Volumetric Analysis & Redox

Content

- Reacting volumes (of solutions)
- Redox processes; electron transfer and/or of changes in oxidation number (oxidation state)

Learning Outcomes required for H2 (9729) and H1 (8873) Chemistry:

[The term relative formula mass or M_r will be used for ionic compounds]

Candidates should be able to

(a) Write and /or construct balanced equations;

(b) Perform calculations, including use of the mole concept, involving volumes and concentrations of solutions;
[when performing calculations, candidates' answers should reflect the no. of significant figures given or asked for in the question]

(c) Deduce stoichiometric relationships from calculations such as those in (b).

(d) Describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state).

(e) Construct redox equations using the relevant half-equations.

1. VOLUMETRIC ANALYSIS (TITRATION)

Success Criteria:

- Understand what the following terms mean: analyte; standard solution; titrant; end-point; equivalence point

Volumetric analysis (or titrimetric analysis) is carried out to obtain quantitative information about chemical reactions, such as the concentration of a solution and/or establish the stoichiometry of a reaction.

Note:

Standard solution is a solution of known concentration.

The standard solution may also be placed in the conical flask, and the reactant of unknown concentration in the burette.

General overview of the titration method:

1. Pipette a portion of the solution of unknown concentration (called the **analyte**) into a conical flask.
2. Add a few drops of a suitable indicator into the conical flask. (Some titrations do not require any indicator)
3. Titrate the solution by adding a **standard solution** from a burette slowly, with **constant swirling** until a **first permanent colour change** is noted (this is the **end-point**).

End-point (experimental): The point during titration at which a sudden sharp colour change (of indicator) is observed.

Equivalence point (theoretical): The point during titration at which stoichiometric amounts of the two reactants have reacted completely with one another, i.e., none of the reactants is in excess.

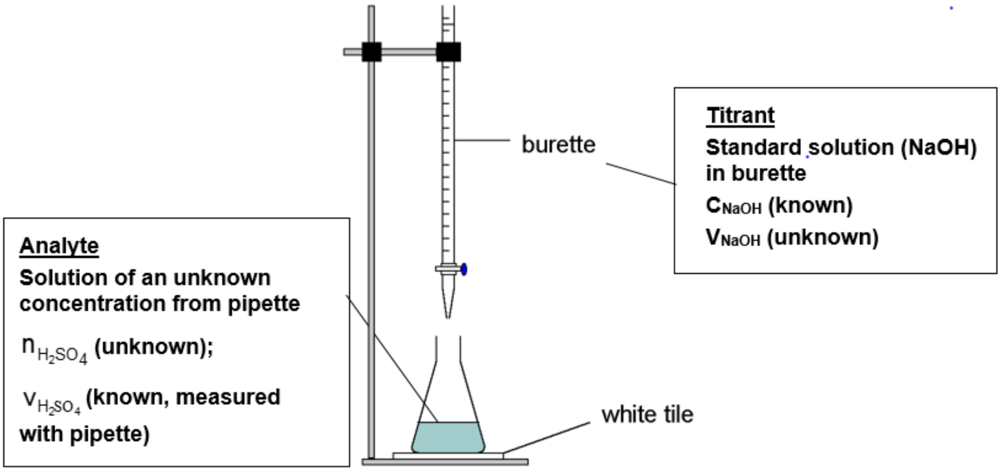
For a titration result to be accurate, the **end-point** must be close to the **equivalence point**.

E.g. Titration between dilute H_2SO_4 and NaOH solution:

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

Note:

Notation for amount of H_2SO_4 is n_{H2SO4}



Analyte

Solution of an unknown concentration from pipette

$n_{H_2SO_4}$ **(unknown);**

$V_{H_2SO_4}$ **(known, measured with pipette)**

Titrant

Standard solution (NaOH) in burette

C_{NaOH} **(known)**

V_{NaOH} **(unknown)**

2. ACID-BASE TITRATION

Common types of titration include:
- Acid-base titration
- Back titration
- Redox titration

Success Criteria:

- Able to state the colour changes (and end-point colours) of common indicators; namely methyl orange & phenolphthalein
- Able to write/construct balanced equations
- Able to perform calculations, using mole concept involving volumes and concentrations of solutions; including scaling up when dilution is performed.

Acid-Base titration usually involves the use of an indicator to determine the end-point.

An indicator consists of either a weak acid or base and is added in a small amount to the solution in the conical flask at the start of an acid-base titration. The indicator causes the colour of the solution in the conical flask to change at the end-point depending on the pH of solution.

This table shows the colour changes of some common indicators used in acid-base titrations.

Different indicators are chosen for specific titrations, so that their end-point corresponds to the equivalence point of the titration.

