Redox, Group 2 & Group 7

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<u>Special thanks to Ms Williams and Ms Matrella for their constant</u> <u>support and inspiration</u> Please note that these guides are a collation of my personal notes, teachers' notes, chemistry books, and websites such as chemguide, chemsheets, chemwiki and wikipedia.

Redox

OIL - Oxidation Is Loss of electrons

RIG - Reduction Is Gain of electrons

Oxidation and reduction can be seen as movement up or down a scale of oxidation states

Also note that Oxidation is gain in oxygen or loss of hydrogen. Reduction is loss of oxygen or gain of hydrogen. However these conditions may not necessary apply. If an element gains oxygen but has its oxidation state reduced, it is said to be reduced.

Rules

Here are the rules for determining oxidation states of elements:

Element	Oxidation State
GROUP 1	+1
GROUP 2	+2
F	-1
Cl	-1 (Except in ClF and Cl ₂ O)
0	-2 (Except in F ₂ O and H ₂ O ₂)
Н	+1
H in Metal Hydride	-1

Writing Half Ionic Equations

- 1. Write an equation for the species
- 2. Work out oxidation states for the element on both sides of the equation
- 3. Balance O with H₂O
- 4. Balance H with H^+
- 5. Balance charges with e⁻

Combining Half Equations

If the electrons on both half equations balance out then add the equations and cancel out the e^{-} . If not, use an appropriate scalar.

Common Reducing Agents

These will react to reduce another species and are themselves oxidized. They do so by giving away electrons.

Metals

 $M(s) \rightarrow M^{n+}(aq) + ne^{-}$

For example: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

Iron(II) salts

 $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}$

Acidified potassium iodide

 $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-}$

Thiosulfate

 $2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^{-}$

Ethanedioic acid and ethanedioates

 $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^{-}$

Sulfuric(IV) acid

 $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$

Hydrogen peroxide in the presence of an acid and absence of a strong oxidising agent

 $H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$

Hydrogen

 $H_2(g) + O^{2-}(s) \rightarrow H_2O(l) + 2e^{-}$

Iron(II) salts

 $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}$

Common Oxidizing Agents

These will react to oxidize another species and are themselves reduced. They do so by gaining electrons.

Oxygen

 $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$

Chlorine

 $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

Bromine

 $Br_2(g) + 2e^- \rightarrow 2Br^-(s)$

lodine

 $I_2(g) + 2e^- \rightarrow 2I^-(s)$

Manganate(VII) in acid solution

 $\begin{array}{l} MnO_{4}^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightarrow Mn^{2+}(aq) + \\ 4H_{2}O(l) \end{array}$

Dichromate(VI) in acid solution

Cr₂O₇^{2−}(aq) + 14H⁺(aq) + 6e⁻ → 2Cr³⁺(aq) + 7H₂O(l)

Iron(III) salts Fe³⁺(aq) + e⁻ \rightarrow Fe²⁺(aq)

Hydrogen ions

 $2\mathrm{H^+(aq)}\,+\,2\mathrm{e^-} \twoheadrightarrow \mathrm{H_2(g)}$

Hydrogen peroxide in absence of another oxidising agent

 $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

Concentrated sulfuric acid

Group 2

Ionisation Energy (IE)

IE decreses down the group because more full electron shells are present each time. Hence more shielding effect will take place. Also, the atomic radius will increase. Both of these will decrease the effective nuclear charge which in turn decreases the attraction between the



nucleus and the valency electron. Therefore the outermost electron is more easily removed. Hence reactivity increases down the group.

Reactions

 $M = Group \ 2 Metal$

 $M_{(s)} + Cl_{2(g)} \rightarrow MCl_{2(s)}$

 $2M_{(s)} + O_{2\,(g)} \mathop{\longrightarrow} 2MO_{(s)}$

Element	Reaction with water or steam
Beryllium	No reaction due to a thick oxide layer on the surface of the metal
Magnesium	Very, very slow reaction with cold water — rapid reaction with steam
Calcium	
Strontium	 reaction with cold water to produce hydrogen reactivity increases down the group
Barium	

table 2.5.4 The reaction of the group 2 metals with water.

Magnesium reacts with steam to form magnesium oxide and hydrogen:

 $Mg(s) \, + \, H_2O(g) \, \textbf{\rightarrow} \, MgO(s) \, + \, H_2(g)$

Calcium, strontium and barium react to form the hydroxide and hydrogen, for example:

 $Ca(s) + 2H_2O(g) \twoheadrightarrow Ca(OH)_2(aq) + H_2(g)$

In each case the hydroxide forms an alkaline solution.

