Chem Factsheet

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Recognising, Constructing & Interpreting Redox Reactions

Before working through this Factsheet you should:
- Understand oxidation and reduction and know how to find the oxidation numbers of elements present in a substance or ion (Factsheet 11);
- Understand oxidation and reduction in terms of both change in oxidation numbers and electron transfer.

After working through this Factsheet you should:
- Recognise, given the equation, whether or not a reaction is redox;
- Be able to construct an overall redox equation using redox half-equations;
- Given an overall redox equation, be able to write the two half-equations showing both oxidation and reduction;
- Be able to identify both the oxidising and reducing agents from a redox equation.

> Be aware that **oxidation numbers** and **oxidation states** are one and the same. If your exam board uses the term 'oxidation state' substitute that term for 'oxidation number' throughout this Factsheet.

Remember

	Oxidation	Reduction
Oxidation number	Increases	Decreases
Electrons	Lost	Gained

Recognising a redox reaction
The simplest way to recognise a redox reaction is to identify the oxidation numbers of all the elements involved in the reaction. Going from reactants to products, if one element increases in oxidation number and another decreases the reaction is ***redox***. If ***none*** of the elements change in oxidation number the reaction is ***not***.

$$\underset{0}{Zn} + \underset{+1}{H_2}SO_4 \rightarrow \underset{+2}{Zn}SO_4 + \underset{0}{H_2}$$ ✓

$$\underset{+1\ -2\ +1}{KOH} + \underset{+1\ +5\ -2}{HNO_3} \rightarrow \underset{+1\ +5\ -2}{KNO_3} + \underset{+1\ -2}{H_2O}$$ ✗

$$\underset{+2}{5Fe^{2+}} + \underset{+7}{MnO_4^-} + 8H^+ \rightarrow \underset{+3}{5Fe^{3+}} + \underset{+2}{Mn^{2+}} + \underset{+1\ -2}{4H_2O}$$ ✓

$$\underset{+2\ +5\ -2}{Pb(NO_3)_2} + \underset{+1\ -1}{2KI} \rightarrow \underset{+1\ +5\ -2}{2KNO_3} + \underset{+2\ -1}{PbI_2}$$ ✗

$$\underset{-1}{5I^-} + \underset{+5}{IO_3^-} + 6H^+ \rightarrow \underset{0}{3I_2} + \underset{+1\ -2}{3H_2O}$$ ✓

$$\underset{+6\ -2}{2CrO_4^{2-}} + \underset{+1}{2H^+} \rightleftharpoons \underset{+6\ -2}{Cr_2O_7^{2+}} + \underset{+1\ -2}{H_2O}$$ ✗

There are a variety of redox reactions to be found at AS/A2, in particular:
- Displacement of $H_2(g)$ from water and acids by elements of groups 1 and 2.
- Change in oxidation states of group 7 elements

	Cl_2	Cl^-	ClO^-	ClO_3^-
Oxidation number:	0	-1	+1	+5

- Change in oxidation states of transition metal ions, eg vanadium:

	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Oxidation number:	+5	+4	+3	+2

Constructing redox reactions
Given sufficient information about reactants and products it is possible to construct redox reactions ***using redox half-equations***.

1. Write the reactants and products *given in the question* as an equation.
2. Using *oxidation numbers* identify those elements involved in oxidation and reduction.
3. Balance ***these elements only*** in the equation.
4. Work out the two half-equations involving ***electrons lost*** and ***gained***
5. Multiply one (or both) the half equations by a number to balance electrons lost and gained.
6. Add the two half-equations together.

At step 4, there may be other elements present in the equation that are **not** changing oxidation state – usually hydrogen or oxygen. These may be unbalanced - eg oxygen only on one side. The table below shows how to deal with this

Problem	Solution	Example
Too many hydrogen on left	Add H^+ on right	$H_2S \rightarrow S + 2H^+$
Too many oxygen on left	Add H^+ on left, H_2O on right	$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
Too many oxygen on right	Add H^+ on right, H_2O on left	$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+$

Once you have dealt with the hydrogen and oxygen in step 4, you need to add the appropriate number of **electrons** to the half equations. You use the principle that the charges must balance - for example, if your total charge is +8 on the left hand side and +3 on the right hand side, then you need to add 5 electrons ($5e^-$) to the left hand side, to make the charges equal.