	Colour		
Indicator	**In base (or alkali)**	**At end-point**	**In acid**
thymol blue	blue	yellow	red
bromothymol blue	blue	green	yellow
methyl orange	**yellow**	**orange**	**red**
screened methyl orange	green	grey	purple
phenolphthalein (no longer used in practical)	**pink**	**pale pink or colourless***	**colourless**
thymolphthalein	blue	pale blue or colourless*	colourless

***depending on the original colour of indicator in conical flask**

Worked Example 1 (Acid-Base Titration)

In a titration experiment, 25.0 cm^3 of dilute H_2SO_4 reacts with 18.00 cm^3 of 0.100 mol dm^{-3} NaOH(aq).
Calculate the concentration of H_2SO_4 in (a) mol dm^{-3}, and (b) g dm^{-3}.

(a) Amount of NaOH used in titration $= 0.100 \times \frac{18.00}{1000} = 1.800 \times 10^{-3}$ **mol (4 s.f.)**

$$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$$

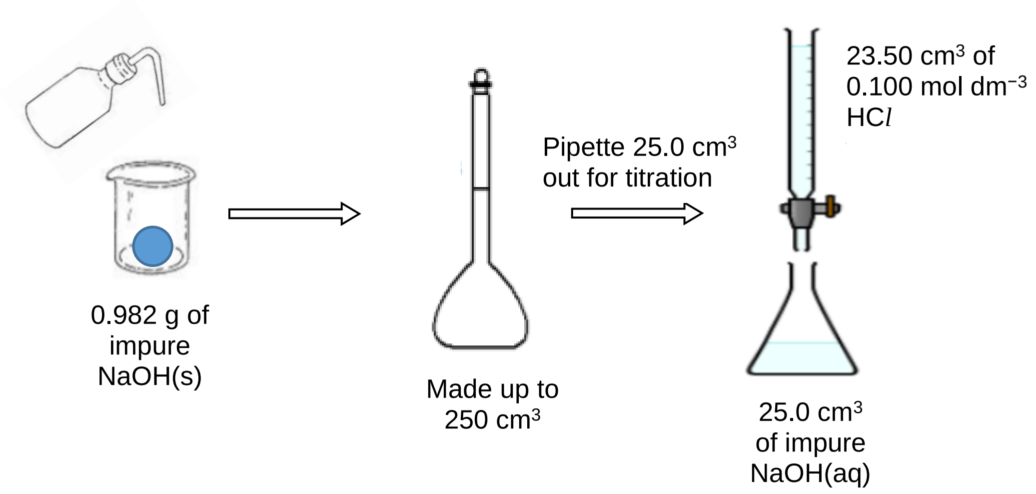
Amount of H_2SO_4 **in 25.0** $cm^3 = \frac{1}{2} \times 1.800 \times 10^{-3} = 9.000 \times 10^{-4}$ **mol**

$$[H_2SO_4] = \frac{9.000 \times 10^{-4}}{(^{25.0}/_{1000})} = \underline{3.60 \times 10^{-2}\ mol\ dm^{-3}}\ (3\ s.f.)$$

(b) conc in g $dm^{-3} = 3.60 \times 10^{-2} \times (2 \times 1.0 + 32.1 + 4 \times 16.0) = \underline{3.53\ g\ dm^{-3}}$

Worked Example 2 (Acid-Base Titration)

0.982 g of an impure sample of solid sodium hydroxide was dissolved in deionised water and made up to 250 cm^3 in a graduated flask. 25.0 cm^3 of this solution was neutralised by 23.50 cm^3 of 0.100 mol dm^{-3} dilute hydrochloric acid. Calculate the percentage purity of sodium hydroxide in the sample.



$$\mathbf{NaOH(aq) + HC\mathit{l}(aq) \longrightarrow NaC\mathit{l}(aq) + H_2O(\mathit{l})}$$

$$\mathbf{n_{HC\mathit{l}}\ in\ 23.50\ cm^3 = 0.100 \times \frac{23.50}{1000} = 2.350 \times 10^{-3}\ mol\ (4.s.f.)}$$

$$\mathbf{n_{NaOH}\ in\ 25.0\ cm^3 = 2.350 \times 10^{-3}\ mol}$$

Note:

Remember to scale up to find the no. of moles in the original solution

$$\mathbf{n_{NaOH}\ in\ 250\ cm^3 = 2.350 \times 10^{-3} \times \frac{250}{25} = 2.350 \times 10^{-2}\ mol}$$

Molar mass of NaOH = 40.0 g mol^{-1}

Mass of pure NaOH = 2.350 × 10^{-2} × 40.0 = 0.940 g

$$\mathbf{percentage\ purity\ of\ NaOH\ in\ sample = \frac{0.940}{0.982} \times 100\% = \underline{95.7\%}}$$

Checkpoint 1 (Acid-Base Titration)

