1

Oxidation and reduction

Definitions

You should remember the following from your Year 12 work.

- An **oxidation-reduction** (redox) reaction is any reaction involving a *transfer of electrons.*
- In all redox reactions, oxidation and reduction occur at the same time.
- **Oxidation** is a *loss* of electrons.
- **Reduction** is a *gain* of electrons.
- **Oxidising agents** (oxidants) are themselves reduced, **reducing agents** (reductants) are themselves oxidised.

REVISION

1A 1 Oxidation-reduction facts

Oxidation numbers

Oxidation numbers are a form of electronic book-keeping. They are particularly useful when working with reactions involving elements which can exist in a number of different oxidation states, such as sulfur, nitrogen and the transition elements.

Rules for assigning oxidation numbers

1 The oxidation number of any free, uncombined element is zero. This includes polyatomic molecules of elements such as H_2, O_3 and S_8.

2 The charge on a simple (monatomic) ion is the oxidation number of the element in that ion. In a polyatomic ion, the sum of the oxidation numbers of the atoms in that ion is equal to the charge on the ion.

3 In compounds (whether ionic or covalent), the sum of the oxidation numbers of all atoms in the compound is zero.

4 The oxidation number of oxygen is –2, except in the case of peroxides where it is –1.

5 The oxidation number of hydrogen is +1, except in the case of metallic hydrides where it is –1.

Example 1.1 **Oxidation numbers**

Write the oxidation numbers for each of the underlined atoms:

a $\underline{Pb}O_2$ **b** $\underline{Br}O_3^-$ **c** $[\underline{Fe}SCN]^{2+}$

a PbO_2 is a compound, so the sum of the oxidation numbers (ON) will be zero (rule 3), and the oxygen has an ON of –2 (rule 4), so we can calculate the ON of the Pb by simple algebra:

$$\begin{aligned} Pb + 2O &= 0 \\ Pb + (2 \times -2) &= 0 \\ Pb - 4 &= 0 \\ Pb &= +4 \end{aligned}$$

POWERPOINT

1A 1 Calculating and using oxidation numbers

b BrO_3^- is an ion, so the sum of its ON will be −1 (rule 2). The oxygen atoms will again have ON of −2 (rule 4), so:

$$\begin{aligned} Br + 3O &= -1 \\ Br + (3 \times -2) &= -1 \\ Br - 6 &= -1 \\ Br &= -1 + 6 \\ Br &= +5 \end{aligned}$$

c $[FeSCN]^{2+}$ is a complex ion, containing the SCN^- ion. It is not necessary to work out the ON for the S, C and N atoms, since we know that their sum will be −1 (rule 2).

$$\begin{aligned} Fe + SCN &= +2 \\ Fe - 1 &= +2 \\ Fe &= +3 \end{aligned}$$

Identifying redox equations

Oxidation numbers can be used to identify what has been oxidised or reduced in an equation.

- If its oxidation number increases, the element has been oxidised.
- If its oxidation number decreases, the element has been reduced.

Example 1.2 Using oxidation numbers

Use oxidation numbers to determine whether the following reaction is a redox reaction, and if so, which element has been oxidised, and which reduced.

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(l)$$

It is simplest to write the oxidation numbers above each element:

$$4\overset{-3}{N}\overset{+1}{H_3}(g) + 3\overset{0}{O_2}(g) \longrightarrow 2\overset{0}{N_2}(g) + 6\overset{+1}{H_2}\overset{-2}{O}(l)$$

The oxidation numbers of N and O have changed: it is a redox reaction.

The oxidation number of N has gone from −3 to 0: it has been oxidised.

The oxidation number of O has gone from 0 to −2: it has been reduced.

REVISION

1A 2 Oxidation number

Quiz 1A 2

Test yourself 1A Electron transfer reactions

1 Define the terms *oxidation* and *reduction* in terms of electron transfer.

2 Determine the oxidation numbers of the underlined atoms:

a $\underline{Cl}O^-$ **b** $\underline{Cr}O_4^{2-}$ **c** $\underline{C}O_2$ **d** $\underline{S}O_3^{2-}$ **e** $H_2\underline{S}$

3 Use oxidation numbers to determine whether the following reactions are redox reactions. For those that are, identify the element oxidised, and the element reduced.

a $HgCl_2(aq) + 2KI(aq) \longrightarrow HgI_2(s) + 2KCl(aq)$

b $3HCl(aq) + HNO_3(aq) \longrightarrow Cl_2(g) + NOCl(g) + 2H_2O(l)$

c $ICl(s) + H_2O(l) \longrightarrow HCl(aq) + HOI(aq)$

d $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

e $2MnO_4^-(aq) + HSO_3^-(aq) + 3OH^-(aq) \longrightarrow 2MnO_4^{2-}(aq) + SO_4^{2-}(aq) + 2H_2O(l)$

