# Section 3
Reduction-Oxidation

- Definitions. Define oxidation in terms of loss or gain of oxygen, hydrogen and electrons; giving examples to illustrate this.
- Oxidation States. The rules for assigning oxidation states to elements, ions, compounds and molecules.
- Equations. Balancing redox equations using the ion-electron method.
- Common oxidising agents. Oxygen, chlorine, dilute acids, nitrate ions (in conc. HNO_3), hydrogen peroxide, acidified permanganate ions and acidified dichromate ions, etc.
- Common reducing agents. Zinc metal, magnesium metal, iron metal, carbon, sulfur dioxide and iron(II) ions, etc
- The behaviour of the following oxidising and reducing agents
a) oxidising agents: H_2O_2, Cl_2, I_2, MnO_4^-, $Cr_2O_7^{2-}/H^+$, HNO_3, Fe^{3+}, Cu^{2+}, IO_3^- or BrO_3^-, etc.
b) reducing agents: Zn, Mg, Fe, H_2, SO_2, CO, $C_2O_4^{2-}$ Fe^{2+}, SO_3^{2-}, $S_2O_3^{2-}$, I^-, etc.
- Volumetric analysis involving oxidation-reduction reactions selected from the oxidising and reducing agents listed above.
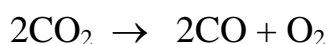
Reduction/Oxidation (Redox) Reactions

Definitions:

In terms of	Reduction	Oxidation
O atom	Loss	Gain
H atom	Gain	Loss
Electron	Gain	Loss
Oxidation number	Decrease	Increase

Oxidation and Reduction always occur together. Below are some examples.
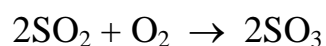
$$2SO_2 + O_2 \rightarrow 2SO_3$$
Sulfur has been oxidised because it has gained oxygen

$$2CO_2 \rightarrow 2CO + O_2$$
Carbon has been reduced because it has lost oxygen.
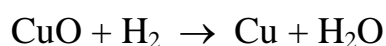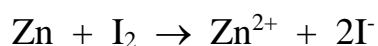
$$CuO + H_2 \rightarrow Cu + H_2O$$
The hydrogen has been oxidised because it has gained oxygen
The copper has been reduced because it has lost oxygen

A better definition of oxidation and reduction uses the gain or loss of electrons.

> **Oxidation is the loss of electrons (OIL)**
> **Reduction is the gain of electrons (RIG)**
> ***or***
> **Loss of electrons is oxidation (LEO)**
> **Gain of electrons is reduction (GER)**

$$Zn + I_2 \rightarrow Zn^{2+} + 2I^-$$
The Zinc has been oxidised because it has lost electrons
$$Zn \rightarrow Zn^{2+} + 2e^-$$
The Iodine has been reduced because it has gained electrons
$$2e^- + I_2 \rightarrow 2I^-$$
Two moles of electrons have been transferred from zinc to iodine.
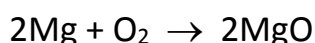
Oxidation Numbers/Oxidation States

Sometimes it is hard to work out what has been reduced and what has been oxidised. Oxidation numbers are a sort of electronic book keeping system to make this task easier. Every atom in an element, compound or ion is assigned an oxidation number according to the following set of rules:

1. The oxidation number of any free, uncombined element is zero. This includes multi-atomic elements such as H_2 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 the sum of the oxidation numbers of the atoms involved is zero.

4. The oxidation number of Group One metals is always +1. The oxidation number of Group Two metals is always +2.

5. The oxidation number of oxygen is -2 except in the case of peroxides such as H_2O_2 where it is -1 and the compound F_2O where it is +2.

6. The oxidation number of hydrogen is +1 except in the case of metal hydrides such as NaH where it is -1.

7. In the interhalogen compounds, the more electronegative halogen atom is assigned the oxidation number of -1. e.g. IF_5, the oxidation number of fluorine is -1 while +5 for iodine; e.g. $BrCl_3$, the oxidation number of chlorine is -1 while +3 for bromine.

