# GROUP VII (A2)

## Relative reactivity of Group VII elements as oxidising agents

- All halogens are oxidising agents
- The oxidising power of the elements decreases down Group VII because,
  - the elements become less reactive as atomic number increases
  - the electron affinity decreases (increasing nuclear charge which should attract electrons more; but is offset by - ↑ sheilding - ↑ atomic radius)
- Down group VII, the $E^{\ominus}$ values become less positive.

$$F_2 + 2e^- \longrightarrow 2F^- \quad E^{\ominus} = +2.87\,V$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \quad E^{\ominus} = +1.36\,V$$

$$Br_2 + 2e^- \longrightarrow 2Br^- \quad E^{\ominus} = +1.07\,V$$

$$I_2 + 2e^- \longrightarrow 2I^- \quad E^{\ominus} = +0.54\,V$$

- Fluorine is the strongest oxidising agent.
- Order of oxidising ability:

$$F_2 > Cl_2 > Br_2 > I_2$$

- Each halide ion can be oxidised by the halogen before it.
- A more reactive halogen (on the left) will displace a less reactive one from its compounds.

- Eqs

$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$ $Cl_2$ oxidises $Br^-$ to $Br_2$

$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$ $Cl_2$ oxidises $I^-$ to $I_2$

$Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$ $Br_2$ oxidises $I^-$ to $I_2$

## Reaction with $Fe^{2+}_{(aq)}$

- $Cl_2$ and $Br_2$ can oxidise $Fe^{2+}$ to $Fe^{3+}$, but not $I_2$

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77V$

$Cl_2 + 2Fe^{2+} \longrightarrow 2Cl^- + 2Fe^{3+}$ $E^\ominus_{cell} = +1.36 - 0.77 = +0.59V$

$Br_2 + 2Fe^{2+} \longrightarrow 2Br^- + 2Fe^{3+}$ $E^\ominus_{cell} = +1.07 - 0.77 = +0.30V$

$I_2 + 2Fe^{2+} \longrightarrow 2I^- + 2Fe^{3+}$ $E^\ominus_{cell} = +0.54 - 0.77 = -0.23V$

## Reaction with $Na_2S_2O_3(aq)$

- $Cl_2$ and $Br_2$ oxidise $Na_2S_2O_3$ to $Na_2SO_4$ (sodium sulfate).

$$4Cl_2 + S_2O_3^{2-} + 5H_2O \longrightarrow 2SO_4^{2-} + 10H^+ + 8Cl^-$$

(+2 → +6: oxidation no increases by +4)

- But $I_2$ oxidises $Na_2S_2O_3$ to $Na_2S_4O_6$ (Sodium tetrathionate)

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$$

(+2 → +2.5: oxidation no increases only +0.5)