4 Put circles around the oxidants, and squares around the reductants, in the following equations:

a $CuO + H_2 \longrightarrow Cu + H_2O$

b $Ag^+(aq) + Fe^{2+}(aq) \longrightarrow Ag(s) + Fe^{3+}(aq)$

c $5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$

Laboratory redox

Identifying species in redox reactions

For many redox reactions there are visible changes in the appearance of one or both of the reacting species. For example, when acidified potassium permanganate is added to hydrogen peroxide solution the purple colour disappears as MnO_4^- is reduced to Mn^{2+}. In other reactions no colour change is visible, so we have to add another reagent if we wish to detect the reaction. You should remember the following tests from Year 12 chemistry:

I_2: turns blue/black with starch solution
SO_4^{2-}: forms a white precipitate with acidified barium chloride solution
Fe^{3+}: forms a blood-red solution with potassium thiocyanate solution
Cl_2: turns damp starch-iodide paper blue/black.

You should be familiar with the following redox reagents from Year 12 chemistry.

Reduced form		Oxidised form	
Formula	**Appearance**	**Formula**	**Appearance**
Cu	brown solid	Cu^{2+}	blue ion
SO_2	colourless gas	SO_4^{2-}	colourless ion
Mn^{2+}	colourless ion	H^+/MnO_4^-	purple ion
H_2O_2	colourless liquid	O_2	colourless gas
H_2O	colourless liquid	H_2O_2	colourless liquid
Cr^{3+}	blue/green ion	$Cr_2O_7^{2-}$	orange ion
Fe^{2+}	pale green ion	Fe^{3+}	orange ion
Cl^-	colourless ion	Cl_2	pale green gas
Br^-	colourless ion	Br_2	red/orange liquid
H_2	colourless gas	H^+	colourless ion

You also need to learn the colours and formulae of the following reagents, which will be probably be new to you this year.

POWERPOINT

1B 1 Chemical tests for redox species

Use coloured pencils or pens to show the colour of each species in this table.

REVISION

1B 1 Formula practice
1B 2 Redox colours

Quizzes 1B 1, 1B 2a, 1B 2b

PRACTICAL

1.1 P 149 Redox reactions: some examples

POWERPOINT

1B 2 Permanganate with neutral and acidified H_2O_2

1B 3 Bromate and sulfur dioxide

1B 4 Reactions involving I_2 and I^-

1B 5 $CuSO_4(aq)$ and $I_2(aq)$

REVISION

1B 3a Testing for redox species

1B 3b–3g Learning redox pairs

1B 4a–4b Studying redox reactions

Quizzes 1B 3, 1B 4a, 1B 4b

Reduced form		Oxidised form	
Formula	Appearance	Formula	Appearance
MnO_2	brown precipitate	H_2O/MnO_4^-	purple ion
MnO_4^{2-}	green ion	OH^-/MnO_4^-	purple ion
I^-	colourless ion	I_2 (in $I^- = I_3^-$)	brown solution
I_2 (in $I^- = I_3^-$)	brown solution	IO_3^-	colourless ion
H_2S	colourless gas	S	yellow/white solid
Pb^{2+}	colourless ion	PbO_2	brown solid
NO_2	brown gas	NO_3^-	colourless ion
$C_2O_4^{2-}$	colourless ion	CO_2	colourless gas
$S_2O_3^{2-}$	colourless ion	$S_4O_6^{2-}$	colourless ion
Br_2	red-orange liquid	BrO_3^-	colourless ion

Use coloured pencils or pens to show the colour of each species in this table.

Important oxidising agents are MnO_4^- (in acid, neutral or alkaline conditions), $H^+/Cr_2O_7^{2-}$, H_2O_2, Cl_2 and IO_3^- or BrO_3^-.

Important reducing agents are SO_2 (or HSO_3^-), $S_2O_3^{2-}$ (thiosulfate), Fe^{2+}, and $C_2O_4^{2-}$ (oxalate—from oxalic acid).

You will meet other redox reagents as well, but those listed above are the important ones.

Test yourself 1B Laboratory redox

1 Describe what you would see when:

a $Cr_2O_7^{2-}$ is reduced

b Br^- is oxidised

c IO_3^- is reduced

d H_2O_2 is oxidised

2 Describe what you would see when:

a Iodine solution, to which a few drops of starch have been added, is reduced to I^- by thiosulfate solution. The thiosulfate is oxidised to $S_4O_6^{2-}$.

b Oxalic acid reduces H^+/MnO_4^- to Mn^{2+}. The oxalic acid is oxidised to CO_2.

c Zinc metal is oxidised to Zn^{2+} by dilute sulfuric acid. The H^+ is reduced.