Remember: **(1)   In most cases, -4 ≤ O.N. ≤ +7**

(2)   O.N. can be a decimal

Find the oxidation number of each species in the following equation:

$$2Mg + O_2 \rightarrow 2MgO$$

Mg = 0 (rule 1)
O_2 = 0 (rule 1)
Oxygen in MgO = -2 (rule 5)
Magnesium in MgO = +2 (rule 3)

In Redox reactions, an increase in oxidation number means a substance has been oxidised. A decrease in oxidation number means a substance has been reduced.
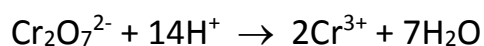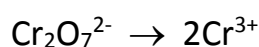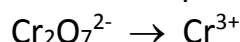
Questions 1

Balancing Redox Equations (The Ion-Electron method)

We balance redox equations by writing two half equations using the following rules:
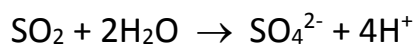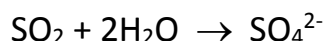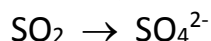
1) Balance the atoms that are not oxygen or hydrogen.
2) Balance the oxygen's by adding water.
3) Balance the hydrogen's by adding hydrogen ions.
4) Balance the charge by adding electrons to the more positive side until the charge is equal.

Write an equation for the overall reactions between sulfur dioxide and dichromate ions.

Step 1: Write the half equation for the reduction of $Cr_2O_7^{2-}$

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$
$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$
$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
$$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Step 2: Write the equation for the oxidation of SO_2

$$SO_2 \rightarrow SO_4^{2-}$$
$$SO_2 + 2H_2O \rightarrow SO_4^{2-}$$
$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+$$
$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

Step 3: Multiply the equations to make the number of electrons equal.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$3SO_2 + 6H_2O \rightarrow 3SO_4^{2-} + 12H^+ + 6e^-$$
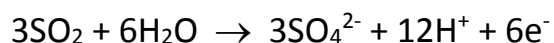
Step 4: Add the two half equations together. Cancel electrons on both sides

$$Cr_2O_7^{2-} + 14H^+ + 3SO_2 + 6H_2O \rightarrow 2Cr^{3+} + 7H_2O + 3SO_4^{2-} + 12H^+$$
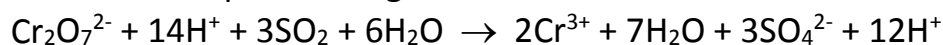
Step 5: Cancel out species appearing on both sides of the equation.

$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$$
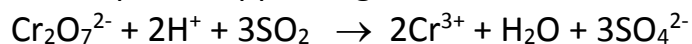
In the final (overall) equation:

(a)   Electrons must be canceled out.

(b)   The same number of atoms of each element on both sides of the equation are equal.

(c)   The electrical charges must be equal on both sides of the equation.

Questions 2

Common Oxidising Agents

Oxidising agents (oxidants) oxidise another substance and gain electrons in a chemical reaction and are themselves reduced. Identifying the substance reduced is one way to identify the oxidising agent in a chemical reaction. Some common oxidising agents are listed below:

Oxidant	Half equation	Observation
Oxygen	$O_2(g) + 4e^- \rightarrow 2O^{2-}$	No obvious change
Chlorine	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	Green gas disappears
Dilute acids	$2H^+ + 2e^- \rightarrow H_2(g)$	Colourless solution forms bubbles or fizzing
Conc. nitric acid	$NO_3^- + 2H^+ + e^- \rightarrow NO_2(g) + H_2O$	Brown gas formed
Dilute nitric acid	$NO_3^- + 4H^+ + 3e^- \rightarrow NO(g) + 2H_2O$	No obvious change
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	No obvious change
Acidified dichromate	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	Orange solution to green/blue solution
Acidified permanganate	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	Purple solution to colourless solution
Neutral permanganate	$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	Purple solution to black/brown solid
Alkaline permanganate	$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	Purple solution to dark green solution
Manganese (IV) oxide	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	Black solid / colourless solution
Bromate ions	$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$	No visible change
Iodate ions	$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$	No visible change
	$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2(aq) + 6H_2O$	Colourless solution to brown solution
Aqueous iodine	$I_2(aq) + 2e^- \rightarrow 2I^-$	Brown solution goes colourless
Iron(III) ion	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	Yellow-brown solution to pale green solution
Copper (II) ions	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	Blue solution to red/pink solid
	$Cu^{2+} + I^- + e^- \rightarrow CuI(s)$	Blue solution to white ppt

Common Reducing Agents

Reducing agents (reductants) reduce another reactant and lose electrons in a chemical reaction and are themselves oxidised. Identifying the substance oxidised is one way to identify the reducing agent in a chemical reaction. Some common reducing agents are listed below:

