	HBr	aqueous ammonia
I-		HI	

# 4.Discussion

Table 1: For chlorine, it can be prepared from the oxidation of chlorine by MnO<sub>2</sub> and conc. HCl Heating will be required.

$$MnO_2 + 4H^+ + 2Cl_{\triangle} \rightarrow Mn^{2+} + 2H_2O + Cl_2$$

The Cl<sub>2</sub> is purified by washing with water to remove HCl and then with conc. H<sub>2</sub>SO<sub>4</sub>, conc. H<sub>3</sub>PO<sub>4</sub>, or anhydrous CaCl<sub>2</sub> to remove moisture.

For bromine, it can be prepared by the action of MnO<sub>2</sub> on KBr and conc. H<sub>2</sub>SO<sub>4</sub>. No heating is required because Br is a stronger agent than Cl. The Br<sub>2</sub> is then dried with anhydrous CaCl<sub>2</sub>. The bromine liquid is purified by distillation.

NaBr + H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  HBr + NaHSO<sub>4</sub> MnO<sub>2</sub> + 4H<sup>+</sup> + 2Br<sup>-</sup>  $\rightarrow$  Mn<sup>2+</sup> + 2H<sub>2</sub>O + Br<sub>2</sub> For iodine, it is similar to Br<sub>2</sub>, using KI + conc. H<sub>2</sub>SO<sub>4</sub>. MnO<sub>2</sub> is not required because I<sup>-</sup> is a strong reducing agent. The I<sub>2</sub> collected is purified by sublimation.

 $KI + H_2SO_4 \rightarrow HI + KHSO_4$  $8HI + H_2SO_4 \rightarrow H_2S + 4H_2O + 4I_2$ 

Table 2: Concentrated sulphric (VI) acid is often said to be an oxidizing acid as it exhibits both oxidizing agent and acidic properties. On treatment with concentrated sulphric acid (VI) acid, chlorides give hydrogen chloride. However, bromides and iodides do not give hydrogen bromide and hydrogen iodide respectively when concentrated sulphuric (VI) acid is added to them. Instead, sulphur dioxide or hydrogen sulphide is formed. Bromides and iodide do not react in the same way with concentrated sulphuric (VI) acid as chlorides. It is because the hydrogen bromide and hydrogen iodide produced are oxidized by concentrated sulphuric (VI) acid to bromine and iodine respectively. However, hydrogen chloride is not oxidized by concentrated sulphuric (VI) acid. In fact, the reaction of chlorides with concentrated sulphuric (VI) acid can be used for the preparation of hydrogen chloride in the laboratory. However, hydrogen bromide and hydrogen iodide cannot be prepared in this way.

Table 3: Phosphoric (V) acid is not an oxidizing agent. It

reacts with halides to form the corresponding hydrogen halides. In fact, this is a general method to prepare hydrogen halides in the laboratory.

## 5. Answers to Question

5.1 Write the chemical equations in each case. Explain the differences in reactivity between concentrated sulphuric(VI) acid and concentrated phosphoric(V) acid.

Table 1:

Table 2:

 $KCl(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HCl(g)$ 

For bromides:

 $KBr(s) + H_2SO_4(1) \rightarrow KHSO_4(s) + HBr(g)$ 

2HBr (g) +  $H_2SO_4(1) \rightarrow SO_2(g) + Br_2(g) + 2H_2O(1)$ 

The chemical equation for the overall reaction is:

2KBr(s) + 3H<sub>2</sub>SO<sub>4</sub>(l) →2KHSO<sub>4</sub>(s) + SO<sub>2</sub>(g) + Br<sub>2</sub>(g) + 2H<sub>2</sub>O (l) For iodides:

 $KI(s) + H_2SO_4(1) \rightarrow KHSO_4(s) + HI(g)$ 

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

The chemical equation for the overall reaction is:

 $8KI(s) + 9H_2SO_4(l) \rightarrow 8KHSO_4(s) + H_2S(g) + 4I_2(g) + 4H_2O(l)$ Table 3:

 $3KCl(s) + H_3PO_4(l) \rightarrow K_3PO_4(s) + 3HCl(g)$ 

 $3KBr(s) + H_3PO_4(1) \rightarrow K_3PO_4(s) + 3HBr(g)$ 

 $3KI(s) + H_3PO_4(1) \rightarrow K_3PO_4(s) + 3HI(g)$ 

5.2 What is the relationship between H-X bond enthalpy and its tendency to undergo further oxidation? [X=Cl/Br/I]

Electron affinity of halogens is the enthalpy change when one mole of electrons is added to one mole of halogen atoms or ions in the gaseous state. The electron affinity decreases from chlorine to iodine. The general decrease in electron affinity is due to the increases in atomic size and number of electrons shells down the group this leads to a decrease in effective charge. Therefore, the tendency of the nuclei of halogen atoms to attract additional electrons decreases.

# 5.3 State the function of manganese (IV) oxide added in experimental procedure (A).

Manganese (IV) oxide is a strong oxidizing agent. When manganese (IV) oxide reacts with reducing agents, it is often reduced to manganese (II) ions

#### 6. Conclusion

The reducing ability of the halide ions increases as we go down the Group when react with an oxidizing acid.