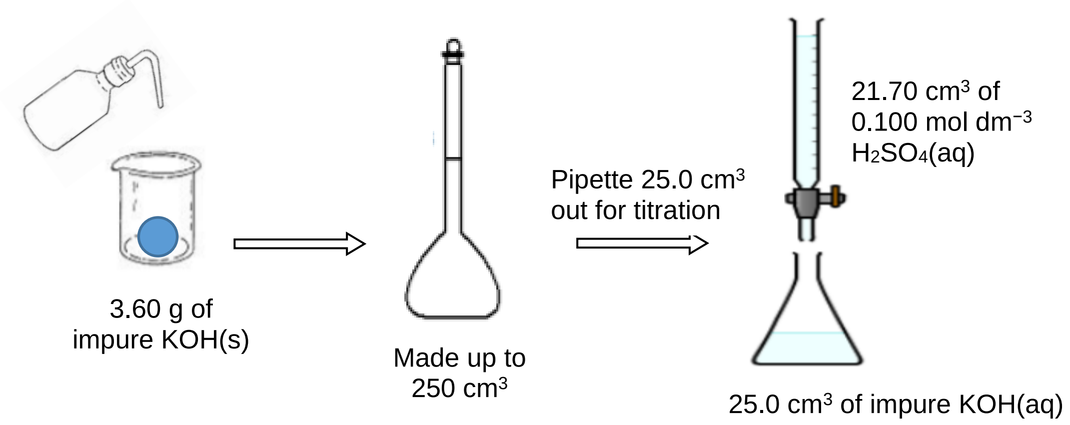
1) Calculate the volume of 0.12 mol dm^{-3} KOH required to react with 25.0 cm^3 of H_3PO_4, containing 4.90g of H_3PO_4 per dm^3 solution.
Equation for the reaction: $2KOH(aq) + H_3PO_4(aq) \longrightarrow K_2HPO_4(aq) + 2H_2O(l)$

[20.8 cm^3]

2) 3.60 g of an impure sample of solid potassium hydroxide was dissolved in deionised water and made up to 250 cm^3 in a graduated flask. 25.0 cm^3 of this solution was neutralised by 21.70 cm^3 of 0.100 mol dm^{-3} dilute sulfuric acid.

Calculate the percentage purity of potassium hydroxide in the sample.

[67.6%]



3. BACK TITRATION

<u>Success Criteria:</u>

- Understand how back titration works and why some experiments use back titration instead of direct titration;
- Able to write/construct balanced equations;
- Able to perform calculations, using mole concept, to determine the amount of unreacted reactant at the end and thus the amount of reactant that reacted by subtracting from its amount at the start, including scaling up, where appropriate.

Back titrations are done when **direct titrations are not feasible** due to one of the following reasons:

- a solid is insoluble in water, but is soluble in an acid or a base.
  - e.g. calcium carbonate is insoluble in water but reacts with acid to form an aqueous solution.
- one of the reactants is volatile.
  - e.g. ammonia may be lost during titration through evaporation.
- a particular reaction is too slow; the end-point of the reaction may be missed if directly titrated as the reaction is too slow for observable changes.

A back titration is generally a two-step analytical technique:

Step 1: Reactant A of unknown concentration is reacted with known amount of excess reactant B (*Start*).

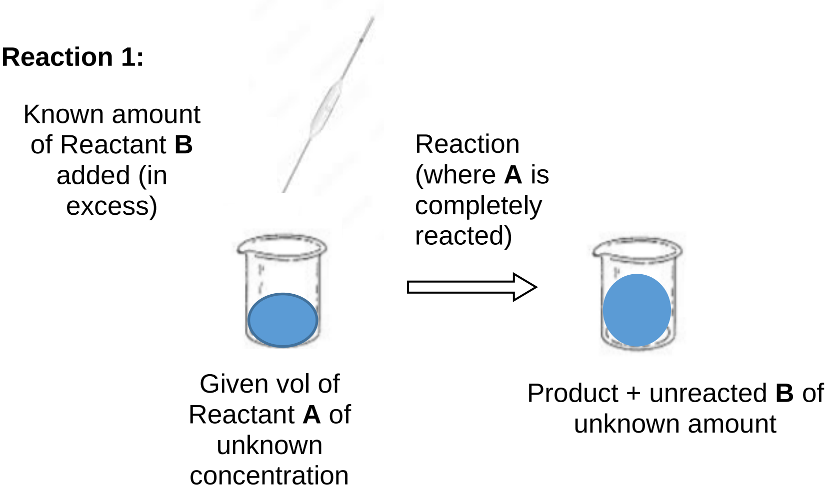
$$\text{A + B (in excess)} \longrightarrow \text{products + B (unreacted)}$$

Step 2: Titration against a standard solution is then performed to determine the amount of unreacted reactant B (*End*)

