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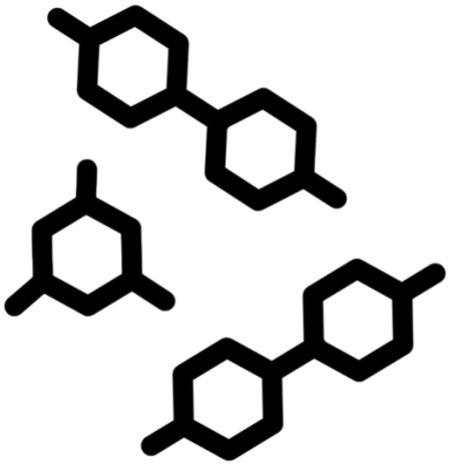
Year 12 ATAR Chemistry

Unit 3: Oxidation and Reduction



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Chemistry ATAR Year 12 Unit 3

Oxidation and Reduction

Oxidation-reduction (redox) reactions involve the transfer of one or more electrons from one species to another.

OXIDATION AND REDUCTION

All chemical changes are, at an atomic level, due to electrical interactions.
One particular group of chemical changes can best be understood by considering them as electron-transfer reactions.

Chemists initially defined oxidation as the process by which a substance gained oxygen. For example:

$$2Hg_{(l)} + O_{2\,(g)} \rightarrow 2HgO_{(s)}$$

The mercury is said to be oxidised. Also when magnesium burns brightly in air, the magnesium is oxidised.

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

Reactions that involved the loss of oxygen from a compound were termed reduction.

$$CuO_{(s)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2O_{(l)}$$

See magnesium burning image https://images.app.goo.gl/vAkVioUzP9BFF62i6

Exercise 1: Identify any substances being oxidised or reduced in each of the following:

a. $2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}$

b. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

c. $PbO_{(s)} + CO_{(g)} \rightarrow Pb_{(s)} + CO_{2(g)}$

The early definition of redox reactions were far too limiting and do not cover many similar reactions which do not involve oxygen.
Redox reactions in fact, simply involve the transfer of electrons from one species to another.

These definitions were then extended to include:

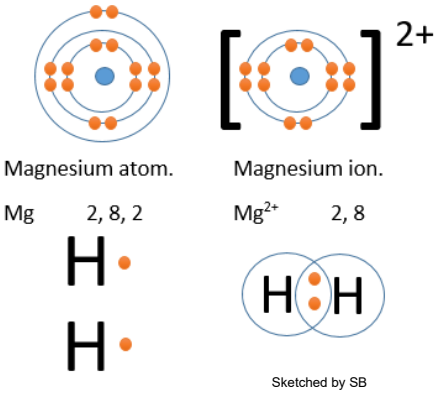
- the addition or removal of oxygen
- the removal or gain of hydrogen.
- loss or gain of electrons which is now the accepted definition of oxidation and reduction

Exercise 2: Consider the reaction between magnesium and HCl.

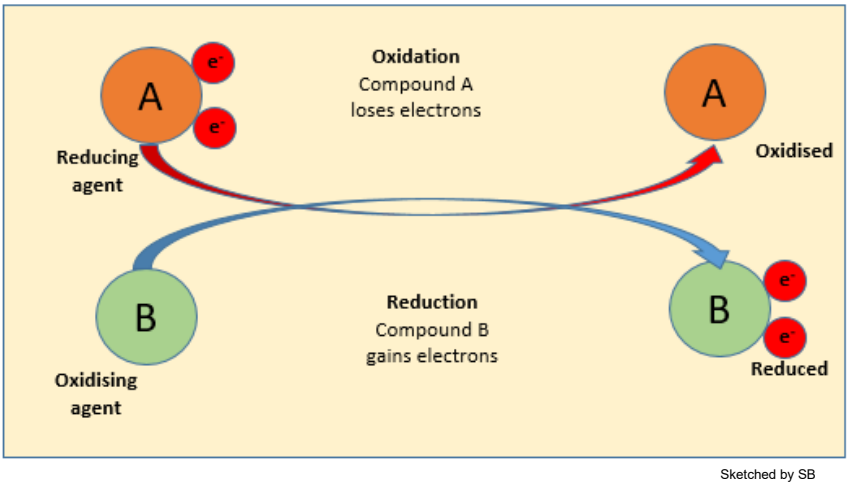
a) What is happening to the Mg?

b) What is happening to the H^+?

c) Discuss, in terms of electron transfer, what is going on in this reaction.



Redox reactions involve the transfer of e^- between reacting species causing **simultaneous** oxidation and reduction.



Oxidation

- originally referred to as the addition of oxygen to other elements.
  - $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ C is oxidised.
- is the *loss of electrons* by a chemical species during a reaction. A species which has lost e^- is **oxidised**.
  - e.g. $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$ Fe^{2+} is oxidised

Reduction

- originally referred to as the removal of oxygen from a compound.
  - $Fe_2O_{3(s)} + C_{(s)} \rightarrow Fe_{(l)} + CO_{2(g)}$ Fe_2O_3 is reduced
- is the *gaining of electrons* by a chemical species during a reaction. A species which has gained e^- is **reduced**.
  - e.g. $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$ Cl_2 is reduced

As one species loses e^- another *must* gain these electrons, thus the process occurs <u>simultaneously</u>. i.e. they are said to be <u>*interdependent*</u>.

Oxidation **I**s **L**oss (of electrons)
Reduction **I**s **G**ain (of electrons)

or **O I L** **R I G** for short

Loss of **E**lectrons is **O**xidation
Gain of **E**lectrons is **R**eduction

or **LEO** **GER** for short

Exercise 3: Complete the following by crossing out the incorrect statement

$Zn_{(s)} + I_{2(s)} \rightarrow ZnI_{2(s)}$ (Zn^{2+}, $2I^-$)

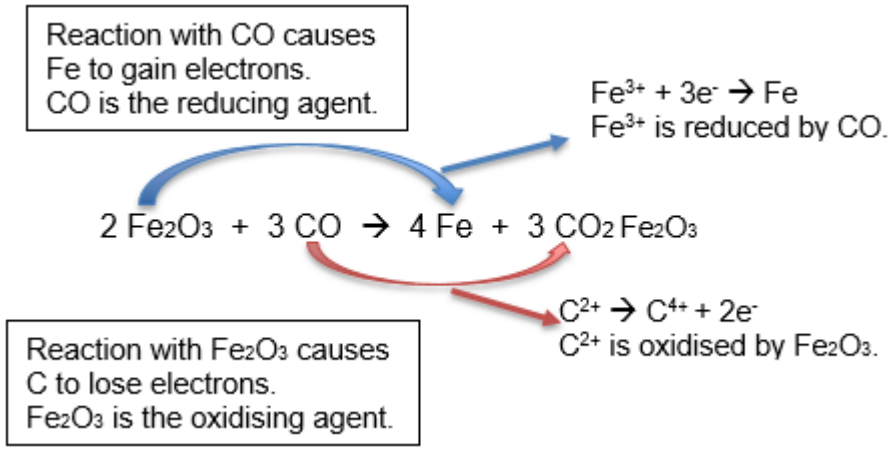
Zn
- donates/accepts electrons
- is oxidised/reduced

I_2
- donates/accepts electrons
- is oxidised/reduced

An **<u>oxidiser</u>** (or oxidising agent or oxidant) is *reduced* during the reaction as it *oxidises* the other chemical species.
e.g. O_2, Cl_2, H_2O_2, MnO_4^-, conc. H_2SO_4 and HNO_3
i.e. it is an e^- acceptor.
ClO^- (hypochlorite ion) used in bleach and water purification.

A **<u>reducer</u>** (or reducing agent or reductant) is *oxidised* as is *reduces* the other substance.
e.g. Zn, C, H_2, Fe^{2+}, $C_2O_4^{2-}$ (oxalate ion)
i.e. it is an e^- donor.

In the extraction of iron from iron ore



Exercise 4: Identify which species is oxidised/reduced and the oxidising/ reducing agents in the following reaction.

$$3Cu^{2+}_{(aq)} + 2Al_{(s)} \longrightarrow 3Cu_{(s)} + 2Al^{3+}_{(aq)}$$

Species	Electron Transfer	Type of Change	Type of Agent
$Cu^{+2}_{(aq)}$			
$Al_{(s)}$			

Non-metal molecules and some ions are often used as oxidising agents: all easily gain e^-'s.

O_2, Cl_2, MnO_4^-, $Cr_2O_7^{2-}$, ClO^-, H^+,conc HNO_3, conc H_2SO_4, H_2O_2, Br_2, I_2, S_8.

Active metals and some ions are among the substances frequently used as reducing agents: all easily lose e^-'s.

Zn, C, H_2, Fe^{2+}, $C_2O_4^{2-}$, Mg, Ca, CO, Al, SO_2.

Exercise 5: Problem Set

1. Identify the species being oxidised and that being reduced in each of the following:
   a. $Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{+2}_{(aq)} + H_{2(g)}$ oxidised: reduced:
   b. $Mg_{(s)} + S_{(s)} \rightarrow MgS_{(s)}$ oxidised: reduced:
   c. $Cu^{+2}_{(aq)} + Fe_{(s)} \rightarrow Cu_{(s)} + Fe^{+2}_{(aq)}$ oxidised: reduced:
2. Identify the oxidising agent and the reducing agent in each of the following:
   a. $Cl_{2(g)} + 2Br^-_{(aq)} \rightarrow Br_{2(l)} + 2Cl^-_{(aq)}$ OA: RA:
   b. $Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$ OA: RA:
   c. $2Ag^+_{(aq)} + Cu_{(s)} \rightarrow Cu^{+2}_{(aq)} + 2Ag_{(s)}$ OA: RA:
3. Identify the oxidising agent in each of the following:
   a. $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(s)} + Cu_{(s)}$
   b. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$
   c. $Zn_{(s)} + Cl_{2(g)} \rightarrow ZnCl_{2(s)}$

4. Identify the reducing agent in each of the following:
   a. $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$
   b. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$
   c. $Zn_{(s)} + Cl_{2(g)} \rightarrow ZnCl_{2(s)}$

Oxidation involves the loss of electrons from a chemical species, and reduction involves the gain of electrons by a chemical species; these processes can be represented using half-equations and redox equations (acidic conditions only).

HALF EQUATIONS

Redox equations are considered in two parts:

- the oxidation reaction
- the reduction reaction.

These are called half equations.

Oxidation half equations:

- show the species which is oxidised - loses electrons.
- electrons are placed on the <u>product side</u> of the half equation.

$Zn_{(s)} \rightarrow Zn^{2+}_{(s)} + 2e^-$

Reduction half equations:

- show the species which is reduced - gains electrons.
- electrons are placed on the <u>reactant side</u> of the half equation.

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Half equations must be balanced for **atoms** and **total charge**.

MORE COMPLEX HALF EQUATIONS

There are two techniques by which we can produce balanced half-equations:-

	Procedure	Example – F is reduced to F_2	
Ion-electron method	1. Write down the reactant and product in a skeleton equation.	FO_3^-	$\rightarrow F_2$
	2. Balance the number of atoms of the element being oxidised or reduced.	$2FO_3^-$	$\rightarrow F_2$
	3. Balance the number of atoms of oxygen by adding H_2O to the side that is deficient in O.	$2FO_3^-$	$\rightarrow F_2 + 6H_2O$
	4. Balance the number of atoms of hydrogen by adding H^+ to the side that is deficient in H.	$2FO_3^- + 12H^+$	$\rightarrow F_2 + 6H_2O$
	5. Balance the charge by adding e^- to the side that is more positive.	$2FO_3^- + 12H^+ + 10e^-$	$\rightarrow F_2 + 6H_2O$
	6. Check that all atoms and charge balance.		✓
	7. Add the states (if required).	$2FO_3^-{}_{(aq)} + 12H^+{}_{(aq)} + 10e^-$	$\rightarrow F_{2(aq)} + 6H_2O_{(l)}$

The other technique will be shown later.