Reductant	Half equation	Observation
Zinc metal	$Zn \rightarrow Zn^{2+} + 2e^-$	Grey metal → colourless solution
Magnesium metal	$Mg \rightarrow Mg^{2+} + 2e^-$	Grey metal → colourless solution
Iron metal	$Fe \rightarrow Fe^{2+} + 2e^-$	Grey metal → pale green solution
Iron(II) ion	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	Pale green solution → yellow-brown solution
Carbon	$C \rightarrow CO_2$	Black solid → colourless gas
Carbon monoxide	$CO \rightarrow CO_2$	(Poisonous) pungent gas → colourless, odourless gas
Oxalate ion /oxalic acid	$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$	Colourless solution → bubbles or colourless gas (which turns limewater milky then clear again)
Thiosulfate ions	$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$	Colourless solution → colourless solution
Hydrogen peroxide	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	Colourless solution → bubbles or colourless gas (which rekindles a glowing splint)
Sulfur dioxide	$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$	Choking/pungent gas → colourless solution
Sulfite ions	$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$	Colourless solution → colourless solution

Remember:

In a redox reaction, the oxidant (oxidising agent) oxidises the reductant and itself gets reduced, undergoing reduction;

The reductant (reducing agent) reduces the oxidant and itself gets oxidised, undergoing oxidation.

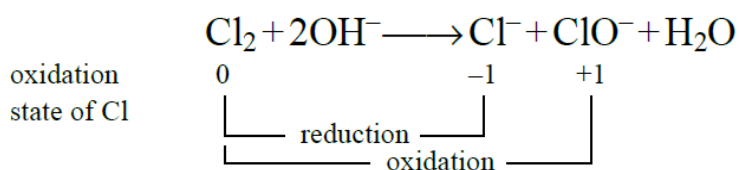**Both oxidant and reductant must be the reactants, not the products.**

Disproportionation Reactions

Disproportionation is a chemical reaction, typically a redox reaction, where a reactant is transformed into two or more dissimilar products. In a redox reaction, the species is simultaneously oxidised and reduced to form at least two different products.
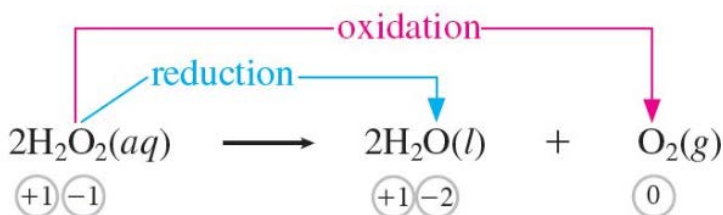
Disproportionation reactions follow the form: $2X \rightarrow X' + X''$ where X, X', and X" are all different chemical species.

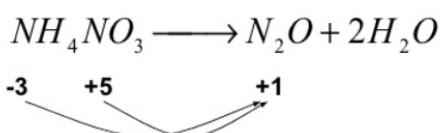The reverse reaction of disproportionation is called comproportionation.

e.g.1

$$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

oxidation state of Cl: 0 ... -1 ... $+1$

reduction
oxidation

e.g.2

—oxidation—
reduction—

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$
$(+1)(-1)$ ... $(+1)(-2)$ ... (0)

e.g.3

Is this a disproportionation reaction?

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$
-3 ... $+5$ ... $+1$

This is NOT a disproportionation reaction
Disproportionation requires that the <u>same</u> atom is both oxidised and reduced simultaneously.
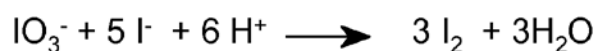In this case, <u>different</u> atoms (of nitrogen) are oxidised and reduced.

e.g.4   Is the following redox reaction a disproportionation reaction?

$$Cu_2O_{(s)} + H_2SO_{4(aq)} \rightarrow Cu_{(s)} + CuSO_{4(aq)} + H_2O_{(l)}$$

e.g.5   Is the following redox reaction a disproportionation reaction?

$$IO_3^- + 5 I^- + 6 H^+ \longrightarrow 3 I_2 + 3H_2O$$

Redox Titrations

In a titration a known mass or volume of substance A is placed in a flask and reacted with solution B, which is added from a burette. The concentration of one of the solutions either A or B must be accurately known. Some kind of indicator may be needed to show when all of substance A or B has reacted. The aim is normally to determine the concentration, volume, mass of A or B.