> ***Exam Hint: -*** *The overall equation must NOT have electrons in it - they are cancelled out in stages 5 and 6.*

1. $Fe^{3+}(aq)$ reacts with $I^-(aq)$ to give $Fe^{2+}(aq)$ and $I_2(s)$.

1. $Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(s)$
2. $+3 \quad -1 \quad +2 \quad 0$
3. $Fe^{3+}(aq) + 2I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(s)$ (Iodine balanced)
4. $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ 1
   $2I^-(aq) \rightarrow I_2(s) + 2e^-$ 2
   (No O or H atoms involved; electrons added to balance charges)
5. Equation 1 $\times$ 2 (to balance electrons lost and gained)
6. $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$

$Fe^{3+}(aq)$ is **reduced** to $Fe^{2+}(aq)$; $I^-(aq)$ is **oxidised** to $I_2(s)$.

2. Bromide ion, Br^- reacts with concentrated sulphuric acid, H_2SO_4 to give bromine, Br_2 and sulphur dioxide, SO_2.

1. $H_2SO_4 + Br^- \rightarrow Br_2 + SO_2$
2. $+6 \quad -1 \quad 0 \quad +4$
3. $H_2SO_4 + 2Br^- \rightarrow Br_2 + SO_2$ (Br balanced)
4. $2Br^- \rightarrow Br_2 + 2e^-$ 1
   $H_2SO_4 + 2H^+ \rightarrow SO_2 + 2H_2O$ (to deal with oxygens)
   $H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$ 2
   (electrons added to balance charges)
5. Electrons lost and gained are balanced
6. $2Br^- + H_2SO_4 + 2H^+ \rightarrow Br_2 + SO_2 + 2H_2O$

H_2SO_4 is **reduced** to SO_2; Br- is **oxidised** to Br_2.

3. Sulphur dioxide, SO_2 reacts with acidified dichromate(VI) ions, $Cr_2O_7^{2-}$ to give sulphate ions, SO_4^{2-} and chromium(III) ions, Cr^{3+}.

1. $SO_2 + Cr_2O_7^{2-} \rightarrow SO_4^{2-} + Cr^{3+}$
2. $+4 \quad +6 \quad +6 \quad +3$
3. $SO_2 + Cr_2O_7^{2-} \rightarrow SO_4^{2-} + 2Cr^{3+}$ (to balance Cr)
4. $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+$ (to balance oxygen)
   $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ 1
   (to balance charges)

   $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$ (to balance oxygen)

   $\underbrace{Cr_2O_7^{2-} + 14H^+}_{(12+)} + 6e^- \rightarrow \underbrace{2Cr^{3+} + 7H_2O}_{(6+)}$ 2
5. Equation 1 $\times$ 3 (to balance electrons lost and gained)
6. $3SO_2 + 6H_2O + Cr_2O_7^{2-} + 14H^+ \rightarrow 3SO_4^{2-} + 12H^+ + 2Cr^{3+} + 7H_2O$
   - Cancelling H^+ and H_2O:
   $3SO_2 + 2H^+ + Cr_2O_7^{2-} \rightarrow 3SO_4^{2-} + H_2O + 2Cr^{3+}$

$Cr_2O_7^{2-}$ is **reduced** to Cr^{3+}; SO_2 is **oxidised** to SO_4^{2-}.

Obtaining oxidation and reduction half-equations from the overall equation

Using oxidation numbers, identify the two elements that are oxidised and reduced.

Take each one in turn and construct the half-equation by
1. writing the appropriate species on each side of the equation,
2. balancing *that element* in the equation,
3. adding or removing oxygen/hydrogen as previously described, balancing the equation and *finally*
4. balancing the charges on each side of the equation by adding electrons to reactants or products.

1. $\underset{+2}{5Fe^{2+}} + \underset{+7}{MnO_4^-} + 8H^+ \rightarrow \underset{+3}{5Fe^{3+}} + \underset{+2}{Mn^{2+}} + 4H_2O$

1. $Fe^{2+} \rightarrow Fe^{3+}$	$MnO_4^- \rightarrow Mn^{2+}$
2. Fe balanced	Mn is balanced
3. No O or H atoms	$\underbrace{MnO_4^- + 8H^+}_{(+7)} \rightarrow \underset{(+2)}{Mn^{2+} + 4H_2O}$
4. $Fe^{2+} \rightarrow Fe^{3+} + e^-$	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

