Chlorates

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Nomenclature

ClO_2 chlorine dioxide

Oxyanion		Corresponding acid	
ClO_4^-	perchlorate	$HClO_4$	perchloric acid
ClO_3^-	chlorate	$HClO_3$	chloric acid
ClO_2^-	chlorite	$HClO_2$	chlorous acid
ClO^-	hypochlorite	$HClO$	hypochlorous acid
Cl^-	chloride	HCl	hydrochloric acid

Generation of Chlorine Dioxide

Originally: Sir Humphrey Davy (early 1800s)
potassium chlorate with sulfuric acid

Nowadays, small scale: reaction of sodium chlorite and chlorine

1 Using chlorine directly

$$Cl_2 + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl$$

2 Chlorine generated *in situ*

$$HCl + NaOCl + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl + NaOH$$

Note: Chlorine dioxide is highly reactive, liable to explode as shock sensitive, so usually generated *in situ*.

ClO_4^- = perchlorate, ClO_3^- = chlorate, ClO_2^- = chlorite, ClO^- = hypochlorite, Cl^- = chloride

Chlorine Dioxide in water

Aqueous solutions (low concentrations) are stable in the dark. However, in light slowly decompose to hydrochloric acid (HCl) and chloric acid ($HClO_3$).

$$ClO_2 + H_2O \rightarrow HCl + HClO_3$$

Basic solutions undergo a rapid reaction to give chlorite and chlorate.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

Acidic solutions are more stable. Evidence it decomposes to chlorous acid ($HClO_2$) first, followed by formation of hydrochloric acid and chloric acid.

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Possible other sources of chlorate

Chlorine initially dissolves in water: $Cl_2(g) \rightarrow Cl_2(aq)$

Then reacts, to form hypochlorous acid: $Cl_2(aq) + H_2O \rightarrow HCl + HOCl$

In *basic solution*: $Cl_2 + 2OH^- \xrightarrow{\text{rapid}} Cl^- + ClO^- + H_2O$ Equation 1

The hypochlorous anion rapidly disproportionates (simultaneous oxidation and reduction):

$3ClO^- \rightarrow 2Cl^- + ClO_3^-$ Equation 2

At, or below, room temperature, Equation 1 most likely.

As temperature increases, Equation 2 becomes more likely.

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