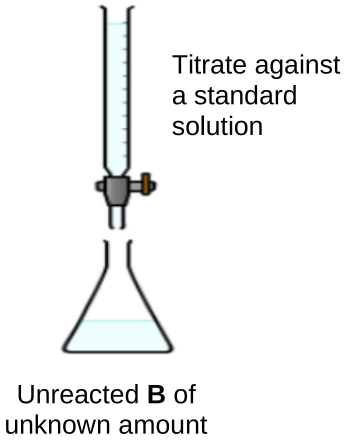
Step 3: Amount of B reacted is then calculated as follows:

$$\boxed{\begin{array}{l}\text{amt. of B } \textit{\underline{R}eacted} = (\text{amt. of B at }\underline{\text{S}}\text{tart}) - (\text{amt. of B at }\underline{\text{E}}\text{nd}) \\ \qquad\qquad\qquad \textit{Reacted} \;\; = \textit{Start} - \textit{End}\end{array}}$$

Reaction 1:



Reaction 2:



Note:

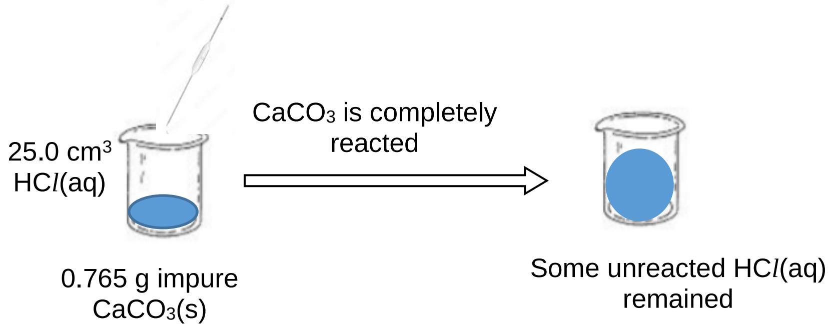
In this calculation, it is assumed that in the impure sample of calcium carbonate, the impurities do not react with HC*l*.

Worked Example 3 (Back Titration)

0.765 g of an impure sample of calcium carbonate was dissolved in 25.0 cm^3 of 1.00 mol dm^{-3} dilute HC*l*. The resulting solution was made up to 250 cm^3 in a volumetric flask. 25.0 cm^3 of this solution was neutralised by 24.35 cm^3 of 0.050 mol dm^{-3} NaOH(aq).

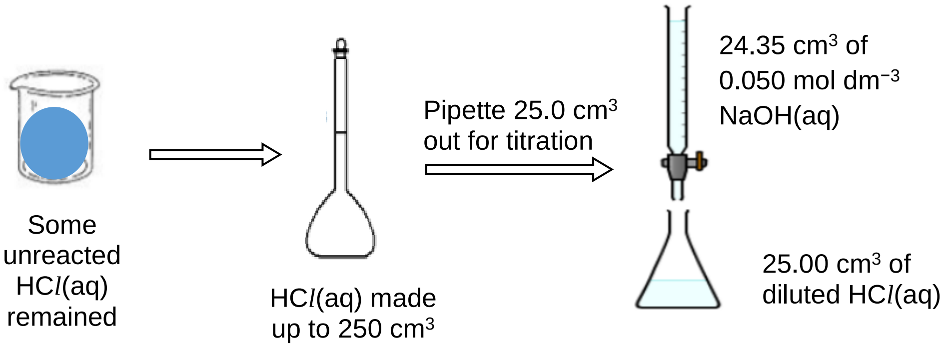
Calculate the mass of calcium carbonate in the impure sample.

Procedure 1:



Reaction 1: $2HCl + CaCO_3 \longrightarrow CaCl_2 + CO_2 + H_2O$

Procedure 2:



Reaction 2: $NaOH(aq) + HCl\,(aq) \longrightarrow NaCl(aq) + H_2O(l)$

(unreacted HC*l*)

Step 1: Find amount of acid at the <u>start</u>

$$n_{HCl} \text{ used for dissolving } CaCO_3 = \frac{25.0}{1000} \times 1.00 = 2.500 \times 10^{-2} \text{ mol}$$

Step 2: Find amount of acid at the <u>end</u>

Reaction 2: $NaOH(aq) + HCl\,(aq) \longrightarrow NaCl(aq) + H_2O(l)$

$$n_{NaOH} \text{ used} = \frac{24.35}{1000} \times 0.050 = 1.218 \times 10^{-3} \text{ mol (4 s.f.)}$$

$$\therefore n_{HCl} \text{ in } 25.0 \text{ cm}^3 \text{ solution} = 1.218 \times 10^{-3} \text{ mol (4 s.f.)}$$

$$\therefore n_{HCl} \text{ in } 250 \text{ cm}^3 \text{ solution} = \frac{250}{25.0} \times 1.218 \times 10^{-3} = 1.218 \times 10^{-2} \text{ mol (4 s.f.)}$$