Example – MnO_4^- is reduced to Mn^{2+}

1. Show the oxidised or reduced species and its product.
2. $MnO_4^- \rightarrow Mn^{2+}$
3. Balance the element that is oxidised or reduced
   - Mn already balanced
4. Balance O atoms by adding H_2O.
   - $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
5. Balance H atoms by adding H^+ ions.
   - $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
6. Balance charge by adding electrons. 7+ on the LHS, 2+ on the RHS – need 5- on RHS
   - $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
7. Subscripts *(aq), (l), (s), (g)* should be added as required
   - $MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$

Exercise 6: Balance this half equation.

$Cl_2 \rightarrow HClO$

BALANCED REDOX EQUATIONS

A redox equation

- must be balanced for charge and atoms.
- electrons do not appear in the redox reaction (they get cancelled out).

The oxidation and reduction half equations are added together - the number of electrons produced in the oxidation half equation **must equal** the number of electrons consumed in the reduction half equation.

Writing Redox Equations

Example: Write the redox equation for the oxidation of Al metal by $H^{+}_{(aq)}$ forming $H_{2(g)}$ and $Al^{+3}_{(aq)}$.

Write oxidation and reduction half equations.

i. $Al_{(s)} \rightarrow Al^{+3}_{(aq)} + \mathbf{3e^{-}}$

ii. $\mathbf{2e^{-}} + 2H^{+}_{(aq)} \rightarrow H_{2(g)}$

Multiply coefficients of each half equation so that electrons are equalised in both.

Multiply **i.** by 2.

$\mathbf{2}Al_{(s)} \rightarrow 2Al^{+3}_{(aq)} + \mathbf{6e^{-}}$

Multiply **ii.** by 3

$\mathbf{6e^{-}} + 6H^{+}_{(aq)} \rightarrow 3H_{2(g)}$

Add the two half equations and cancel the electrons.

$\mathbf{2}Al_{(s)} + 6H^{+}_{(aq)} \rightarrow 3H_{2(g)} + 2Al^{+3}_{(aq)}$

Simplify coefficients for any species common to both sides.
(No species common to both sides, equation is complete.)

Exercise 7: Balancing redox equations.

a) Write a redox equation for the oxidation of $Fe^{+2}_{(aq)}$ by $Cl_{2(g)}$ forming $Fe^{+3}_{(aq)}$ and $Cl^{-}_{(aq)}$.

b) Write a redox equation for the oxidation of $Mg_{(s)}$ by $Br_{2(g)}$ forming $MgCl_{2(s)}$.

Harder Example: Write the redox equation for the oxidation of $H_2C_2O_4$ solution by acidified $KMnO_4$ solution producing $Mn^{+2}_{(aq)}$ ions and $CO_{2(g)}$.

Write oxidation and reduction half equations.

i. $\mathbf{5e^-} + MnO_4^- + 8H^+ \rightarrow Mn^{+2} + 4H_2O$ (NOTE: K^+ will be a spectator ion)

ii. $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + \mathbf{2e^-}$

Multiply coefficients of each half equation so that electrons are equalised in both.

Multiply **i.** by 2.

$\mathbf{10e^-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{+2} + 8H_2O$

Multiply **ii.** by 5.

$5H_2C_2O_4 \rightarrow 10CO_2 + 10H^+ + \mathbf{10e^-}$

Add the two half equations and cancel the electrons.

$5H_2C_2O_4 + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{+2} + 8H_2O + 10CO_2 + 10H^+$

Simplify coefficients for any species common to both sides.

Eliminate 10 H^+ from both sides.

$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{+2} + 8H_2O + 10CO_2$

Subscripts *(aq), (l), (s), (g)* should be added as required.

$5H_2C_2O_{4(aq)} + 2MnO_4^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 2Mn^{+2}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(g)}$

Exercise 8: Balancing harder redox equations.

a) Acidified $\mathbf{K_2Cr_2O_7}_{(aq)}$ [$H^+_{(aq)}$, $K^+_{(aq)}$ and $Cr_2O_7^{-2}{}_{(aq)}$] is added to $\mathbf{Na_2S}_{(aq)}$ [$Na^+_{(aq)}$ and $S^{-2}_{(aq)}$] forming **sulfur** and **chromium (III) ions.**

b) Hydrogen peroxide is added to sodium oxalate to form water and carbon dioxide

COMMON OXIDISING AND REDUCING AGENTS and REDOX EQUATIONS

Some Common Oxidising Agents

Oxidising Agent			Reduction Product	
Name	**Characteristic**	**Half-Equation**	**Name**	**Characteristic**
flourine	pale yellow gas	$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$	fluoride ion	colourless solution
hydrogen peroxide	colourless solution	$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons 2H_2O_{(l)}$	water	colourless solution
hypochlorous acid	colourless solution	$2HClO_{(aq)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons Cl_{2(aq)} + 2H_2O_{(l)}$	chlorine solution	pale yellow solution
permanganate ion	purple solution	$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^+ \rightleftharpoons Mn^{+2}_{(aq)} + 4H_2O_{(l)}$	manganese (II) ion	colourless solution
gold ion		$Au^{3+}_{(aq)} + 3e^- \rightleftharpoons Au_{(s)}$	gold solid	gold coloured metal
hypochlorite ion	colourless solution	$ClO^-_{(aq)} + H_2O_{(l)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)} + 2OH^-_{(aq)}$	chloride ion	colourless solution
chlorine gas	greenish-yellow gas	$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	chloride ion	colourless solution
dichromate ion	orange solution	$Cr_2O_7^{-2}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{+3}_{(aq)} + 7H_2O_{(l)}$	chromium (III) ion	green solution
oxygen	colourless gas	$O_{2(g)} + H_2O_{(l)} + 4e^- \rightleftharpoons 4OH^-_{(aq)}$	hydroxide ion	colourless solution

Some Common Reducing Agents

Reducing Agent			Oxidation Product	
Name	**Characteristic**	**Half-Equation**	**Name**	**Characteristic**
calcium solid	silver, grey	$Ca_{(s)} \rightleftharpoons Ca^{+2}_{(aq)} + 2e^-$	calcium ion	colourless solution
magnesium solid	silver, grey	$Mg_{(s)} \rightleftharpoons Mg^{+2}_{(aq)} + 2e^-$	magnesium ion	colourless solution
hydrogen in basic soln	colourless solution	$H_{2(g)} + 2OH^-_{(aq)} \rightleftharpoons 2H_2O_{(l))} + 2e^-$		
oxalic acid	colourless solution	$H_2C_2O_{4(aq)} \rightleftharpoons 2CO_{2(g)} + 2H^+_{(aq} + 2e^-$	carbon dioxide	colourless gas
hydrogen gas	colourless gas	$H_{2(g)} \rightleftharpoons 2H^+_{(aq)} + 2e^-$	hydrogen	colourless solution

Adapted from SCSA Chemistry Data Booklet

The species being oxidised and reduced in a redox reaction can be identified using oxidation numbers

Oxidation Numbers or States

The oxidation number of an atom is an arbitrary charge assigned to the atom. It represents e^- gained or lost by a species and the charge an atom would have if it existed as an ion in a compound.

Oxidation numbers (O.N.) indicate the extent to which an atom has been oxidised. The larger the O.N. the greater the greater its degree of oxidation.

An atom's O.N. is defined as "the charge an atom would have if the bonds were purely ionic".

O.N.s are assigned according to the **following rules**.

Atoms in the free state have an oxidation number of zero.

	H_2	H	O_2	Al	Cl_2	Fe
Oxidation Number	0	0	0	0	0	0

Monatomic ions have an oxidation number equal to their charge.

	H^+	Al^{+3}	Fe^{+2}	$AlCl_3$	Na_2O
Oxidation Number	+1	+3	+2	(+3)(-1)	(+1)(-2)

Hydrogen atoms that are combined to other elements have an oxidation number of +1.
The **exception** is metal hydrides when hydrogen is -1.

	HCl	H_2O	CH_4	H_3PO_4	H_2CO_3	NaH
Oxidation Number	+1	+1	+1	+1	+1	-1

Oxygen atoms that are combined to other elements have an oxidation number of -2.
The exception is peroxides where oxygen is -1.

	H_2O	H_3PO_4	CO_2	SO_4^{-2}	NO_3^-	Na_2O_2
Oxidation Number	-2	-2	-2	-2	-2	-1

The sum of the oxidation numbers of all the atoms of any formula equals the net charge shown on the formula.

Al_2O_3: Net charge on formula is 0.
This is the same as the sum of oxidation numbers: (+3) x 2 + (-2) x 3 = 0

H_3O^+: Net charge on formula is +1.
This is the same as the sum of oxidation numbers: (+1) x 3 + (-2) x 1 = +1

An easy method is to use a table to determine the unknown oxidation number.

e.g. Mn in $KMnO_4$

O.N.	+1	+7	-2	
	K	Mn	O_4	
Total O.N.	+1	+7	-8	= 0

O.N. of Mn = +7

e.g. Cr in $Cr_2O_7^{2-}$

O.N.	+6	-2	
	Cr_2	O_7	
Total O.N.	+12	-14	= -2

O.N. of Cr = +6

Exercise 9: Oxidation numbers

a) Find the O.N. of

P in PO_4^{3-} C in $H_2C_2O_4$

b) What is the oxidation state of the following?

(a) zinc in zinc metal

(b) zinc in zinc ions, Zn^{2+}

(c) zinc in zincate ions, $Zn(OH)_4^{2-}$

(d) sulphur in sulphur dioxide, SO_2

(e) nitrogen in ammonia, NH_3

(f) nitrogen in nitrate ions, NO_3^-

O.N.'s may be different for the same element in different compounds.
Cr is +3 in $CrCl_3$ but it is +6 in $Cr_2O_7^{2-}$
Fe is +3 in Fe_2O_3 but it is +2 in $FeCl_2$

c) What is the oxidation state of chlorine in each of the following?

(a) perchlorate ion, ClO_4^-

(b) chlorate ion, ClO_3^-

(c) chlorite ion, ClO_2^-

(d) hypochlorite ion, ClO^-

(e) chlorine gas, Cl_2

(f) chloride ion, Cl^-

Oxidation and Reduction – Alternative Definitions

Oxidation can also be redefined as an <u>increase in O.N.</u>

e.g. $Fe^{2+} \rightarrow Fe^{3+} + e^-$
(+2) → (+3)

$Zn \rightarrow Zn^{2+} + 2e^-$
(0) → (+2)

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$
(+3) → (+4)

Reduction can be redefined as a <u>decrease in O.N.</u>
e.g. $MnO_4^- + 14H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$
(+7) → (+4)

Note: gain of $3e^-$ to give a decrease of O.N. of Mn from +7 to +4.

Redox reactions

For a chemical change to be a redox reaction there must be an increase and a decrease in the O.N.s of some reactant species.

Atoms that have an **increase** in O.N. have lost e^- i.e. have been **oxidised**.