2. $\underset{+5}{2VO_2^+} + \underset{0}{3Zn} + 8H^+ \rightarrow \underset{+2}{2V^{2+}} + \underset{+2}{3Zn^{2+}} + 4H_2O$

1. $Zn \rightarrow Zn^{2+}$	$VO_2^+ \rightarrow V^{2+}$
2. Zn balanced	V is balanced
3. No O or H atoms	$\underbrace{VO_2^+ + 4H^+}_{(+5)} \rightarrow \underset{(+2)}{V^{2+} + 4H_2O}$
4. $Zn \rightarrow Zn^{2+} + 2e^-$	$VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 4H_2O$

***Exam Hint: -** A common error is to try to balance charges too early. This has to be done **after** H^+ etc are included - i.e. at the last stage.*

Disproportionation reactions

During a **disproportionation** reaction the **same** element is both **oxidised and reduced**.

For example, in the reaction between Cl_2 and cold, dilute alkali, eg NaOH(aq), the chlorine disproportionates.

$\underset{0}{Cl_2} + 2NaOH \rightarrow \underset{-1}{NaCl} + \underset{+1}{NaClO} + H_2O$

Cl_2 is both **reduced** to Cl^- ($Cl_2 + 2e^- \rightarrow 2Cl^-$)
and **oxidised** to ClO^- ($Cl_2 + 4OH^- \rightarrow 2ClO^- + 2H_2O + 2e^-$).

At a higher temperature, with concentrated alkali, the ClO^- (chlorate(I) ion) further disproportionates to give Cl^- and ClO_3^- (chlorate(III)) ions:

$[ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O] \times 2$ ——— *reduction*
$ClO^- + 2H_2O \rightarrow ClO_3^- + 4H^+ + 4e^-$ ——— *oxidation*
$3ClO^- \rightarrow 2Cl^- + ClO_3^-$ ——— *overall redox equation*

Copper(I) chloride is stable when *dry*. In aqueous solution, however, the copper(I) ion is unstable and disproportionates into $Cu^{2+}(aq)$ and Cu(s).

$\underset{+1}{2CuCl} + aq \rightarrow \underset{+2}{Cu^{2+}(aq)} + 2Cl^-(aq) + \underset{0}{Cu(s)}$

$Cu^+ + e^- \rightarrow Cu$ ——— *reduction*
$Cu^+ \rightarrow Cu^{2+} + e^-$ ——— *oxidation*

Oxidising and reducing agents

Many students get confused about which is which. One way to think of it is that a **cleaning agent** does not clean itself, it cleans the article to which it is applied. In the process it does itself become **dirty**!

An **oxidising agent** causes the *other* reactant to be oxidised. It is itself **reduced**.

In terms of electrons, oxidation involves **electron loss**. The oxidising agent **receives** those electrons and is therefore **reduced**. The converse is true of the **reducing agent**.

oxidation

$\underset{0}{Cl_2} + \underset{-1}{2Br^-} \rightarrow \underset{-1}{2Cl^-} + \underset{0}{Br_2}$

reduction

or $Cl_2 + 2e^- \rightarrow 2Cl^-$ **reduction**

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

Cl_2 is the **oxidising** agent; Br^- is the **reducing** agent.

***Exam Hint: -** When describing redox reactions some candidates use the oxidation state of the element rather than the **actual** formula of the reactant. E.g. in the following equation*

$$\underset{0}{Cu} + 4H\underset{+5}{N}O_3 \rightarrow \underset{+2}{Cu^{2+}} + 4\underset{+4}{N}O_2 + 2H_2O$$

-1

*HNO_3 is the oxidising agent, **not** N^{5+} - There is no such ion!*
The redox half-equation is

$$\underset{(+5)}{HNO_3} + H^+ + e^- \rightarrow \underset{(+4)}{NO_2} + H_2O$$

*and **not*** $N^{5+} + e^- \rightarrow N^{4+}$

Questions

1. Which of the following equations are redox reactions?
   - A $Br_2 + 2I^- \rightarrow I_2 + 2Br^-$
   - B $3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$
   - C $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$
   - D $2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2[Fe(OH)_3(H_2O)_3] + 3CO_2 + 3H_2O$
   - E $Na_2S_2O_8 + 2NaI \rightarrow I_2 + 2Na_2SO_4$
   - F $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
   - G $2Na + Cl_2 \rightarrow 2NaCl$
   - H $Mg + Zn^{2+} \rightarrow Mg^{2+} + Zn$
   - I $K_2CO_3 + 2HCl \rightarrow 2KCl + H_2O + CO_2$
   - J $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