Common laboratory equipment

    (a) electronic balance

    (b) volumetric flask

    (c) burette

    (d) pipette

    (e) conical flask

    (f) measuring cylinder

    (g) wash bottle

    (h) beaker

    (i) safety googles

Titration terminology

    (a)   Titration – a volumetric analysis using burette and pipette to accurately determine the concentration or mass of a reactant whose concentration or mass is unknown.

    (b)   Primary standard – a pure solid (or liquid) that is stable under normal conditions and can be easily used to make up a standard solution.

    (c)   Standard solution – a solution whose concentration is accurately known.

    (d)   Standardised solution – a solution whose concentration has been accurately determined by titrating the solution against a standard solution.

    (e)   Aliquot – an accurate volume of a reactant measured and transferred by a pipette.

    (f)   Titre – in a titration, the volumes of solution needed to be dispensed from the burette in order to reach the equivalence point.

(g)   Equivalence point – the point in a titration at which the correct amounts of reactants have been added to complete the reaction according to the mole ratio in the balanced equation.

(h)   Endpoint – the point in a titration that occurs when the indicator changes the colour.

(i)   Indicator – a substance that shows a distinct colour change at the endpoint in a titration.

(j)   Concordant results – three titres or more agree to within 0.10 mL.

Primary standard

Can be measured accurately usually by weighting and dissolved in an accurately measured known volume of water to prepare a standard solution.

To be a good primary standard the following properties are required:
- The sample must be pure.
- It must not lose water of crystallisation on storage.
- It must be stable in air and not pick up water or carbon dioxide while standing.
- It must have a large molar mass so weighing errors are minimal.
- It must react quickly to completion.

Oxalic acid dihydrate ($H_2C_2O_4.2H_2O$), potassium bromate ($KBrO_3$) and potassium iodate (KIO_3) all make good primary standards.

Secondary standard

A solution whose concentration has been determined by a chemical reaction (i.e. another titration). Some examples are aqueous solutions of

potassium permanganate, $KMnO_4$ (OA);

iron(II) sulfate, $FeSO_4$ (RA);

iodine, I_2 (OA);

sodium thiosulfate, $Na_2S_2O_3$ (RA);

etc.

Practical Techniques

The following are the steps that must be followed in undertaking each titration.

➢ Make sure all glassware is clean.

➢ Before using a pipette, rinse it with a small amount of the solution to be used. To use a pipette properly make sure that the bottom of the meniscus comes exactly opposite the mark on the pipette.

➢ Rinse out the burette with a small amount of the solution it will contain. Use a filter funnel to fill the burette and stand it in such a position that spilt solution cannot possibly fall into your eyes.

➢ Ensure that no solution is left dripping down the outside of the burette.

➢ Do not leave the funnel in the burette during the titration; a small drop of solution can be caught between the burette and the funnel and fall down during the titration which affects the volume used.

➢ Run a little of the solution through the burette before starting the titration to ensure that no air bubble is caught in the trap.

➢ Make sure the burette is vertical.

➢ Read the burette immediately before and after the titration as accurately as possible (to 0.05 mL) by placing a piece of white paper behind the burette and reading from the bottom of the meniscus.

➢ Gently swirl the flask during the titration with your right hand to mix the solution. Use your wash bottle to rinse off any solution splashed on the inside of the conical flask. As you near the endpoint of the titration add the solution a few drops at a time. At the endpoint one drop is normally enough to change the colour of the indicator.

➢ Do at least three titrations for any unknown solutions. If one differs a lot from the other two ignore it and carry on doing more titrations until you have three titres within experimental error – i.e. within 0.1 mL

➢ Rinse the conical flask three times (twice with tap water; last time with distilled water) between titrations.

Calculation Formulae:

(a) $n = \dfrac{m}{M}$

(b) $c = \dfrac{n}{V}$

(c)   mol L^{-1} $\underset{\div M}{\overset{\times M}{\longleftrightarrow}}$ g L^{-1}

(d)   Average titre, $\bar{V} = \dfrac{\sum concordant\,titres}{number\,of\,titres}$

Calculations involving redox titrations follow the following steps:

1)   Write a balanced equation

2)   Perform the titration

3)   Calculate the amount (in mol) of the known chemical in the burette (n(B)) using

$$n(B) = V(B) \times c(B)$$

   Where: $V(B)$ = volume of burette solution used to reach the equivalence point.

   $c(B)$ = concentration of burette solution in mol L^{-1}

4)   Calculate the amount (in mol) of the other (unknown) substance pipetted into the flask ($n(P)$), using the mole ratio from the balanced equation and the amount (in mol) of the known substance.