Atoms that have a **decrease** in O.N. have gained e^- i.e. have been **reduced**.

Atoms which show **no change** in O.N. have neither gained or lost e^-.

In any oxidation-reduction reaction one species is oxidised while another species is reduced.

Example:

$Cu_{(s)}$	+	$4H^+_{(aq)}$	+	$2NO_3^-{}_{(aq)}$	→	$2NO_{2(g)}$	+	$Cu^{+2}{}_{(aq)}$	+	$2H_2O_{(l)}$
0		**+1**		**+5 -2**		**+4 -2**		**+2**		**+1 -2**

- Cu has been oxidised (OXD No. 0 → +2)
  N has been reduced (OXD No. 5 → -4)
- All other species have retained the same oxidation number; hence they have neither been reduced nor oxidised.
- This reaction is a redox reaction (both oxidation and reduction have taken place.

If none of the elements in reaction shows a change in oxidation number; then this not an electron transfer (redox) reaction.

Example:

$$2Fe^{3+} + 3O^{2-} + 3CO \rightarrow 2Fe + 3CO_2$$

- Fe^{3+} - accepts electrons
  - is reduced
  - is the oxidising agent
  - O.N. changes from +3 to 0 (decrease = red)
- CO - donates electrons
  - is oxidised
  - is the reducing agent
  - C O.N. changes from +2 to +4 (increase = ox)

Example:

Rxn showing O.N.s of all atoms	Ox atom	Red atom	O.A.	R.A.	Type of rxn
$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + H_{2(g)}$ 0 +1 –2 +2–2+1 0	Ca 0→2	H +1→ 0	H_2O	Ca	Redox
$Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Ca(OH)_{2(s)}$ +2 -2+1 +2 –2+1	none	none	none	none	Not redox

Exercise 10: Redox Consolidation

1. Indicate the change in O.N. (if any) for the element in brackets.

a) (Cu) in $Cu(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow Cu(NH_3)_2^{+}{}_{(aq)} + 2OH^{-}{}_{(aq)}$

b) (Cr) in $Cr_2O_7^{2-} + 14H^{+} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe_3^{+}$

c) (Ag) in $AgBr_{(s)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow Ag(S_2O_3)_2^{3-}{}_{(aq)} + Br^{-}{}_{(aq)}$

2. Identify whether the reaction is a redox reaction and state why?

a) $Ba(NO_3)_{2(aq)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + 2HNO_{3(aq)}$

b) $3Mg_{(s)} + N_{2(g)} \rightarrow Mg_3N_{2(s)}$

c) $OF_{2(g)} + H_2O_{(l)} \rightarrow O_{2(g)}\ 2HF_{(aq)}$

3. Indicate the change in O.N. for the element in brackets. Is it ox. or red.?

a) (I in IO_3^{-}) in $5I^{-} + IO_3^{-} + 6H^{+} \rightarrow 2I_2 + 3H_2O$

b) (Xe) in $XeO_3 + 6I^{-} + 6H^{+} \rightarrow Xe + 3H_2O + 3I_2$

c) (N in NH_4^{+}) in $NH_4NO_3 \rightarrow N_2O + 2H_2O$

d) (O in OF_2) in $OF_2 + H_2O \rightarrow O_2 + 2HF$

4. Balance the following half equation and state whether it is ox. or red..

a) $Mg \rightarrow Mg^{2+}$

b) $Cl_2 \rightarrow ClO^-$

c) $NO_3^- \rightarrow NH_4^+$

5. Some of the following balanced equations represent **redox reactions**. Examine the oxidation numbers of the elements in reach reaction and decide which represent redox reactions. For each of the **redox reactions** state the following:
   i. the element that is **reduced.**
   ii. the element that is **oxidised.**
   iii. the **oxidising agent.**
   iv. the **reducing agent.**

Equation	Redox?	Element reduced	Element oxidised	Oxidising agent	Reducing agent
$Cl_{2(g)} + 2Na_{(s)} \rightleftharpoons 2NaCl_{(s)}$					
$Ag^+_{(aq)} + Br^-_{(aq)} \rightleftharpoons AgBr_{(s)}$					
$Zn_{(s)} + 2H^+_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + H_{2(g)}$					
$OH^-_{(aq)} + H^+_{(aq)} \rightleftharpoons H_2O_{(l)}$					
$2H_{2\ (g)} + O_{2\ (g)} \rightleftharpoons 2H_2O_{\ (g)}$					
$2H_2O_{2(l)} \rightleftharpoons 2H_2O_{(l)} + O_{2(g)}$					
$Ca_{(s)} + 2H_2O_{(l)} \rightleftharpoons Ca(OH)_{2(s)} + H_{2(g)}$					
$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$					
$H_2O_{(l)} + Cr_2O_7^{-2} \rightleftharpoons CrO_4^{-2}{}_{(aq)} + 2H^+_{(aq)}$					

Balancing redox reactions using oxidation numbers

Oxidation number method

Procedure	Example – F is reduced to F_2
1. Write down the reactant and product in a skeleton equation. Include their oxidation numbers to decide the elements being oxidised and reduced.	FO_3^- → F_2 (+5)(-2) (0) fluorine is reduced
2. Balance the number of atoms of the element being oxidised or reduced.	$2FO_3^-$ → F_2
3. Determine the total change in oxidation number and balance this with electrons.	$2FO_3^-$ → F_2 2 x (+5) (0) x 2 10 e^- are needed to balance change in ON. $2FO_3^- + 10e^-$ → F_2
4. Balance the number of atoms of oxygen by adding H_2O to the side that is deficient in O.	$2FO_3^- + 10e^-$ → $F_2 + 6H_2O$
5. Balance the number of atoms of hydrogen by adding H^+ to the side that is deficient in H.	$2FO_3^- + 10e^- + 12H^+$ → $F_2 + 6H_2O$
6. Check that all atoms and charge balance.	✓
7. Add the states (if required).	$2FO_3^-{}_{(aq)} + 10e^- + 12H^+{}_{(aq)}$ → $F_{2(aq)} + 6H_2O_{(l)}$

Worked Example – MnO_4^- is reduced to Mn^{2+}

- Show the oxidised or reduced species with their ON's.

  MnO_4^- → Mn^{2+}
  (7+) (2+)

- Balance the element that is oxidised or reduced

  Mn already balanced

- Determine the total change in ON and balance with e^-s 7+ on LHS, 2+ on RHS – $5e^-$ on LHS

  $MnO_4^- + 5e^-$ → Mn^{2+}

- Balance O atoms by adding H_2O.

  $MnO_4^- + 5e^-$ → $Mn^{2+} + 4H_2O$

- Balance H atoms by adding H^+ ions.

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

Subscripts *(aq), (l), (s), (g)* should be added as required

$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^-$ → $Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$

Exercise 11: chlorine gas is oxidised to hypochlorous acid
Cl_2 → HClO

Additional Comments

1. In a balanced redox equation, the total **increase** in O.N. is equal to the total **decrease** in O.N.

2. Strong reducers usually contain an element in a low oxidation state; which is capable of increasing O.N. Similarly, strong oxidisers have an element with a high O.N.

3. When the same element exists in different states, the one with the higher oxidation state is usually the more powerful oxidiser – i.e. is more capable of reduction.
   e.g. MnO_4^- (+7) is a stronger oxidiser than MnO_2 (+4).
   Fe^{3+} is stronger than Fe^{2+}

4. An element with an intermediate O.N. may act as an oxidiser or a reducer depending on the other reagent.
   e.g. Fe^{2+} compared to Fe and Fe^{3+}.
   Oxygen in peroxide – O.N. in H_2O_2 = -1 is between 0 in O_2 and -2 in H_2O.

5. **Disproportionation**, or **self-oxidation and reduction**, can occur if part of a substance is oxidised and part reduced.

   e.g. hydrogen peroxide as a reducer is oxidised to oxygen

   $H_2O_{2(l)} \rightarrow O_{2(g)} + 2H^+_{(aq)} + 2e^-$

   +1 –1 0 +1 O –1→0 O.N. ↑ = Ox

   hydrogen peroxide as an oxidiser is reduced to water

   $H_2O_{2(l)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{(l)}$

   +1 –1 +1 +1-2 O –1→-2 O.N. ↓ = Red

   this is why H_2O_2 slowly decomposes at room temperature

   $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

   i.e. it oxidises and reduces itself.

Exercise 12: Prove that the following reactions undergo disproportionation:

a) $Cu^+_{(aq)} + Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

b) $NH_4NO_{2(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)}$

c) $I_{2(aq)} \rightarrow I^-_{(aq)} + IO_3^-{}_{(aq)}$

Exercise 13: Problem Set

1. Write separate half equations and an overall redox equation for the following reactions.

   a. $H_2S_{(aq)} + Cl_{2(g)} \rightarrow S_{(s)} + Cl^-_{(aq)}$

   b. $Cu_{(s)} + NO_3^-{}_{(aq)} \rightarrow Cu^{+2}_{(aq)} + NO_{2(g)}$

   c. $MnO_4^-{}_{(aq)} + C_2O_4^{-2}{}_{(aq)} \rightarrow Mn^{+2}_{(aq)} + CO_{2(g)}$

   d. $Zn_{(s)} + VO_3^-{}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + VO^{+2}_{(aq)}$

2. For each of the following:

   i. Identify the species being oxidised and reduced.
   ii. Write half equations for the oxidation and reduction processes.
   iii. Write and overall redox equation.

   a. Tin (II) nitrate solution reacts with acidified hydrogen peroxide to form tin (IV) nitrate and water.

   b. Acidified potassium permanganate solution reacts with sulphur dioxide gas to form manganese (II) ions and sulphate ions.

   c. Challenge question.
   Develop an oxidation and a reduction half equation for the following, then write a balanced redox equation.

   $TeCN^- + FO_3^- + Cl^- \rightarrow TeO_4^{2-} + HCN^- + FCl$

   Oxidation half-equation

   Reduction half-equation

   Overall equation

Redox Titrations

Volumetric analysis to determine unknown amounts of samples or concentrations of solutions can be done using redox reactions.

These are similar to acid/base titrations.

An advantage is that an indicator is sometimes not required as many substances have different colours for their various ions.

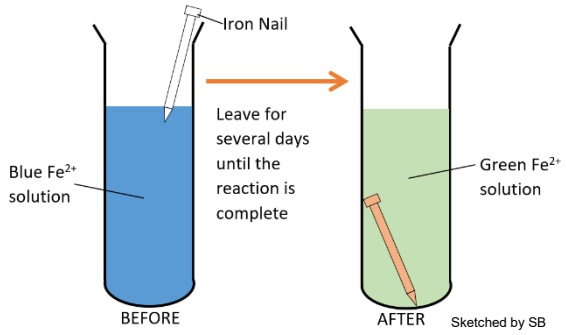
- Mn^{2+} is very pale pink (~colourless), MnO_4^- is purple.
- Cr^{3+} is green, $Cr_2O_7^{2-}$ is orange.
- Fe^{2+} is pale green, Fe^{3+} is pale brown.

Exercise 14: An approximately 0.02 mol L^{-1} potassium permanganate solution was standardised against 0.05120 mol L^{-1} oxalic acid solution. An average volume of 21.24 mL of the permanganate solution was required to titrate acidified 20.00 mL aliquots of the oxalic acid solutions. Calculate the concentration of the potassium permanganate solution.