Step 3: Find amount of acid <u>reacted in reaction 1</u>

$$n_{HCl} \text{ reacted in reaction 1} = 2.500 \times 10^{-2} - 1.218 \times 10^{-2} = 1.282 \times 10^{-2} \text{ mol}$$

Reaction 1: $2HCl + CaCO_3 \longrightarrow CaCl_2 + CO_2 + H_2O$

$$\therefore n_{CaCO_3} = \frac{1}{2} \times n_{HCl} \text{ reacted} = \frac{1}{2} \times 1.282 \times 10^{-2} = 6.410 \times 10^{-3} \text{ mol}$$

$$\therefore \text{mass of } CaCO_3 \text{ in sample} = 6.410 \times 10^{-3} \times [40.1 + 12.0 + 3(16.0)]$$

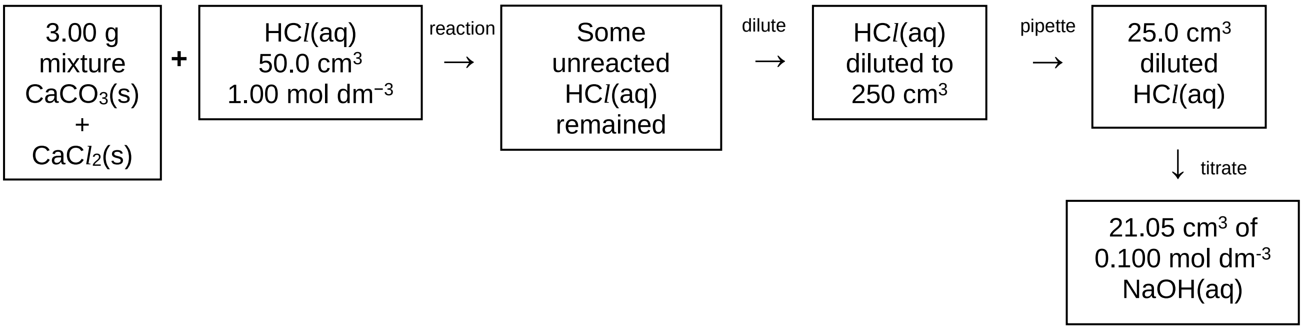
$$= \underline{0.642 \text{ g}} \text{ (3 s.f.)}$$

Checkpoint 2 (Back Titration)

A 3.00 g mixture of calcium carbonate and calcium chloride was added to 50.0 cm^3 of 1.00 mol dm^{-3} HC*l*, which was in excess. The resultant solution was made up to 250 cm^3 in a graduated flask with deionized water. 25.0 cm^3 of this solution was neutralised by 21.05 cm^3 of 0.100 mol dm^{-3} NaOH(aq).

Calculate the percentage by mass of calcium carbonate in the mixture. **[48.3%]**

[**Hint: Calculate the amount of HC*l* at the start, at the end, and hence the amount of HC*l* reacted. Remember to scale up since dilution was carried out.]



4. REDOX TITRATION

Success Criteria:

- Able to define oxidation & reduction in terms of loss/gain of electrons and the change in oxidation numbers;
- Able to determine the oxidation number of an atom in any given species, and hence deduce if oxidation/reduction has taken place;

The term 'redox' is used by chemists as an abbreviation for the processes of **red**uction and **ox**idation.

In a redox reaction, one reactant is reduced while the other is oxidised. These two processes always occur simultaneously. Redox titrations are similar to acid–base titrations, except that the reactions involve oxidising and reducing agents.

Oxidising agent: oxidises another species, while itself is reduced in the process

Reducing agent: reduces another species, while itself is oxidised in the process

4.1 Definition of Oxidation and Reduction

A gain or loss of oxygen or hydrogen is often used as an indicator of a redox reaction. At A levels, a simple observation of gain or loss of oxygen or hydrogen atom is not sufficient in determining whether a reaction is a redox reaction, instead, electron transfer (electron loss or gain) and hence a change in oxidation number is more widely used as an indicator of a redox reaction.

Note:

OIL RIG

Oxidation Is Loss of e⁻ (OIL)

Reduction Is Gain of e⁻ (RIG)

Electron Transfer & Oxidation number	Oxidation involves **loss of electrons** (hence **increase in oxidation number**) Reduction involves **gain of electrons** (hence **decrease in oxidation number)**	Example: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ Oxidising agent: Cu^{2+} Reducing agent: Zn [O]: $Zn \longrightarrow Zn^{2+} + 2e^-$ [R]: $Cu^{2+} + 2e^- \longrightarrow Cu$ Oxidation number of Zn increases from 0 in Zn to +2 in Zn^{2+}, thus Zn is oxidised. Oxidation number of Cu decreases from +2 in Cu^{2+} to 0 in Cu, thus Cu^{2+} is reduced.

4.2 Oxidation Numbers

The oxidation number or oxidation state of an atom in a substance is:

- the actual charge of the atom if it is a monoatomic ion; otherwise,
- the hypothetical charge assigned to the atom using a set of rules (refer to Table 1).
- '+' or '–' signs must be indicated clearly before the number.