5)   Calculate the concentration of the unknown solution using:

$$c(P) = n(P) / V(P)$$

   Where: $V(P)$ is the known volume pipetted into the flask.

A 5.026 g sample of an ore of iron was dissolved in 50 mL of dilute sulfuric acid. The iron was converted to Fe^{2+}(aq). The resulting solution was then titrated against 0.0640 mol L^{-1} $KMnO_4$ solution and required an average 30.68 mL to oxidise all of the iron. Calculate the mass of iron in the ore and hence the percentage of iron in the ore.

The mass of the ore has been given accurately, but the ore is impure, so we won't need that number until the end of the problem. The key reaction is that between Fe^{2+} and MnO_4^-. It is done under acid conditions, so the MnO_4^- will be reduced to Mn^{2+}. We need to work out the amount of Fe^{2+} which reacted, first in moles, then in grams.

$c(MnO_4^-)$ = 0.06402 mol L^{-1}; $V(MnO_4^-)$ = 30.68 mL
$M(Fe)$ = 55.85 g mol^{-1}; $m(ore)$ = 5.026 g
$n(Fe^{2+})$ = ?
$m(Fe)$ = ?
$\%(Fe)$ = ?

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+}\ 4H_2O$
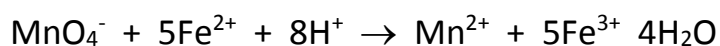
$n(MnO_4^-)$ = cV = 0.0640 x 0.03068   = 1.96 x 10^{-3} mol

$n(Fe^{2+})$ = $5n(MnO_4^-)$ = 5 x (1.96 x 10^{-3}) = 9.82 x 10^{-3} mol

$m(Fe^{2+})$ = nM = (9.82 x 10^{-3}) x 55.85 = 0.548 g = $m(Fe)$

$\%(Fe)$ = (mass of iron found / mass of ore) x 100

    = (0.548 g / 5.026 g) x 100

    = 10.91%

Questions 3

Questions 1

1. Find the oxidation number of chromium in the following species.

   a. Cr_2O_3 b. CrO_3

   c. Na_2CrO_4 d. Cr

   e. $Cr_2O_7^{2-}$ f. CrO_4^{2-}

2. Find the oxidation number of sulfur in the following species.

   a. SO_2 b. S_8

   c. Na_2SO_4 d. SO_3

   e. K_2SO_3 f. H_2S
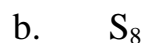
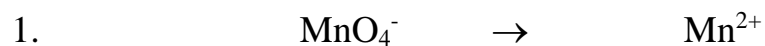3. Find the oxidation number of chlorine in the following species.

   a. Cl_2 b. $LiCl$

   c. $HClO_3$ d. ClO_4^-

   e. Cl_2O f. ClF_3
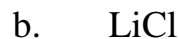
Questions 2

Balance the following half equations using ion-electron method.

Write the overall equation, ensuring that you cancel any species that occur on both sides.

Identify the oxidising agent and reducing agent in each reaction.