A range of reactions involve the oxidation of one species and reduction of another species, including metal and halogen displacement reactions, combustion and corrosion

DISPLACEMENT REACTIONS

Metal Displacement Reactions



In a displacement reaction, a more reactive metal will displace (remove) the less reactive metal ion from a solution causing the reactive metal to become an ion and the ion to become a metal e.g.

Iron + copper (II) sulfate → iron (II) sulfate + copper

$Fe_{(s)} + Cu^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Cu_{(s)}$

Displacement reactions are redox reactions in which one or more products are separated from solution as a gas, liquid or solid. $Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

Reactive metals tend to form ions in solution that are difficult to displace (remove).

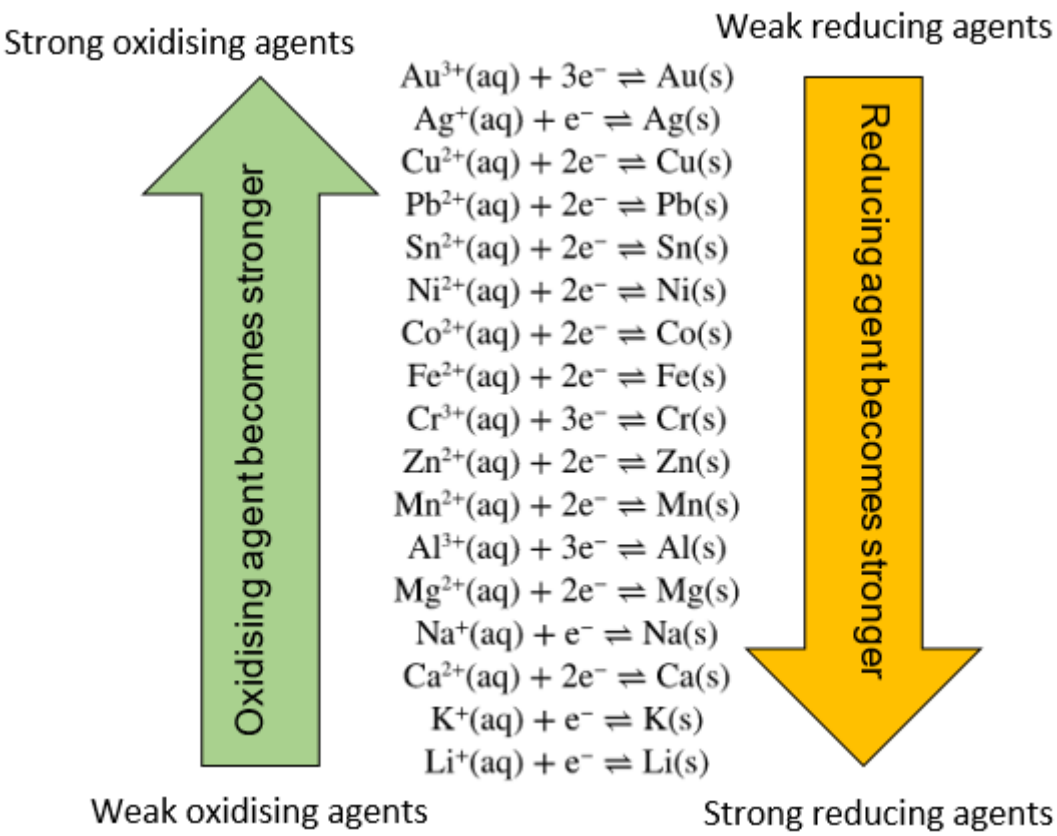
- Metal displacement reactions will occur if a more reactive solid metal is placed in a solution of a less reactive metal ion.

K Na Mg Al Zn Fe Pb H_2 Cu Ag

Au

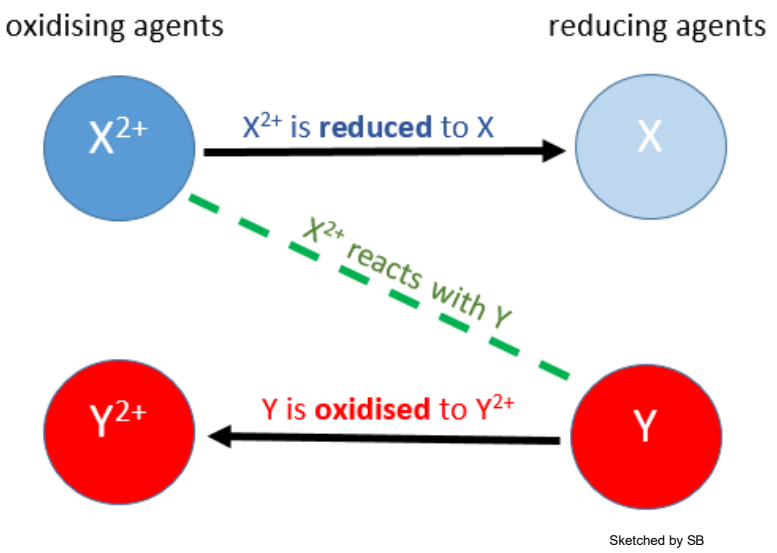
Reactive ⟶ inert

(metal easily oxidised) (ion easily reduced)



The relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and can be used to predict reaction tendency.

How to determine if a reaction will occur



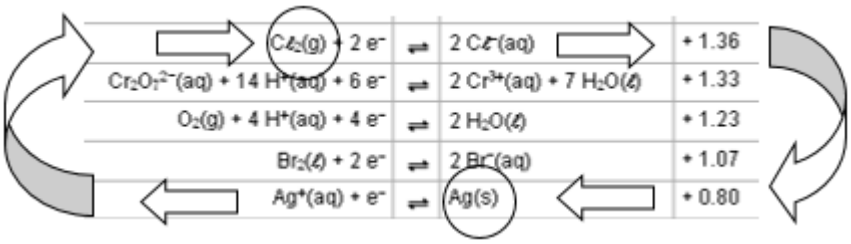
Oxidising agents only react significantly with reducing agents that are lower in the electrochemical series.

X^{2+} reacts with Y.
No reaction occurs for other combinations.
X and Y, X^{2+} an Y^{2+}, X^{2+} and X, X and X^{2+}, Y^{2+} and Y.

An easy way to determine if a reaction between two half equations will go ahead or not is to see if a CLOCKWISE LOOP can be created from the Standard Reduction Potential table.

Example: What will happen when chlorine gas is added to silver metal?

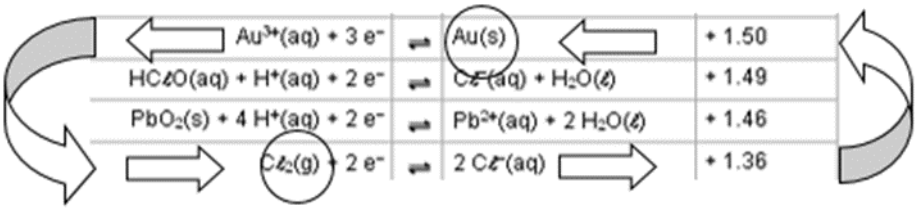
$Cl_2 \rightarrow 2Cl^-$ $Ag \rightarrow Ag^+$



The loop goes CLOCKWISE so the reaction will go ahead

Example: What will happen when chlorine gas is added to gold metal?

$Cl_2 \rightarrow 2Cl^-$ $Au \rightarrow Au^{3+}$



The loop goes ANTI-CLOCKWISE so the reaction will NOT go ahead.

How to determine if a reaction will occur using Standard Reduction Potentials

Example: A strip of zinc metal is added to an aluminium nitrate solution. Predict the reaction if any.

x3 $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ $E^o = +0.76$ V

x2 $Al^{+3}_{(aq)} + 3e^- \rightarrow Al_{(s)}$ $E^o = -1.66$ V

NOTE: Changing the coefficient of the half equation has no effect of the E^0 value.

$3Zn_{(s)} \rightarrow 3Zn^{+2}_{(aq)} + 6e^-$ $E^o = +0.76$ V

$2Al^{+3}_{(aq)} + 6\ e^- \rightarrow 2Al_{(s)}$ $E^o = -1.66$ V

$3Zn_{(s)} + 2Al^{3+}_{(aq)} \rightarrow 3Zn^{+2}_{(aq)} + 2Al_{(s)}$ $E^o = -0.90$ V

Negative E^0 value so this reaction will not proceed.

Example: A strip of magnesium metal is placed in aluminium nitrate solution.

x3 $Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2e^-$ $E^0 = +2.37$ V

x2 $Al^{3+}{}_{(aq)} + 3e^- \rightarrow Al_{(s)}$ $E^0 = -1.66$ V

$3Mg_{(s)} + 2Al^{3+}{}_{(aq)} \rightarrow 3Mg^{2+}{}_{(aq)} + 2Al_{(s)}$ $E^0 = +0.71$ V

Positive E^0 value so this reaction will proceed.

Exercise 15: Determine if a reaction will occur. Show your working.

a. A strip of copper is placed in silver nitrate solution.

b. A strip of iron is placed in aluminium nitrate solution. (NB: the iron may form Fe^{2+})

The further down the table of reduction potentials a metal is, the more easily oxidised it will be.

That is, the strongest reducing agents are found at the bottom right of the table.

The higher the number, the stronger the reducing agent.

- $K \rightarrow K^+ + e^-$ $E^0 = 2.94$ V is the strongest reducing agent on the table

Metal + dilute acid

Acids have the ability to act as oxidising agents – H^+ ion in dilute acid is reduced to form $H_{2(g)}$.

$2H^+{}_{(aq)} + 2e \rightarrow H_{2\,(g)}$

The exception is nitric acid which forms nitrogen monoxide.

Dilute acids have the ability to oxidise many metals (exceptions: Au, Pt, Hg, Ag and Cu)

Example: Chromium metal added to dilute sulfuric acid solution:

Reduction: $(2H^+{}_{(aq)} + 2e \rightarrow H_{2(g)}) \times 3$ $E^0 = 0.00$

Oxidation: $(Cr_{(s)} \rightarrow Cr^{3+}{}_{(aq)} + 3e) \times 2$ $E^0 = +0.73$

$2Cr_{(s)} + 6H^+{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3H_{(g)}$ $E^0 = +0.73$

Acid solutions which the concentration H^+ is 1 $molL^{-1}$, the E^0 for the evolution of hydrogen is 0.0 V.

Metals with $E^o < 0.0$ V react with dilute acids to produce hydrogen gas.

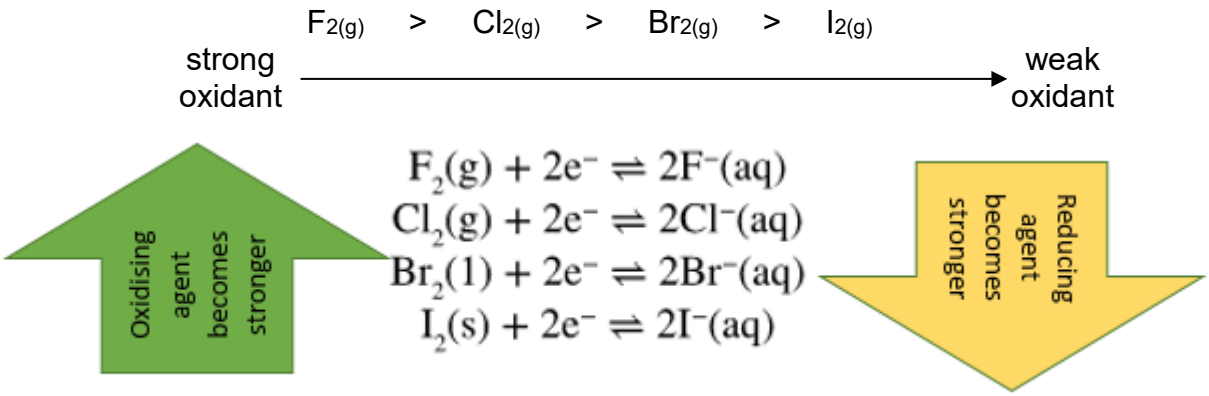
Metals $E^o > 0.0$ V do not react with dilute acids.