Table 1: Rules for assigning oxidation number (O.N.)

<table>
<tr><th>Rule</th><th>Example / Remarks</th></tr>
<tr><td>1 For an atom in its elemental form, the oxidation number is <u>always zero</u>.</td><td>O.N. of H in hydrogen gas, H_2 = 0
O.N. of Mg in magnesium = 0
O.N. of C in diamond and graphite = 0</td></tr>
<tr><td>2 For any monoatomic ion, the O.N. <u>equals the charge</u> on the ion.
This applies to simple ionic compounds.</td><td>O.N. of K in KOH (exists as K^+) = +1
O.N. of Mg in $MgCl_2$ (exists as Mg^{2+}) = +2
O.N. of Cl $MgCl_2$ (exists as Cl^-) = −1</td></tr>
<tr><td>3 Some elements always have fixed oxidation numbers in their compounds. Some exceptions are shown.</td><td>
<table>
<tr><th></th><th>O.N. in all their compounds</th><th>Remarks / Exceptions</th></tr>
<tr><td>Group 1 metals</td><td>+1</td><td></td></tr>
<tr><td>Group 2 metals</td><td>+2</td><td></td></tr>
<tr><td>Al</td><td>+3</td><td></td></tr>
<tr><td>F</td><td>−1</td><td>F is the most electronegative element.</td></tr>
<tr><td>H</td><td>+1</td><td>0 in H_2 gas;
–1 in metal hydrides e.g. NaH</td></tr>
<tr><td>O</td><td>−2</td><td>0 in O_2 gas;
–1 in peroxides e.g. H_2O_2
–½ in superoxides e.g. NaO_2
+2 when bonded to more electronegative F in OF_2</td></tr>
</table>
</td></tr>
<tr><td>4(a) Sum of all the oxidation numbers in a neutral compound is <u>zero</u>.
(b) Sum of all the oxidation numbers in a polyatomic ion <u>equals to the charge</u> of the ion.</td><td>In $Na_2S_2O_3$, Na has O.N. +1 and O has O.N.−2.
Thus, S has an O.N. <u>+2</u> to maintain electrical neutrality in the compound.
In the carbonate ion, CO_3^{2-}, oxygen is assigned O.N. –2 as it is more electronegative than carbon.
To calculate O.N. of carbon, let O.N. of carbon be a:
$a + 3(-2) = -2$
$a = +4$
O.N of C = +4</td></tr>
<tr><td>5 In any covalent compound, the more electronegative atom is given a negative O.N.</td><td>Electronegativity increases across the period and decreases down the group.
The <u>three</u> <u>most</u> electronegative elements, in decreasing order, are: F, O and N.
O.N. of O in CO = –2
O.N. of C in CO = +2</td></tr>
</table>

Checkpoint 3

State whether each of the reactions below is a redox reaction and give your reasons.

a) $2HC\mathit{l}(aq) + Mg(s) \longrightarrow MgC\mathit{l}_2(aq) + H_2(g)$

b) $2NaOH(aq) + MgC\mathit{l}_2(aq) \longrightarrow 2NaC\mathit{l}(aq) + Mg(OH)_2(s)$

4.3 Limitations of the Oxidation Number Concept *(FYI only)*

When calculating the oxidation number of an atom of an element in a polyatomic ion or molecule, it is assumed that all the atoms of the same element have the same oxidation number. Hence the calculated oxidation number is the *average* oxidation number.

In actual fact, the oxidation number of each atom *may* differ depending on the number of the valence electrons used for bonding and the electronegativity of the atoms they are attached to.

Worked Example 4

What is the (*average*) oxidation state of S in tetrathionate ion, $S_4O_6^{2-}$?

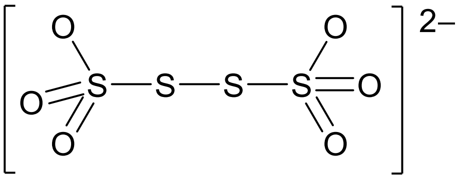
Let a = O.N. of S in $S_4O_6^{2-}$

$\therefore$ $4a + 6(-2) = -2$

$a = +2.5$

O.N. of S in $S_4O_6^{2-}$ = +2.5

The rules give each S an O.N. of +2.5. However, in actual fact, the S atoms have two different O.N. of 0 and +5.



4.4 Balancing Redox Equations

Success Criteria:

- Able to construct balanced half-equations in both acidic & alkaline medium, taking into consideration conservation of mass & balance of charges on both sides of the equation;
- Able to construct full (balanced) equations, by making use of the reduction & oxidation half equations.