Balancing redox equations

When writing equations for redox reactions, we normally write two half-equations (for the oxidation and the reduction processes), then add them together. Usually we keep things simple by leaving out the spectator ions.

Balancing redox equations in acidic or neutral conditions

For each half-equation:

1 Balance the atoms that are not O or H.
2 Balance the O by adding water.
3 Balance the H by adding H^+.
4 Balance the charge by adding electrons to the more positive side.

To put the half-equations together:

5 Multiply the half-equations by the factors needed to make the number of electrons transferred in each half-equation the same.
6 Add the two equations together, cancelling out the electrons and any other duplicated species.

Example 1.3 Balancing a redox equation in acid conditions

Acidified potassium permanganate is decolourised by iron(II) sulfate solution. Write an ionic equation for this reaction.
Break the reaction into two half-equations. The Fe^{2+} will be oxidised to Fe^{3+}. The ion-electron half-equation is simple:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

The MnO_4^- will be reduced to Mn^{2+}. Follow the steps above to write the ion-electron half-equation:

$$MnO_4^- \longrightarrow Mn^{2+}$$
$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$
$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

In combining the two half-equations, multiply the Fe^{2+} equation by 5, since there are $5e^-$ in the MnO_4^- equation:

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^-$$

Finally, add the two equations together:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Balancing redox equations in alkaline conditions

The method shown above is used for all reactions done in acidic or neutral conditions. To balance reactions done in strongly alkaline conditions we modify step **3** of the above method.

3 Balance the H by adding H^+, then add an equal amount of OH^- to both sides of the equation (which changes the H^+ into H_2O).

Example 1.4 Balancing a redox equation in alkaline conditions

Write an ion-electron half-equation for the reduction of MnO_4^- to MnO_2 in alkaline conditions.

$$MnO_4^- \longrightarrow MnO_2$$

Balance the atoms that aren't O or H.

$$MnO_4^- \longrightarrow MnO_2$$

Balance the O by adding H_2O.

$$MnO_4^- \longrightarrow MnO_2 + 2H_2O$$

Balance the H by adding H^+.

$$MnO_4^- + 4H^+ \longrightarrow MnO_2 + 2H_2O$$

Cancel out the H^+ by adding OH^-.

$$MnO_4^- + 4H^+ + 4OH^- \longrightarrow MnO_2 + 2H_2O + 4OH^-$$
$$MnO_4^- + 4H_2O \longrightarrow MnO_2 + 2H_2O + 4OH^-$$

Cancel out extra waters, etc.

$$MnO_4^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$$

Balance the charge by adding electrons.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

PRACTICAL

1.2 P 152 — Redox reactions involving the halogens

ENCOUNTER

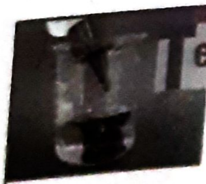
1A — Sodium percarbonate — a modern bleach

POWERPOINT

1C 1 — Permanganate with alkaline hydrogen sulfite
1C 2 — Lead dioxide and conc HCl
1C 3 — Hydrogen sulfide gas and iodine solution

Quizzes 1C 1a, 1C 1b, 1C 1c

To check whether you have balanced a complex redox half-equation correctly: the change in oxidation number should equal the number of electrons transferred. In this equation the ON has changed from +7 to +4 and there are 3 electrons transferred.



Test yourself 1C Redox equations

Write ion-electron half-equations, and hence the full ionic equations, for the following redox reactions.

1 Sodium thiosulfate solution decolourises iodine solution.

2 Oxalic acid decolourises acidified potassium permanganate solution.

3 A brown solution forms when potassium bromate is added to acidified potassium iodide solution.

4 To balance this equation under alkaline conditions, first divide it into two half-equations.

$$TeO_3^{2-} + V^{4+} \longrightarrow Te + V^{5+}$$

Key learning outcomes for Chapter 1

By now you should be able to:

1 Determine the oxidation number of any atom in a compound or ion and use oxidation numbers to identify the oxidised and reduced species in a given reaction.

2 Recall common oxidising and reducing agents, state the colours of the reagents and their products, and recall any other observations or conditions characteristic of their use.

3 Write ion-electron equations for oxidation and reduction half-reactions and combine the half-equations to give a balanced ionic equation.

EXAM QUESTIONS

Practice questions