2. (a) Identify the *oxidising agent* in each of the following equations:
   - A $3Cl_2 + 2Fe \rightarrow 2FeCl_3$
   - B $2H_2S + SO_2 \rightarrow 3S + 2H_2O$
   - C $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$
   - D $5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$
   - E $H_2O_2 + H_2S \rightarrow S + 2H_2O$

   (b) Identify the *reducing agent* in each of the following equations:
   - A $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$
   - B $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$
   - C $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$
   - D $3SO_3^{2-} + Cr_2O_7^{2-} + 8H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$
   - E $2VO^{2+} + Zn + 4H^+ \rightarrow 2V^{3+} + Zn^{2+} + 2H_2O$

3. (a) Fe^{2+} is changed into Fe^{3+} by reaction with acidified $Cr_2O_7^{2-}$ which becomes Cr^{3+}. Using redox ½-equations construct the overall redox equation for this reaction. Which species is the oxidising agent? Give a reason for your answer.

   (b) During the course of a redox reaction between iodine, I_2 and the thiosulphate ion, $S_2O_3^{2-}$, the products formed are the iodide, I^- and tetrathionate, $S_4O_6^{2-}$ ions. Using redox ½-equations, construct the overall equation for the reaction. Identify the reducing agent, giving reasons for your decision.

4. From the two equations given below, construct and identify the two redox ½-equations:
   (a) $2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$
   (b) $I^- + IO_3^- + 6H^+ \rightarrow I_2 + 3H_2O$

5. The manganate(VI) ion in acid solution undergoes a disproportionation reaction as follows:
   $3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2MnO_4^- + MnO_2(s) + 2H_2O(l)$
   (a) What is a disproportionation reaction?
   (b) Show, using both oxidation numbers and ½-equations, that this is an example of such a reaction.

Answers

1. A (*Cl changes oxidation number from 0 to –1, Br- from –1 to 0*).
   B (*Cu from +2 to 0, N from –3 to 0*).
   C (*N from +5 to +4, O from –2 to 0 in O_2*)
   E (*S from +7 to +6, I from –1 to 0*).
   G (*Na from 0 to +1, Cl from 0 to –1*)
   H (*Mg from 0 to +2, Zn from 2+ to 0*)

2. (a) A Cl_2: (*Cl decreases oxidation number from 0 to –1 and is reduced*).
   B SO_2 (*S from +4 to 0*)
   C HNO_3 (*N from +5 to +4 in NO_2*).
   D MnO_4^- (*Mn from +7 to +2*).
   E H_2O_2 (*O from –1 to –2*). [Note that the oxidation number of O in H_2O_2 is –1, not –2. If it was –2, H would be +2 which is not possible because a H atom only has one electron and cannot form H^{2+}].

   (b) A Ca (*increases oxidation number from 0 to +2 and is oxidised*).
   B I^- (*I from –1 to 0*).
   C Cu (*from 0 to +2*).
   D SO_3^{2-} (*S from +4 to +6*).
   E Zn (*from 0 to +2*).

3. (a) $[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 6$ OXIDATION
   $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ REDUCTION

   $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$
   $Cr_2O_7^{2-}$ (acidified) is the oxidising agent. It receives electrons from Fe^{2+} and is reduced.

   (b) $I_2 + 2e^- \rightarrow 2I^-$ REDUCTION
   $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$ OXIDATION

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

   $S_2O_3^{2-}$ is the reducing agent. It gives electrons to I_2 and is oxidised.

4. (a) $2I^- \rightarrow I_2 + 2e^-$ OXIDATION
   $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ REDUCTION

   (b) $2I^- \rightarrow I_2 + 2e^-$ OXIDATION
   $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

5 (a) A disproportionation reaction is one in which the same element is both oxidised and reduced.
   (b) Manganese is both oxidised and reduced:
   $\underset{+6}{MnO_4^{2-}} \rightarrow \underset{+7}{MnO_4^-} + e^-$ OXIDATION
   $\underset{+6}{MnO_4^{2-}} + 4H^+ + 2e^- \rightarrow \underset{+4}{MnO_2} + 2H_2O$ REDUCTION

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