All balanced equations must satisfy the following:

1. Conservation of mass, i.e. the number of atoms of each element must be the same for both reactants and products

2. Balance of charge, i.e. the sum of actual charges on the left and right sides of the equation must be equal.

4.4.1 Balancing redox equations in ACIDIC medium

Use the mnemonic to help you remember!

Elephant On High Chair

Balance the Elements
Balance the Oxygen
Balance the Hydrogen
Balance the Charge

Steps to derive half-equation in ACIDIC medium:

(1) Construct unbalanced oxidation / reduction half-equations by writing the reagent and product involved.

(2) Balance the element undergoing oxidation / reduction.

(3) Balance oxygen atoms by adding H_2O molecules.

(4) Balance hydrogen atoms by adding H^+ ions.

(5) Balance overall charges by adding electrons. (oxidation half-equations should have e^- on RHS of the equation, reduction half-equations should have e^- on LHS)

Note:

Some of the commonly used redox half equations are found inside the *Data Booklet* as the reduction half equation.

Redox half equations that are not found in the *Data Booklet*, we are to balance the half equations using this method.

Worked Example 5

Write the reduction half-equation of dichromate(VI) ions, $Cr_2O_7^{2-}$, to chromium(III) ions, Cr^{3+}, in an acidic solution.

Step 1: Construct unbalanced reduction half-equations by writing the reagent and product involved.

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

Step 2: Balance the element (Cr) undergoing reduction.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

Step 3: Balance oxygen atoms by adding H_2O molecules.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Step 4: Balance hydrogen atoms by adding H^+ ions.

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Step 5: Balance overall charges by adding electrons to the LHS.

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

4.4.2 Balancing redox equations in ALKALINE medium

Steps to derive half-equation in ALKALINE medium:

(1) – (5) Use steps 1 to 5 to get the balanced half-equations in acidic medium.

(6) Add the required number of OH^- ions to both sides of the half-equation to neutralise the H^+ ions.

(7) Combine the H^+ ions and OH^- ions on the same side to form H_2O.

(8) Simplify to get the final balanced half-equation.

Worked Example 6

Write the oxidation half-equation of iodine, I_2, to iodate(V), IO_3^-, in an alkaline solution.

Step 1: Construct unbalanced reduction half-equations by writing the reagent and product involved.

$$I_2 \longrightarrow IO_3^-$$

Step 2: Balance the element (I) undergoing oxidation.

$$I_2 \longrightarrow 2IO_3^-$$

Step 3: Balance oxygen atoms by adding H_2O molecules.

$$I_2 + 6H_2O \longrightarrow 2IO_3^-$$

Step 4: Balance hydrogen atoms by adding H^+ ions.

$$I_2 + 6H_2O \longrightarrow 2IO_3^- + 12H^+$$

Step 5: Balance overall charges by adding electrons to the RHS.

$$I_2 + 6H_2O \longrightarrow 2IO_3^- + 12H^+ + 10e^-$$

Step 6: Add the required number of OH^- ions to both sides of the half-equation to neutralise the H^+ ions.

$$I_2 + 6H_2O + 12OH^- \longrightarrow 2IO_3^- + 12H^+ + 10e^- + 12OH^-$$

Step 7: Combine the H^+ ions and OH^- ions on the same side to form H_2O.

$$I_2 + 6H_2O + 12OH^- \longrightarrow 2IO_3^- + 12H_2O + 10e^-$$

Step 8: Simplify to get the final balanced half-equation.

$$I_2 + 12OH^- \longrightarrow 2IO_3^- + 6H_2O + 10e^-$$

4.4.3 Writing Full (Balanced) Equations

The key concept in writing a full balanced equation is that:

no. of e^- lost = no. of e^- gained

(1) Write out the oxidation half-equation and reduction half-equation.

(2) Multiply the oxidation half-equation & reduction half-equation by an appropriate integer such that the no. of electrons lost = no. of electrons gained.

(3) Add both half-equations together. Simplify if necessary. Check that the overall balanced equation has no electrons.

Worked Example 7

Write a balanced equation for the reaction between iron(II) sulfate, $FeSO_4$, and potassium dichromate(VI), $K_2Cr_2O_7$, in acidic medium to give Fe^{3+} and Cr^{3+} respectively.

Step 1: **Write out the oxidation and reduction balanced half–equations.**

Oxidation: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ *(1)*

Reduction: $6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$ *(2)*

Step 2: **Multiply the oxidation half-equation & reduction half-equation by an appropriate integer such that the no. of electrons lost = no. of electrons gained.**

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ *(1)* **x 6**

$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$ *(2)* **x 1**

Step 3: **Add both half-equations together. Simplify if necessary. Check that the overall balanced equation has no electrons.**

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

On simplifying, we get:

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

Checkpoint 4

In the reaction between acidified MnO_4^- and SO_3^{2-}, MnO_4^- is reduced to Mn^{2+} and SO_3^{2-} is oxidised to SO_4^{2-}. Write the balanced equation for this reaction.