Solubility

	nitrates	chlorides	sulphates	hydroxides
magnesium			solubility	solubility
calcium	all	all	decreases	increases
strontium	soluble	soluble	down	down
barium			group	group

A more generalised picture for solubility:

Symbol	Soluble	Insoluble
Na/K/NO ₃ /NH ₄ +	ALL	NO EXCEPTIONS
SO4 ²⁻	MOST	Pb/Ba/Ca
Cl	MOST	Pb/Ag
O ²⁻ /OH ⁻ /CO ₃ ²⁻	Na/K/	THE REST
	Ba^{2+} , Sr^{2+} , Ca^{2+} are considered	
	slightly soluble.	

Thermal Stability

Group 2 Carbonates

The carbonates become more stable to heat as you go down the Group. The smaller the positive ion is, the higher the charge density, and the greater effect it will have on the carbonate ion. As the ionic radius of the cations increases as you go down Group 2, they have less effect on the carbonate ions near them. This means that you have to heat the compound more in order to help the carbon dioxide to break free and leave the metal oxide.



Group 1 Carbonates

Group 1 carbonates are **more** stable to heat than Group 2 carbonates. Only Li_2CO_3 decomposes when heated with a bunsen burner. This is because the charge on cations in Group 1 is only +1 and the polarising power is weaker.

Group 2 Nitrates

 $2X(NO_3)_{2\,(s)} \rightarrow 2XO_{\ (s)} + 4NO_{2\,(g)} + O_{2\,(g)}$

Like the carbonates, the nitrates become more stable to heat as you go down Group 2.

Group 1 Nitrates

In Group 1, only LiNO₃ breaks down to lithium oxide, NO₂ and O₂ when heated. The rest of Group 1 nitrates break down to form the nitrite and O_2 .

 $2KNO_{3\,(s)} \rightarrow 2KNO_{2\,(s)} + O_{2\,(g)}$

Note: The nitrates are easier to break down than the carbonates.

Flame Tests

Dip a clean nichrome or platinum wire into a sample that has been mixed with a few drops of concentrated hydrochloric acid. This is to remove impurities. Hold the wire in a hot blue bunsen flame to see the colours.

How?

Flame colours are produced from the movement of electrons in the metal ions. When heated, electrons gain energy and can jump into empty orbitals at higher levels. We say the atom is excited. When an electron drops back to its ground state, the atom emits a photon of light. Each element has its own characteristic wavelength of light, e.g. 800 nm for lithium ions.

The spacing between energy levels in an atom determines the sizes of the transitions that occur, and thus the energy and wavelengths of the collection of photons emitted. Larger transition – higher energy photon released (shorter wavelength). Small transition – lower energy photon released (longer wavelength).

Smaller transitions tend to occur in the top of the table. From there we say that going down a group, a blue shift tends to occur in Group 1. As for Group 2, the pattern is harder to explain.



Group 7

Strong oxidizing agents due to a very high electronegative character. They only need one electron to be stable. The oxidizing ability decreases down a group since the valence electron is further away from nucleus, more shielded, etc...

Going down a group, the reactivity increases. The colour gets darker and boiling temperature increases: $F(pale yellow gas) \rightarrow Cl$ (greenish yellow gas) $\rightarrow Br$ (dark red liquid) $\rightarrow I$ (shiny/greyish-black crystalline solid).

Reactions

Displacement

As the reactivity decreases down a group, the top elements will displace the bottom ones from their compounds. Sometimes the colour change can be confused, for example Bromine molecules for Iodine molecules. Hence an organic solvent is used to distinguish between them. In the image, the order is Cl_2 , Br_2 , I_2 . The top layer is organic solvent + halogen while the bottom layer is aqueous solution. Another test for presence of iodine molecules is adding starch. If I_2 is present, starch goes from colourless to blue/black. This test is essential when carrying out iodine/thiosulfate titration as it sharpens the end point of the reaction.

	Cl ₂ (aq)	Br ₂ (aq)	l ₂ (aq)
Cl⁻(aq)		Stays yellow solution (no reaction)	Stays brown solution (no reaction)
Br⁻(aq)	Yellow solution forms (Br ₂ forms) $Cl_2 + 2 Br^- \rightarrow 2 Cl^- + Br_2$		Stays brown solution (no reaction)
l⁻(aq)	Brown solution forms (I_2 forms) $CI_2 + 2 I^- \rightarrow 2 CI^- + I_2$	Brown solution forms (I_2 forms) Br ₂ + 2 I ⁻ \rightarrow 2 Br ⁻ + I_2	



Here, the top layer is organic and the bottom is aqueous...The far left is Cl, Br then I

Disproportionation Reactions

In the 3rd reaction, you can see Cl being oxidized to be Cl^- and also reduced to Cl^+ . This is called a disproportionation reactions where a species is both oxidized and reduced at the same time.