1. MnO_4^- $\rightarrow$ Mn^{2+}

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

2. $Cr_2O_7^{2-}$ $\rightarrow$ Cr^{3+}

          SO_2 $\rightarrow$ SO_4^{2-}

3. MnO_4^- $\rightarrow$ Mn^{2+}

                $H_2C_2O_4$ $\rightarrow$ CO_2

4. $Cr_2O_7^{2-}$ $\rightarrow$ Cr^{3+}

                $CH_3CH_2OH \rightarrow$ CH_3COOH

5. MnO_2 $\rightarrow$ Mn^{2+}

                Cl^- $\rightarrow$ Cl_2

6. IO_3^- $\rightarrow$ I_2

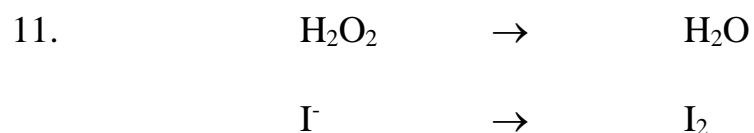 I^- $\rightarrow$ I_2

7. Cu $\rightarrow$ Cu^{2+}

                NO_3^- $\rightarrow$ NO_2

8. MnO_4^- $\rightarrow$ Mn^{2+}

                H_2O_2 $\rightarrow$ O_2

9. I_2 $\rightarrow$ I^-

    $S_2O_3^{2-}$ $\rightarrow$ $S_4O_6^{2-}$

10. MnO_4^- $\rightarrow$ MnO_4^{2-}

    SO_3^{2-} $\rightarrow$ SO_4^{2-}

11. H_2O_2 $\rightarrow$ H_2O

    I^- $\rightarrow$ I_2
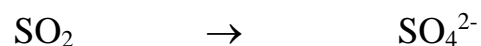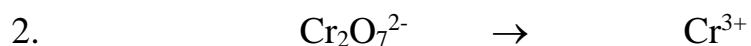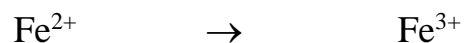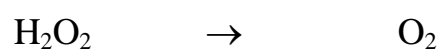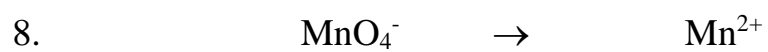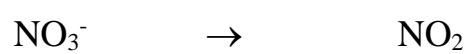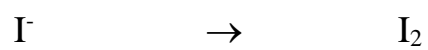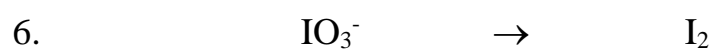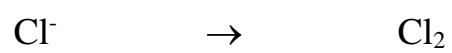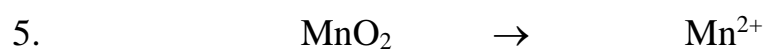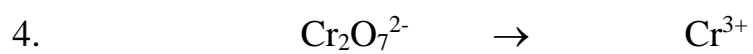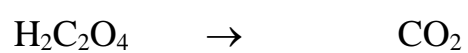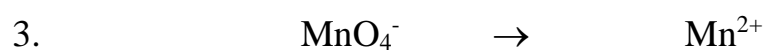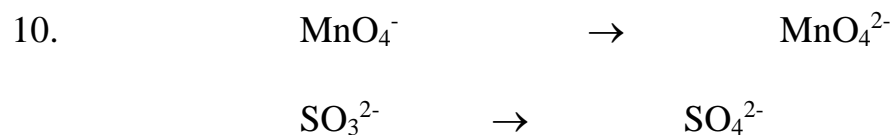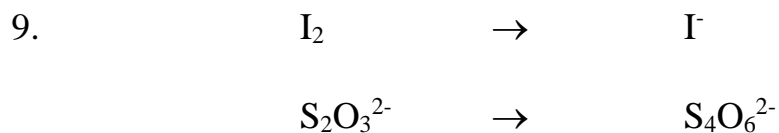
Questions 3

1. Oxalic acid can be used to standardise potassium permanganate solution. A student found that 20.00 mL of 0.172 mol L^{-1} oxalic acid reacted with 22.40 mL of potassium permanganate solution.

    a. Write two ion electron half-equations, and hence the balanced ionic equation for the reaction.

    b. Calculate the amount, in moles, of oxalic acid reacting.

    c. Calculate the amount, in moles, of potassium permanganate that reacted.

    d. Calculate the concentration of the potassium permanganate solution.

2   One analytical method for determining blood alcohol levels involves two stages:

Separation of the alcohol (assumed to be ethanol) from the blood by diffusion, in a closed container, into a known volume of acidified standard potassium dichromate ($K_2Cr_2O_7$) solution. Determination of the amount of dichromate ion consumed in stage 1, by titration.

a.   Write the ion electron half equation for the oxidation of ethanol (C_2H_5OH) to ethanoic acid (CH_3COOH).

b.   Write down the ion electron half-equation for the reduction of the dichromate ions to chromium (III) ions in acid solution.

c.   Write the balanced overall equation for the reaction.

d.   In such an analysis, the ethanol from a 10.0 mL sample of blood required 14.4 mL of 0.0200 mol L^{-1} acidified potassium dichromate solution for oxidation to ethanoic acid. Calculate the amount (in moles) of potassium dichromate solution that was used in the process.

e.   Calculate the amount (in moles) of ethanol in the 10.0 mL blood sample.

f.   In New Zealand, it is an offence to drive a vehicle when the alcohol concentration in blood is over 80 milligrams per 100 mL of blood. Calculate the ethanol concentration in the blood sample determined in (e) in milligrams of ethanol per 100 mL of blood and hence determine if this sample is over the legal limit.

g.   Suggest one reason why it is necessary to separate the alcohol from the blood before carrying out this titration.