Exercise 16: Show that silver metal placed in hydrochloric acid will not react.

Displacement of Halogens

All halogens are good oxidising agents with Fluorine being the strongest.

The trend in oxidising ability is related to their position on the periodic table:



This means, for example, that $F_{2\,(g)}$ will displace the halide ions (eg. Cl^-) of any of the other halogens.

$$2Cl_{2(g)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(l)}$$

Example: Predict the reaction between $Cl_{2\,(g)}$ and a solution of $KBr_{(aq)}$.

$Cl_{2\,(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	$E^o = +1.36$ V
$2Br^-_{(aq)} \rightarrow Br_{2\,(l)} + 2e^-$	$E^o = -1.07$ V
$Cl_{2\,(g)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2\,(l)}$	$E^o = +0.30$ V

Reaction will proceed.

Exercise 17: Using Standard Reduction Potentials show that there is no reaction between $KBr_{(aq)}$ and $I_{2\,(s)}$.

The higher up the table of reduction potentials a substance is, the more easily reduced it will be.
That is, the strongest oxidising agents are found at the top left of the table.

The higher the number, the stronger the oxidising agent.

- $F_2 + 2e^- \rightarrow 2F^-$ $E^0 = 2.89$ V the strongest oxidising agent on the table.

Exercise 18: PROBLEM SET

1. Some of the following balanced equations represent redox reactions. Examine the oxidation numbers of the elements in each reaction and decide which represent redox reactions. For each of the redox reactions state the following: (The first has been done to help you.)

- the element that is reduced.
- the element that is oxidised.
- the oxidant or oxidising agent.
- the reductant or reducing agent.

a. $Cl_{2(g)} + 2Na_{(s)} \rightarrow 2NaCl_{(s)}$

0 0 +1 -1 Na: 0 → +1 Cl: 0 → -1

element reduced: Cl_2 element oxidised: Na oxidant: Cl_2 reductant: Na

b. $Ca_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + H_{2(g)}$

element reduced: element oxidised: oxidant: reductant:

c. $FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$

element reduced: element oxidised: oxidant: reductant:

d. $Cu_{(s)} + 4H^+_{(aq)} + 2NO_3^-{}_{(aq)} \rightarrow 2NO_{2(g)} + 2H_2O_{(l)} + Cu^{2+}_{(aq)}$

element reduced: element oxidised: oxidant: reductant:

e. $H_2O_{(l)} + Cr_2O_7^{2-}{}_{(aq)} \rightarrow CrO_4^{2-}{}_{(aq)} + 2H^+_{(aq)}$

element reduced: element oxidised: oxidant: reductant:

2. Write balanced half equations for each of the chemical changes described here:

a. reduction of $H^+_{(aq)}$ producing $H_{2(g)}$.

b. reduction of $MnO_4^-{}_{(aq)}$ giving $Mn^{2+}_{(aq)}$.

c. reduction of $H_2SeO_{3(aq)}$ giving $Se_{(s)}$.

d. reduction of $Cr_2O_7^{2-}{}_{(aq)}$ forming $Cr^{3+}_{(aq)}$.

3. Several partially written redox equations are listed below. For each example write:
   i. the oxidation half equation.
   ii. the reduction half equation.
   iii. the overall redox equation.

   a. $Cl_{2(g)} + Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Cl^{-}_{(aq)}$

   b. $K_{(s)} + H_2O_{(l)} \rightarrow H_{2(g)} + OH^{-}_{(aq)} + K^{+}_{(aq)}$

   c. $H^{+}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + Cr^{3+}_{(aq)} + H_2O_{(l)}$

   d. $H^{+}_{(aq)} + NO_3^{-}{}_{(aq)} + Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + NO_{(g)} + H_2O_{(l)}$

4. Each of the questions that follow gives some information about the reactants and products of a redox reaction. Write a redox equation for each of these reactions and describe any observations you would expect as the reaction proceeds.

   a. Granules of Zn are added to $HCl_{(aq)}$ liberating H_2 and forming $ZnCl_2$.

   b. Acidified $K_2Cr_2O_{7\,(aq)}$ is added to $Na_2S_{\,(aq)}$ forming sulfur and chromium (III) ions.

   c. Bromine water is added to sodium iodide solution causing the formation of aqueous iodine and sodium bromide.

   d. Concentrated nitric acid is added to copper metal resulting in the formation of nitrogen dioxide gas and copper II nitrate solution.

5. Write balanced redox equations for each of the experiments listed below:

   a. A small piece of barium metal is added to hydrochloric acid solution. The metal dissolves rapidly giving a colourless solution and a colourless gas.

   b. A strip of lead reacted vigorously when placed in a concentrated nitric acid solution. A brown gas was formed as the metal dissolved giving a colourless solution.

   c. Chlorine gas was bubbled through a solution of sodium iodide. The solution went from colourless to brown in colour.

   d. Excess acidified hydrogen peroxide solution was added drop wise to a hydrogen sulfide solution. The mixture slowly changed from colourless to cloudy yellow.

Corrosion of Metals

Corrosion occurs when an uncombined metal decomposes into one of its more stable compounds.
e.g. the rusting of Fe by air (O_2) in a moist environment (H_2O) to form $Fe_2O_3.H_2O_{(s)}$.

The metal is attacked by substances in its surrounding (e.g. O_2 and H_2O) and is oxidised.
e.g. exposed surface of Mg metal

$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

i.e. $Mg_{(s)} \rightarrow Mg^{2+} + 2e^-$ <u>oxid</u>
and $O_{2(g)} + 4e^- \rightarrow 2O^{2-}$ <u>red</u>

Thus, corrosion is a **redox** reaction and involves some form of electrochemical cell.

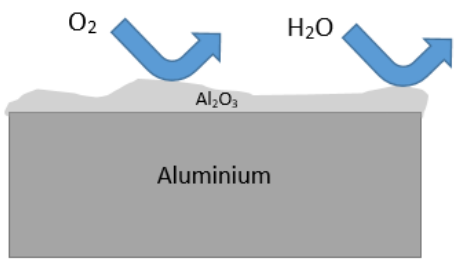
Some active metals show little to no corrosion due to the formation of protective coatings (e.g. Al_2O_3 on Al) which excludes O_2.

The products of corrosion are classified into

- <u>Soluble products</u> – readily dissolve and washed away leaving holes or pits in the metal. e.g. corrosion of Mg in sea water.

- <u>Sparingly soluble products</u> – form layers which are not washed away.
  Two types

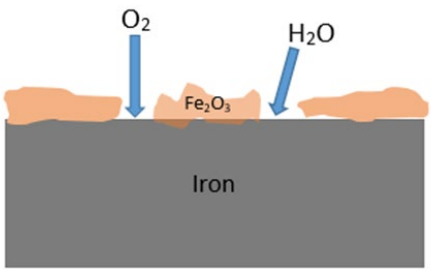
coherent coatings
stay in one piece to form a continuous coating of the metal surface. e.g. Zn and Al in air. This stops further corrosion. i.e protective.



Al_2O_3 forms a tightly bound layer that prevents the metal reacting with many substances

Sketched by SB

incoherent coatings
are flaky, powdery or peel off the metal surface. e.g. rusting of iron. Corrosion can occur below this layer. i.e non protective



The Fe_2O_3 oxide layer is non-protective and can be penetrated by water and air so corrosion continues to occur.

Sketched by SB

Conditions required for corrosion are;

1. metal surface free from protective films e.g. paint, oil.
2. suitable oxidising agent(s) present (i.e. something high on the SRP table).
3. solution containing ions for conducting charge. i.e. in the electrochemical cell created.

Corrosion protection

Most corrosion problems are caused by failure to apply known principles of corrosion.

Techniques for preventing corrosion are:

1. Keep metal **dry** e.g. silica gel used to absorb moisture when storing microscopes etc.
2. Use **pure** water – this is a poor electrolyte due to low conc. of ions. e.g. cooling systems in cars with Al in the engines.
3. Using metals of **high purity** – impurities form electrode sites. e.g. expensive cars such as Mercedes use high quality steel.
4. Using **sacrificial anodes** – these are metals that will corrode; more easily oxidised; in preference to the main structure. e.g. solar hot water systems have a Mg anode; Al ships and boat hulls have Mg/Zn bolts or lumps to protect the hull.
5. Electrical Protection – DC voltage is applied with the metal to be protected connected to the –ve terminal. An ample supply of e^- prevents this metal being oxidised. e.g. wharf piles, underground pipes.
6. Alloying – produces alloys with non-corroding properties. e.g. stainless steel.
7. Surface coatings – important and often used.

Rusting

This is a special example of corrosion related to iron and its alloys (steel).

The oxidation or rusting of iron is a complex process which involves an **electrochemical** reaction.

The process involves the reaction of iron with oxygen and water. On the wet surface of the iron, anodic and cathodic sites form.

- As with all corrosion, rusting is a redox reaction with the half reactions being:

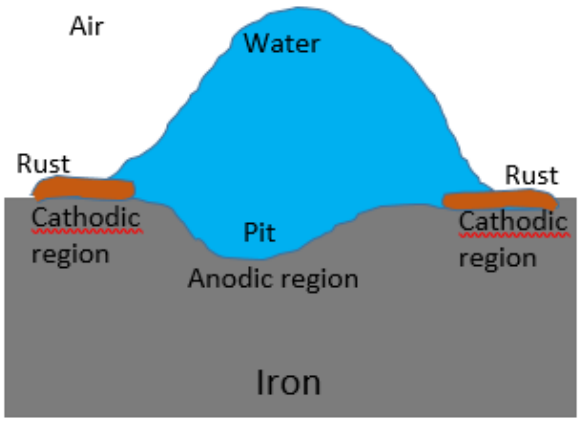
  At the anodic sites
  Oxidation of Fe

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

  At the cathodic sites (often a C particle)
  Reduction of O_2

  $$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

  (note: water and oxygen are required for rusting)



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- Next step is **precipitation of $Fe(OH)_2$** as the Fe^{2+} ions and the OH^- ions migrate towards each other.

  $$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$$

- **Further oxidation of $Fe(OH)_{2(s)}$** forms brown $Fe(OH)_{3(s)}$.

  $$4Fe(OH)_{2(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)}$$

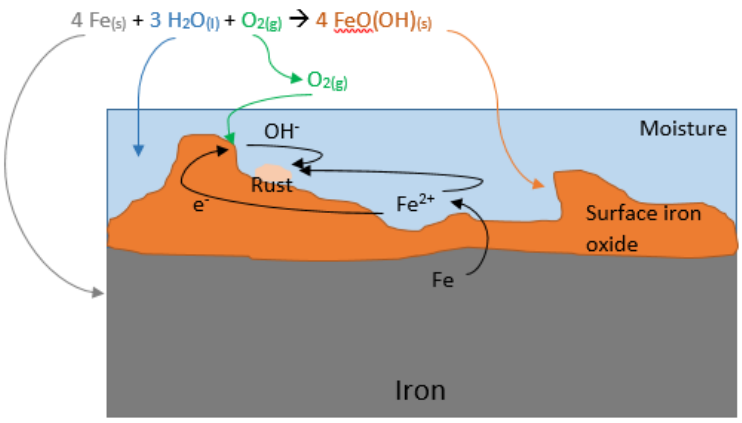
- **Dehydration of $Fe(OH)_{3(s)}$** forms rust. The extent of dehydration and thus, the formula of rust, varies.

  $$2Fe(OH)_{3(s)} \rightarrow Fe_2O_3.H_2O_{(s)} + 2H_2O_{(l)}$$

- $Fe_2O_3.H_2O$ may be written as $FeO(OH)$.