$$\begin{array}{rcl} {\rm Cl}_2 + & 2{\rm Fe}^{2+} \rightarrow & 2{\rm Cl}^- + 2{\rm Fe}^{3+} \\ {\rm Br}_2 + & 2{\rm Fe}^{2+} \rightarrow & 2{\rm Br}^- + & 2{\rm Fe}^{3+} \\ {\rm Cl}_2 + & 2{\rm OH}^- \rightarrow & {\rm OCl}^- + & {\rm Cl}^- + & {\rm H}_2{\rm O} \\ {\rm Cl}_2 + & 2{\rm I}^- \rightarrow & 2{\rm Cl}^- + & {\rm I}_2 \\ {\rm 2S}_2{\rm O}_3^{2^-} + & {\rm I}_2 \rightarrow & {\rm S}_4{\rm O}_6^{2^-} + & 2{\rm I}^- \end{array}$$

Testing for the	halides and	solubility in N	IH _{3 (aq)}
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Halide ion	Action of AgNO ₃ (aq)	Action of dilute NH ₃ (aq)	Action of conc. NH ₃ (aq)
F⁻(aq)	No precipitate		
Cl⁻(aq)	Ag⁺(aq) + Cl⁻(aq) → AgCl(s) white ppt	Soluble AgCl(s) + 2 NH ₃ (aq) \rightarrow [Ag(NH ₃) ₂] ⁺ (aq) + Cl ⁻ (aq)	Soluble AgCl(s) + 2 NH ₃ (aq) \rightarrow [Ag(NH ₃) ₂] ⁺ (aq) + Cl ⁻ (aq)
Br⁻(aq)	Ag⁺(aq) + Br⁻(aq) → AgBr(s) cream ppt	Insoluble	Soluble AgBr(s) + 2 NH ₃ (aq) \rightarrow [Ag(NH ₃) ₂] ⁺ (aq) + Br ⁻ (aq)
l⁻(aq)	Ag⁺(aq) + I⁻(aq) → AgI(s) yellow ppt	Insoluble	Insoluble

Reactions Of Halides With Concentrated H₂SO₄

 $NaCl_{(s)} + H_2SO_{4(l)} \rightarrow HCl_{(g)} + NaHSO_{4(s)}$

 $NaBr_{(s)} + H_2SO_{4(l)} \rightarrow HBr_{(g)} + NaHSO_{4(s)}$

But we can distinguish between NaBr and NaCl using conc. sulphuric acid because for bromides, the H_2SO_4 acts as an oxidising agent on the HBr formed to form Br_2 :

 $2HBr(g) + H_2SO_{4(l)} \rightarrow Br_{2(g)} + 2H2O_{(l)} + SO_{2(g)}$

And iodides get oxidised even more. The sulphuric acid is reduced to hydrogen sulphide as the HI is a stronger reducing agent than HBr.

 $8HI_{(g)}+H_2SO_{4(l)} { \longrightarrow } 4I_{2(aq)}+H_2S_{(g)}+4H_2O_{(l)}$

halide	products	observation	reaction type	equation
Cl⁻	HCI	steamy fumes	acid-base	$NaCI + H_2SO_4 \rightarrow NaHSO_4 + HCI$
	HBr	steamy fumes	acid-base	$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$
Br⁻	Br ₂	brown fumes	oxidation of Br [–]	$2 \operatorname{Br}^{-} + \operatorname{H}_2 \operatorname{SO}_4 + 2 \operatorname{H}^{+} \rightarrow \operatorname{Br}_2 + \operatorname{SO}_2 + 2 \operatorname{H}_2 \operatorname{O}$
	SO ₂	colourless gas	reduction of H_2SO_4	$2 \operatorname{Br}^{-} + \operatorname{H}_2 \operatorname{SO}_4 + 2 \operatorname{H}^{+} \rightarrow \operatorname{Br}_2 + \operatorname{SO}_2 + 2 \operatorname{H}_2 \operatorname{O}$
	н	steamy fumes	acid-base	Nal + $H_2SO_4 \rightarrow NaHSO_4 + HI$
	I_2	purple fumes	oxidation of I⁻	$2 \text{I}^- + \text{H}_2 \text{SO}_4 + 2 \text{H}^+ \rightarrow \text{I}_2 + \text{SO}_2 + 2 \text{H}_2 \text{O}$
I-	SO ₂	colourless gas	reduction of H_2SO_4	$2 \text{I}^- + \text{H}_2 \text{SO}_4 + 2 \text{H}^+ \rightarrow \text{I}_2 + \text{SO}_2 + 2 \text{H}_2 \text{O}$
	S	yellow solid	reduction of H_2SO_4	$6 \mid^{-} + H_2 SO_4 + 6 H^+ \rightarrow 3 \mid_2 + S + 4 H_2 O$
	H₂S	gas (bad egg smell)	reduction of H_2SO_4	$8 I^{-} + H_2 SO_4 + 8 H^{+} \rightarrow 4 I_2 + H_2 S + 4 H_2 O$