- This compound is not coherent, thus the corrosion process continues until all the metal is rusted.

  Note: if the water is sufficiently acidic, iron corrodes as
  $Fe_{(s)} + 2H^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)}$



Sketched by SB

Combustion

Combustion reactions produce heat energy that we use to cook food, heat our homes and run our cars.

In many parts of Australia, combustion of coal is an energy source for the production of electricity.

Respiration, which takes part in every cell of our body, is also a combustion reaction.

Combustion reactions involve the oxidation of a fuel by oxygen.

Where there is an abundance of oxygen, complete combustion occurs and the products are carbon dioxide and water.

Complete combustion of octane: $2C_8H_{18}(l)+25O_2(g) \rightarrow 16CO_2(g)+18H_2O(l)$

If oxygen is in short supply, incomplete combustion occurs and the products may be carbon monoxide and water, or simply carbon and water.

Image : free to use - www.pixabay.com

Incomplete combustion of octane:

$2C_8H_{18}(l)+17O_2(g) \rightarrow 16CO(g)+18H_2O(l)$

Oxidation numbers in combustion reactions

1. Oxidation numbers can be used to show that carbon is oxidised and oxygen is reduced in these reactions.

Incomplete combustion of methane	-4 +1 0 +2 -2 +1 -2 $2\ CH_{4(g)} + 3\ O_{2(g)} \rightarrow 2\ CO_{(g)} + 4\ H_2O_{(i)}$
Complete combustion of methane	-4 +1 0 +4 -2 +1 -2 $CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(i)}$

2. The oxidation number of carbon increases from −4 to +4 in the complete combustion of methane, whereas it only increases to +2 during incomplete combustion.
3. Less energy is produced during incomplete combustion.

Oxidation and Reduction
Questions in Oxidation and Reduction have been shared with permission from Canning College

1. Find the oxidation numbers of the underlined elements in the following formulae:

(a)	$K\underline{Cl}O_3$	(b)	$\underline{Pb}O_2$	(c)	$\underline{Pb}SO_4$
(d)	$Na_2\underline{S}O_4$	(e)	$Na_2\underline{O}_2$	(f)	$\underline{Cr}O_4^{2-}$
(g)	$\underline{I}O_4^-$	(h)	$\underline{Zn}(NH_3)_4^{2+}$	(i)	$\underline{Cu}(CN)_3^{2-}$
(j)	$\underline{N}O_2^-$	(k)	$\underline{N}_2O$		

2. What is the oxidation number of manganese in each of the following compounds?

(a)	Na_2MnO_4	(b)	MnO_3	(c)	$NaMnO_4$
(d)	MnO	(e)	Mn_2O_7		

3. Which of the following equations represent redox reactions? Name the oxidizing agent where appropriate.

(a)	$2Na(s)$	+	$2H_2O(l)$	$\rightarrow$	$2NaOH(aq)$	+	$H_2(g)$			
(b)	$Pb^{2+}(aq)$	+	$S^{2-}(aq)$	$\rightarrow$	$PbS(s)$					
(c)	$3CuO(s)$	+	$2NH_3(g)$	$\rightarrow$	$3Cu(s)$	+	$3H_2O(l)$	+	$N_2(g)$	
(d)	$NaClO(aq)$	+	$Na_2SO_3(aq$	$\rightarrow$	$NaCl(aq)$	+	$Na_2SO_4(aq)$			
(e)	$Mg(s)$	+	$2HCl(aq)$	$\rightarrow$	$MgCl_2(aq)$	+	$H_2(g)$			
(f)	$2H^+(aq)$	+	$CO_3^{2-}(aq)$	$\rightarrow$	$CO_2(g)$	+	$H_2O(l)$			
(g)	$Cu(s)$	+	$2H_2SO_4(aq)$	$\rightarrow$	$CuSO_4\ (aq)$	+	$SO_2(g)$	+	$2H_2O(l)$	

4. The reaction of magnesium and silver nitrate solution can be represented by the following equation:

$$Mg(s) + 2AgNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + 2Ag(s)$$

(a) Name the substance which is oxidized and write an equation in terms of electron transfer to represent the oxidation process.
(b) Name the substance which is reduced and write an equation in terms of electron transfer to represent the reduction process.
(c) From the equations obtained in (a) and (b), construct a balanced ionic equation for the redox reaction.

5. Hydrogen peroxide may act as a reducing agent or an oxidizing agent. The change of hydrogen peroxide in each case may be represented by either one of the following half equations:

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

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

(a) Which one of the above equations shows hydrogen peroxide acting as an oxidising agent?
Explain your answer.

(b) Which one of the above equations shows hydrogen peroxide acting as a reducing agent?
Explain your answer.

(c) When hydrogen peroxide solution is mixed with each of the following substances, state whether it is acting as an oxidizing agent or a reducing agent. Write half-cell equations for the oxidation and reduction and construct a balanced redox equation in each case.

(i) A solution containing Fe^{2+} ions
(ii) A solution containing I^- ions

6. Balance the following equations by using half equations. Show both half-reactions and identify them as oxidation or reduction.

(a) $Fe^{2+}(aq) + Cl_2(g) \rightarrow Fe^{3+}(aq) + Cl^-(aq)$

(b) $SO_3^{2-}(aq) + MnO_4^-(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2O(l)$

(c) $Cu(s) + Hg^{2+}(aq) \rightarrow Cu^{2+}(aq) + Hg(s)$

(d) $MnO_4^-(aq) + H^+(aq) + S^{2-}(aq) \rightarrow Mn^{2+}(aq) + H_2O(1) + S(s)$

(e) $I_2(s) + H_2S(aq) \rightarrow H^+(aq) + I^-(aq) + S(s)$

(f) $Cr_2O_7^{2-}(aq) + I^-(aq) \rightarrow Cr^{3+}(aq) + I_2(s) + H_2O(l)$

(g) $Cu(s) + HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + NO_2(g) + H_2O(l)$

(h) $SO_3^{2-}(aq) + IO_3^-aq) + H+(aq) \rightarrow I_2(s) + SO_4^{2-}(aq) + H_2O(l)$

Answers to Exercises

Exercise 1: Identify any substances being oxidised or reduced in each of the following:

a. **OX = Zn (add O)** **RED = O_2 (O removed)**
b. **OX = SO_2 (add O)** **RED = O_2 (O removed)**
c. **OX = CO (add O)** **RED = PbO (O removed)**

Exercise 2: Consider the reaction between Mg and HCl.

a) **Mg is being corroded by the acid and is being turned into Mg^{2+} ions in solution.**
(b) **H^+ ions are turning into H_2 gas.**
(c) **When Mg turns into Mg^{2+}, each Mg atom is losing two electrons. These electrons are being picked up by the H^+ ions which then form H_2.**

Exercise 3: **Zn**
- donates/~~accepts~~ electrons
- is oxidised/~~reduced~~

I_2
- ~~donates~~/accepts electrons
- is ~~oxidised~~/reduced

Exercise 4:

Species	Electron Transfer	Type of Change	Type of Agent
$Cu^{+2}_{(aq)}$	**Each Cu^{+2} $_{(aq)}$ ion gains 2 electrons in forming $Cu_{(s)}$ atom.**	**reduced**	**oxidising agent**
$Al_{(s)}$	**Each Al $_{(s)}$ atom loses 3 electrons in forming an $Al^{+3}_{(aq)}$ ion.**	**oxidised**	**reducing agent**

Exercise 5 Problem Set

1.
a. oxidised: **Zn** reduced: **H^+**
b. oxidised: **Mg** reduced: **S**
c. oxidised: **Fe** reduced: **Cu^{2+}**

2.
a. OA: **Cl_2** RA: **Br^-**
b. OA: **Cl_2** RA: **Mg**
c. OA: **Ag^+** RA: **Cu**

3. Identify the oxidising agent in each of the following:
a. **Cu^{2+}**
b. **O_2**
c. **Cl_2**

4. Identify the reducing agent in each of the following:
a. **CO**
b. **H_2**
c. **Zn**

Exercise 6: $Cl_2 \rightarrow 2HClO$

$Cl_2 + 2H_2O \rightarrow 2HClO$

$Cl_2 + 2H_2O \rightarrow 2HClO + 2H^+$

$Cl_2 + 2H_2O \rightarrow 2HClO + 2H^+ + 2e^-$

Exercise 7:

a) $2Fe^{+2} \rightarrow 2Fe^{3+} + 2e^-$ x 2

$Cl_2 + 2e^- \rightarrow 2Cl^-$

$2Fe^{2+}_{(aq)} + Cl_{2\,(g)} \rightarrow 2Fe^{3+}_{(aq)} + 2Cl^-_{(aq)}$

b) $Mg \rightarrow Mg^{2+} + 2e^-$

$Br_2 + 2e^- \rightarrow 2Cl^-$

$Mg_{(s)} + Br_{2\,(g)} \rightarrow Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$ $(MgCl_{2(s)})$

Exercise 8: Balancing harder redox equations.

a)

$Cr_2O_7^{-2}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{+3}_{(aq)} + 7H_2O_{(l)}$

$3S^{2-} \rightarrow 3S_{(s)} + 6\ \cancel{2}e^-$ x3

$Cr_2O_7^{-2}{}_{(aq)} + 3S^{2-}_{(aq)} + 14H^+_{(aq)} \rightarrow 2Cr^{+3}{}_{(aq)} + 3S_{(s)} + 7H_2O_{(l)}$

b)

$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$

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

$H_2O_{2(aq)} + 2H^+_{(aq)} + C_2O_4^{-2}{}_{(aq)} \rightarrow 2H_2O_{(l)} + 2CO_{2(g)}$

Exercise 9: Oxidation numbers

a)

P in PO_4^{3-} **+5**

C in $H_2C_2O_4$ **+3**

b) What is the oxidation state of the following?

(a) **0**
(b) **+2**
(c) **+2**
(d) **+4**
(e) **-3**
(f) **+5**

c) What is the oxidation state of chlorine in each of the following?

(a) **+7**
(b) **+5**
(c) **+3**
(d) **+1**
(e) **0**
(f) **-1**

Exercise 10: Redox Consolidation

1.

a) **+2 → +1**

b) **+6 → +3**

c) **+1 → +1**

2.
a) **Not Redox → No change in ON**
b) **Redox 0 → +2**
c) **Redox +2 → 0 (O has ON = +2 in OF_2)**

3.
a) **+5 → 0 Reduction**
b) **+6 → 0 Reduction**
c) **-3 → +1 Oxidation**
d) **+2 → 0 Reduction**

4.
a) **$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ Oxidation**
b) **$Cl_2 + 2H_2O \rightarrow 2ClO^- + 4H^+ + 2e^-$ Oxidation**
c) **$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$ Reduction**

5.

Equation	Redox?	Element reduced	Element oxidised	Oxidising agent	Reducing agent
$Cl_{2(g)} + 2Na_{(s)} \rightleftharpoons 2NaCl_{(s)}$	Yes	Cl_2	Na	Cl_2	Na
$Ag^+_{(aq)} + Br^-_{(aq)} \rightleftharpoons AgBr_{(s)}$	No	-	-	-	-
$Zn_{(s)} + 2H^+_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + H_{2(g)}$	Yes	H	Zn	H^+	Zn
$OH^-_{(aq)} + H^+_{(aq)} \rightleftharpoons H_2O_{(l)}$	No	-	-	-	-
$2H_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2H_2O_{\,(g)}$	Yes	O	H	O_2	H_2
$2H_2O_{2(l)} \rightleftharpoons 2H_2O_{(l)} + O_{2(g)}$	Yes	O	O	H_2O_2	H_2O_2
$Ca_{(s)} + 2H_2O_{(l)} \rightleftharpoons Ca(OH)_{2(s)} + H_{2(g)}$	Yes	H	Ca	H_2O	Ca
$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$	Yes	Fe	C	FeO	CO
$H_2O_{(l)} + Cr_2O_7^{-2} \rightleftharpoons CrO_4^{-2}{}_{(aq)} + 2H^+_{(aq)}$	No	-	-	-	-

Exercise 11: $Cl_2 \rightarrow HClO$

$Cl_2 \rightarrow HClO$
(0) (+1)
$Cl_2 \rightarrow 2HClO$ 0 on LHS, 2+ on RHS – $2e^-$ on RHS
$Cl_2 \rightarrow 2HClO + 2e^-$
$Cl_2 + 2H_2O \rightarrow 2HClO + 2H^+ + 2e^-$
$Cl_{2(g)} + 2H_2O_{(l)} \rightarrow 2HClO_{(aq)} + 2H^+_{(aq)} + 2e^-$

Exercise 12: Prove that the following reactions undergo disproportionation:

a) $Cu^+_{(aq)} + Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$
+1 oxidation +2
+1 reduction 0

b) $NH_4NO_{2(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)}$
-3 oxidation 0
+3 reduction 0

c) $I_{2(aq)} \rightarrow I^-_{(aq)} + IO_3^-{}_{(aq)}$
0 reduction -1
0 oxidation +5

Exercise 13: Problem Set

1.

a. $H_2S \rightarrow S + 2H^+ + 2e^-$ Oxidation

$Cl_2 + 2e^- \rightarrow 2Cl^-$ Reduction

$H_2S_{(aq)} + Cl_{2(g)} \rightarrow S_{(s)} + 2H^+_{(aq)} + 2Cl^-_{(aq)}$

b. $Cu \rightarrow Cu^{2+} + 2e^-$ Oxidation

$2NO_3^- + 4H^+ + 2e^- \rightarrow 2NO_2 + 2H_2O$ Reduction

$Cu_{(s)} + 2NO_3^-{}_{(aq)} + 4H^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$

c. $5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$ Oxidation

$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 2H_2O$ Reduction

$5C_2O_4^{2-}{}_{(aq)} + 2MnO_4^-{}_{(aq)} + 16H^+_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 10CO_{2(g)} + 8H_2O_{(l)}$

d. $Zn \rightarrow Zn^{2+} + 2e^-$ Oxidation

$2VO_3^- + 8H^+ + 2e^- \rightarrow 2VO^{+2} + 4H_2O$ Reduction

$Zn_{(s)} + 2VO_3^-{}_{(aq)} + 8H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2VO^{2+}_{(aq)} + 4H_2O_{(l)}$

2.

a. $Sn(NO_3)_2 + H_2O_2 \rightarrow Sn(NO_3)_4 + 2H_2O$

+2 +1 -1 +4 +1 -2

oxidised reduced

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ Oxidation

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ Reduction

$Sn^{2+}_{(aq)} + H_2O_{2(l)} + 2H^+_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2H_2O_{(l)}$

b. $MnO_4^- + SO_2 \rightarrow Mn^{2+} + SO_4^{2-}$

+7 -2 +4 -2 +2 +6 -2

reduced oxidised

$5SO_2 + 10H_2O \rightarrow 5SO_4^{2-} + 20H^+ + 10e^-$ Oxidation

$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$ Reduction

$2MnO_4^-{}_{(aq)} + 5SO_{2(g)} + 2H_2O_{(l)} \rightarrow 2Mn^{2+}_{(aq)} + 5SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)}$

c)

Oxidation half-equation $TeCN^- + 4H_2O \rightarrow TeO_4^{2-} + HCN + 7H^+ + 6e^-$ x 2

Reduction half-equation $FO_3^- + Cl^- + 6H^+ \; 4e^- \rightarrow FCl + 3H_2O$ x3

Overall equation $2TeCN^- + 3FO_3^- + 3Cl^- \; 4H^+ \rightarrow 2TeO_4^{2-} + 2HCN + 3FCl + H_2O$

Exercise 14: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ x2

$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$ x5

$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

$n(H_2C_2O_4) = cV = 0.05120 \times 0.02000 = 0.001024$ mol

$n(MnO_4^-) = 2/5 \times 0.001024 = 0.0004096$ mol

$c(MnO_4^-) = \frac{n}{V} = \frac{0.0004096}{0.02124} = 0.01928 \text{ mol L}^{-1}$

Exercise 15:

a. $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e$ $E^0 = -0.34$ V

$Ag^+_{(aq)} + e \rightarrow Ag_{(s)}$ $E^0 = \underline{+0.80 \text{ V}}$

$E^0 = +0.46$ V reaction will proceed

b. $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e$ $E^0 = +0.44$ V

$Al^{3+}_{(aq)} + 3e \rightarrow Al_{(s)}$ $E^0 = \underline{-1.66 \text{ V}}$

$E^0 = -1.22$ V so reaction will NOT proceed

Exercise 16: $2H^+_{(aq)} \rightarrow H_{2(g)} + 2e^-$ $E^0 = 0.00$ V

$Ag_{(s)} + e \rightarrow Ag^+_{(aq)}$ $E^0 = \underline{-0.80 \text{ V}}$

Exercise 17: Using Standard Reduction Potentials show that there is no reaction between $KBr_{(aq)}$ and $I_{2\,(s)}$.

$Br^-_{(aq)} \longrightarrow Br_{2(l)} + 2e^-$ $E^0 = -1.08$ V

$I_{2(s)} + 2e^- \longrightarrow 2I^-_{(aq)}$ $E^0 = +0.54$ V

$2Br^-_{(aq)} + I_{2(s)} \longrightarrow Br_{2(l)} + 2I^-_{(aq)}$ $E^0 = -0.54$ V

Negative E^0 value so this reaction will not proceed.

Oxidation is increase in o.n.
Reduction is decrease in o.n.

Exercise 18: PROBLEM SET

1.

b. $Ca_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + H_{2(g)}$

0 +1 -2 +2 -2 +1 0

element reduced: H (+1 to 0) element oxidised: Ca (0 to +2) oxidant: H_2O reductant: Ca

c. $FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$

+2 -2 +2 -2 0 +4 -2

element reduced: Fe (+2 to 0) element oxidised: C (+2 to +4) oxidant: FeO reductant: CO

d. $Cu_{(s)} + 4H^+_{(aq)} + 2NO_3^-{}_{(aq)} \rightarrow 2NO_{2(g)} + 2H_2O_{(l)} + Cu^{2+}_{(aq)}$

0 +1 +5 -2 +4 -2 +1 -2 +2

element reduced: N (+5 to +4) element oxidised: Cu (0 to +2) oxidant: NO_3^- reductant: Cu

e. $H_2O_{(l)} + Cr_2O_7^{2-}{}_{(aq)} \rightarrow CrO_4^{2-}{}_{(aq)} + 2H^+_{(aq)}$

+1 -2 +6 -2 +6 -2 +1

element reduced: - element oxidised: - oxidant: - reductant: -

2.

a. $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

b.

$MnO_4^-{}_{(aq)} \longrightarrow Mn^{2+}$

add 8H+ $MnO_4^-{}_{(aq)} \longrightarrow Mn^{2+}_{(aq)}$ add $4H_2O$ balance with e^-

$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$

c.

$H_2SeO_{3(aq)} \longrightarrow Se_{(s)}$

add 4H+ $H_2SeO_{3(aq)} \longrightarrow Se_{(s)}$ add $3H_2O$ balance with e^-

$4H^+_{(aq)} + H_2SeO_{3(aq)} + 4e^- \longrightarrow Se_{(s)} + 3H_2O_{(l)}$

d.

$Cr_2O_7^{2-}{}_{(aq)} \longrightarrow Cr^{3+}$ balance Cr

add 14H+ $Cr_2O_7^{2-}{}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)}$ add $7H_2O$ balance with e^-

$14H^+_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 6e^- \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

3.

a. 2 x $Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$ (ox)

1 x $Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$ (red)

$Cl_{2(g)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Cl^-_{(aq)} + 2Fe^{3+}_{(aq)}$

b. 2 x $K_{(s)} \longrightarrow K^+_{(aq)} + e^-$ (ox)

1 x $2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$ (red)

$2K_{(s)} + 2H_2O_{(l)} \longrightarrow H_{2(g)} + 2OH^-_{(aq)} + 2K^+_{(aq)}$

c. 3 x $Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2e^-$ (ox)

1 x $14H^+_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 6e^- \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$ (red)

$14H^+_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 3Sn^{2+}_{(aq)} \longrightarrow 3Sn^{4+}_{(aq)} + 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

d. 3 x $Ni_{(s)} \longrightarrow Ni^{2+}_{(aq)} + 2e^-$ (ox)

2 x $4H^+_{(aq)} + NO_3^-{}_{(aq)} + 3e^- \longrightarrow NO_{(g)} + 2H_2O_{(l)}$ (red)

$8H^+_{(aq)} + 2NO_3^-{}_{(aq)} + 3Ni_{(s)} \longrightarrow 3Ni^{2+}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$

4.

a.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$2H^+ + 2e^- \longrightarrow H_2$$
$$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow H_{2(g)} + Zn^{2+}_{(aq)}$$

A colourless liquid is added to a grey metal, a colourless, odourless gas evolves leaving a colourless solution

b.

$$14H^+_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 6e^- \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$
$$3\text{ x} \quad S^{2-}_{(aq)} \longrightarrow S_{(s)} + 2e^-$$
$$14H^+_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 3S^{2-}_{(aq)} \longrightarrow 3S_{(s)} + 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

An orange solution added to a colourless solution changes to a green solution.

c.

d.

$$Br_{2(aq)} + 2e^- \longrightarrow 2Br^-_{(aq)}$$
$$2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2e^-$$
$$Br_{2(aq)} + 2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2Br^-_{(aq)}$$

A red brown solution added to a colourless solution changes to a purple solution.

$$2\text{ x} \quad 2H^+_{(aq)} + NO_3^-{}_{(aq)} + e^- \longrightarrow NO_{2(g)} + H_2O_{(l)}$$
$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$
$$4H^+_{(aq)} + 2NO_3^-{}_{(aq)} + Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

Copper coloured metal reacts in a colourless solution producing a blue solution and a brown choking gas.

5. a.

$$Ba_{(s)} \longrightarrow Ba^{2+}_{(aq)} + 2e^-$$
$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$
$$Ba_{(s)} + 2H^+_{(aq)} \longrightarrow H_{2(g)} + Ba^{2+}_{(aq)}$$

b.

$$2\text{ x} \quad 2H^+_{(aq)} + NO_3^-{}_{(aq)} + e^- \longrightarrow NO_{2(g)} + H_2O_{(l)}$$
$$Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2e^-$$
$$4H^+_{(aq)} + 2NO_3^-{}_{(aq)} + Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

c.

$$Cl_{2(aq)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$$
$$2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2e^-$$
$$Cl_{2(aq)} + 2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2Cl^-_{(aq)}$$

d.

$$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \longrightarrow 2H_2O_{(l)}$$
$$S^{2-}_{(aq)} \longrightarrow S_{(s)} + 2e^-$$
$$H_2O_{2(aq)} + 2H^+_{(aq)} + S^{2-}_{(aq)} \longrightarrow S_{(s)} + 2H_2O_{(l)}$$

Oxidation and Reduction ANSWERS

1.

a) $KClO_3$ = $K^+ + ClO_3^-$ (divide ionic compound into its ions!)

In ClO_3^-, [Cl] + 3[O] = –1
∴ [Cl] – 6 = –1 ∴ [Cl] = +5

PbO_2 Either: PbO_2 = $Pb^{4+} + 2O^{2-}$
∴ [Pb] = +4

OR [Pb] + 2(–2) = 0
∴ [Pb] – 4 = 0 ∴ [Pb] = +4

b) $PbSO_4$ = Pb^{2+} + SO_4^{2-} ∴ [Pb] = +2

Na_2SO_4 = $2Na^+ + SO_4^{2-}$
In SO_4^{2-}, [S] + 4 [O] = –2
∴ [S] – 8 = –2 ∴ [S] = +6

Na_2O_2 This is sodium peroxide.
Rule In a peroxide, [O] = –1
OR 2 [Na] + 2 [O] = 0
2 (1) + 2 [O] = 0
2 [O] = –2 ∴ [O] = –1

c) CrO_4^{2-}
[Cr] + 4 [O] = –2
[Cr] – 8 = –2 ∴ [Cr] = +6

IO_4^-
[I] + 4(–2) = –1
[I] = –1 + 8 = +7

d) $Zn(NH_3)_4^{2+}$

Note: The (NH_3) is a molecule and has no charge! (∴ O.N = 0)
Hence: [Zn] + 4 (O) = +2
∴ [Zn] + 0 = +2 ∴ [Zn] = +2

e) $Cu(CN)_3^{2-}$
Note : the (CN) is the cyanide ion, and has a charge of –1.
[This is due to C having an O.N of +4 and N having an O.N. of –5]

Hence [Cu] + 3 (–1) = –2
∴ [Cu] – 3 = –2
∴ [Cu] = +1

f) $\underline{N}O_2^-$

$[N] + 2(-2) = -1$
$[N] - 4 = -1 \quad \therefore \quad [N] = +3$

g) $\underline{N}_2O$

$2[N] + [O] = 0$
$\therefore \quad 2[N] - 2 = 0 \quad \therefore \quad 2[N] = +2$
$[N] = +1$

2.

a) $Na_2MnO_4 = 2Na^+ + MnO_4^{2-}$

ie we have the <u>manganate</u> ion
$[Mn] + 4(-2) = -2$
$[Mn] - 8 = -2 \quad \therefore \quad [Mn] = 8 - 2 = +6$

b) MnO_3

$[Mn] + 3(-2) = 0$
$[Mn] - 6 = 0$
$\therefore \quad [Mn] = +6$

c) $NaMnO_4 = Na^+(aq) + MnO_4^-(aq)$

ie we have the <u>permanganate</u> ion
$[Mn] + 4(-2) = -1$
$[Mn] - 8 = -1$
$\therefore \quad [Mn] = +7$

d) $MnO = Mn^{2+} + O^{2-}$

$\therefore \quad [Mn] = +2$
OR $[Mn] + (-2) = 0$
$\therefore \quad [Mn] = +2$

e) Mn_2O_7

$2[Mn] + 7(-2) = 0$
$2[Mn] - 14 = 0$
$2[Mn] = +14$
$\therefore \quad [Mn] = +7$

3.

a) $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

Represents redox because O.N of H changes from +1 to 0
and O.N of Na changes from 0 to +1

b) Not redox. Pb^{2+} on LHS. Pb^{2+} on RHS
S^{2-} on LHS. S^{2-} on RHS

c) $3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(l) + N_2(g)$

Represents redox because O.N of Cu changes from +2 to 0
O.N of N changes from –3 to 0

d) $NaClO(aq) + Na_2SO_3(aq) \rightarrow NaCl(aq) + Na_2SO_4(aq)$

Represents redox because the chlorine has been reduced (from +1 to –1) and the sulfur has been oxidised (from +4 to +6)

e) $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

Redox has occurred.
Reason : O.N of Mg has changed from 0 to +2
O.N of H has changed from +1 to 0

f) Not redox. There is no change in any oxidation number.

g) $Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + SO_2(g) + 2H_2O(l)$

Redox has occurred in the above reaction because:
Cu has been OXIDISED (O.N from 0 to +2)
and S has been REDUCED (O.N from +6 to +4)

4. $Mg(s) + 2AgNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + 2Ag(s)$

a) Mg has been OXIDISED.

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$.....(1)

b) $Ag^+(aq)$ has been reduced:

$Ag^+(aq) + e^- \rightarrow Ag(s)$.....(2)

c) To combine equations (1) and (2) we must multiply eq (2) x 2, then add:

$Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$

5. a) "Oxidising behaviour" means "acting as an oxidising agent". The O.A. must accept electrons, enabling the other substance to lose the electrons and become oxidised.

Hence: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$
shows hydrogen peroxide accepting electrons ie. it is acting as an oxidising agent in the above reaction.

b) The "reducing behaviour" of H_2O_2 means it is acting as a reducing agent. It must therefore be donating electrons to allow the other substance to gain the electrons and become reduced!

Hence: $H_2O_2 \rightarrow 2H^+ + 2e^- + O_2(g)$
shows hydrogen peroxide acting as a reducing agent.

c) i) A solution containing Fe^{2+} (aq) may be oxidised OR reduced:

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ $E° = -0.77V$
or $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E° = -0.44V$

Since the first reaction is oxidation, it can only happen with an oxidising agent. We note that $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$
shows H_2O_2 acting as an oxidising agent, the E° for this reaction is + 1.78 V.

Hence:
$2Fe^{2+}(aq) \rightarrow 2Fe^{3+} + 2e^-$ $E° = -0.77V$
and $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E° = +1.78V$
$2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O$ $E° = +1.01V$

(A reaction between $Fe^{2+}(aq)$ and $H_2O_2(aq)$ could NOT produce Fe(s) because in this case, the E would be negative! (ie not spontaneous)

ii) A solution containing $I^-(aq)$ ions could ONLY be oxidised to $I_2(s)$.

ie $2I^-(aq) \rightarrow I_2(s) + 2e^-$ $E° = -0.54V$

Hence, for the above to occur, the $H_2O_2(aq)$ must act as an oxidising agent.

The two reactions are:
$2I^-(aq) \rightarrow I_2(s) + 2e^-$ $E° = -0.54V$
and $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ $E° = +1.78V$
$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(s) + 2H_2O(l)$ $E° = +1.24V$

Due to the positive value of the overall 'E', a spontaneous reaction is predicted!

6.

a) $Fe^{2+} \rightarrow Fe^{3+}(aq) + e^-$ (Oxidation ½ equation)
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$ (Reduction ½ equation)

To add the above reactions, multiply (1) by 2:

$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$
$2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

b) $SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$
$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

Now balance each half equation by adding H_2O to balance O, adding $H^+(aq)$ to balance H and adding e^- to balance overall charge:

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \quad (1)$$
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O \quad (2)$$

To equalise electrons, multiply -(1) by 5 and multiply -(2) by 2.

$$5SO_3^{2-} + 5H_2O \rightarrow 5SO_4^{2-} + 10H^+ + 10e^-$$
$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$
$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$$

c) $Cu(s) \rightarrow Cu^{2+}(aq)$ (oxidation)
$Hg^{2+}(aq) \rightarrow Hg(l)$ (reduction)

ie $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$
$Cu(s) + Hg^{2+} \rightarrow Cu^{2+}(aq) + Hg(l)$

d) $S^{2-}(aq) \rightarrow S(s)$ (oxidation)
$MnO_4^- \rightarrow Mn^{2+}$ (reduction)

$$S^{2-}(aq) \rightarrow S(s) + 2e^- \quad - \quad (1)$$
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O \quad (2)$$

To add the above equations, multiply (1) by 5 and (2) by 2:

$$5S^{2-}(aq) \rightarrow 5S(s) + 10e^-$$
$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$
$$5S^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5S(s) + 2Mn^{2+}(aq) + 8H_2O$$

e) $I_2 \rightarrow I^-$ (reduction)
$H_2S \rightarrow S(s)$ (oxidation)

Balance each equation:

$$I_2(s) + 2e^- \rightarrow 2I^-(aq)$$
$$H_2S(g) \rightarrow S(s) + 2H^+(aq) + 2e^-$$
$$I_2(s) + H_2S(g) \rightarrow 2I^-(aq) + S(s) + 2H^+(aq)$$

f) $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$ (REDUCTION)
$I^-(aq) \rightarrow I_2(s)$ (OXIDATION)

$$Cr_2O_7^{2-}(aq) + 14H^+ + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad (1)$$
$$2I^-(aq) \rightarrow I_2(s) + 2e^- \quad - \quad (2)$$

Multiply equation - (2) by 3 to equalise the electrons.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$6I^-(aq) \rightarrow 3I_2(s) + 6e^-$$
$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2(s) + 7H_2O(l)$$

g) $Cu(s) \rightarrow Cu^{2+}(aq)$ (as $Cu(NO_3)_2$)

$NO_3^-(aq) \rightarrow NO_2(g)$

In the first equation, copper has been OXIDISED. In the second equation, nitrogen (in NO_3^-) has been reduced (to $NO_2(g)$).

Balance each equation:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ - (1)

$NO_3^-(aq) + 2H^+ + e^- \rightarrow NO_2(g) + H_2O$ (2)

To add the above equations, multiply equation (2) by 2.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$
$$2NO_3^- + 4H^+ + 2e^- \rightarrow 2NO_2(g) + 2H_2O(l)$$
$$Cu(s) + 2NO_3^- + 4H^+ \rightarrow Cu^{2+} + 2NO_2(g) + 2H_2O(l)$$

(This equation is different to the one which shows nitric acid as a molecular formula and not in ionic form. The reason is that only SOME of the NO_3^- ions are reduced.
ie. some NO_3^- remains as NO_3^- (not redox) and some NO_3^- are reduced to $NO_2(g)$).

The "FULL" equation could be written:

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l).$$

h) $SO_3^{2-} \rightarrow SO_4^{2-}$ (Oxidation)

$IO_3^- \rightarrow I_2(s)$ (Reduction)

Balance each half equation:

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+(aq) + 2e^-$$
$$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2(s) + 6H_2O(l)$$

To combine the above two equations, multiply first by 5 and the second by 2:

$$5SO_3^{2-} + 5H_2O \rightarrow 5SO_4^{2-} + 10H^+ + 10e^-$$
$$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2(s) + 6H_2O(l)$$

Ans (c): $5SO_3^{2-} + 2IO_3^- + 2H^+ \rightarrow 5SO_4^{2-} + I_2(s) + H_2O(l)$