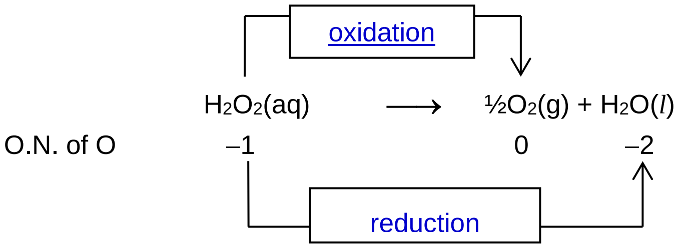
4.5 Disproportionation Reaction

Success Criteria:

- Able to define the term disproportionation;
- Able to identify, based on the change in oxidation numbers, the species undergoing reduction & oxidation simultaneously.

Disproportionation is a redox reaction where a single substance is oxidised and reduced **simultaneously**.

E.g. Spontaneous disproportionation of hydrogen peroxide, H_2O_2, to give oxygen and water



O.N. of O increases from –1 in H_2O_2 to 0 in O_2. Thus H_2O_2 is oxidised.

O.N. of O decreases from –1 in H_2O_2 to –2 in H_2O. Thus H_2O_2 is reduced.

Checkpoint 5

Explain in terms of change in oxidation number why the following unbalanced equation represents a disproportionation reaction. Fill in the coefficients to balance the equation.

$$MnO_4^{2-}(aq) + H^+(aq) \longrightarrow MnO_4^-(aq) + MnO_2(s) + H_2O(l)$$

4.6 Manganate(VII) Titrations

Success Criteria:

- Able to state the observations (colour changes) when performing titrations involving the use of manganate(VII);
- Able to write/construct balanced redox equations by making use of the half-equations;
- Able to perform calculations, using mole concept involving volumes and concentrations of solutions; including scaling up when dilution is performed.

The table below shows some examples of oxidizing and reducing agents. Potassium manganate(VII), $KMnO_4$, is a strong oxidizing agent and is commonly used in redox titrations with other reducing agents.

oxidising agent (O.A.)	reducing agent (R.A.)
manganate(VII) in acidic medium: $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ purple colourless manganate(VII) in alkaline medium: $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ brown/black solid	iron(II): $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ pale green yellow
dichromate(VII) in acidic medium: $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ Orange green	ethanedioate: $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$
Iodine: $I_2 + 2e^- \longrightarrow 2I^-$	thiosulfate: $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$
hydrogen peroxide in acidic medium: $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	hydrogen peroxide: $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$
iodate(V) in acidic medium: $2IO_3^- + 12H^+ + 10e^- \longrightarrow I_2 + 6H_2O$	iodide: $2I^- \longrightarrow I_2 + 2e^-$

Note:
H_2O_2 can act as either an O.A. or a R.A.

Selection of appropriate acid medium for redox titration

Titrations are usually carried out in acidic medium using dilute sulfuric acid. Nitric acid and hydrochloric acid are not used because:

- nitric acid is an oxidising agent itself.
- chloride ions can be oxidised to chlorine by strong oxidizing agents such as potassium manganate(VII):
  $2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 4H_2O + 5Cl_2$

These will affect the accuracy of the titration results.

Indicator and End-point

Manganate(VII) ion, MnO_4^-, is deep purple in colour, while its reduced form, Mn^{2+} ion, is faint pink or colourless in dilute solution. Hence, MnO_4^- can act as its own indicator due to its drastic change in colour before and after reaction.

Change in colour at the end-point depends on whether

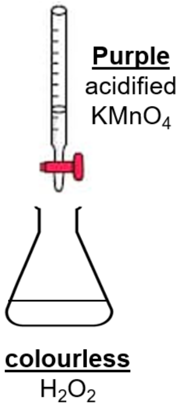
- **(i)** the other reactant is colourless;
- **(ii)** the other reactant is also coloured (e.g. a transition metal cation);
- **(iii)** $KMnO_4$ is in the conical flask or burette during titration.

Example:

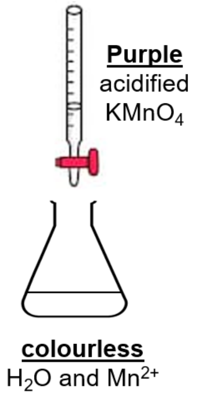
Species in conical flask	Species in burette	Expected colour change at the end-point
$KMnO_4$ (purple)	H_2O_2	purple to colourless
H_2O_2 (colourless)	$KMnO_4$	colourless to first permanent pink
$KMnO_4$ (purple)	Fe^{2+}	purple to yellow (due to Fe^{3+} formed)
Fe^{2+} (pale green)	$KMnO_4$	Pale green to first permanent pink

For example, $5H_2O_2 + 2MnO_4^- + 6H^+ \longrightarrow 5O_2 + 2Mn^{2+} + 4H_2O$

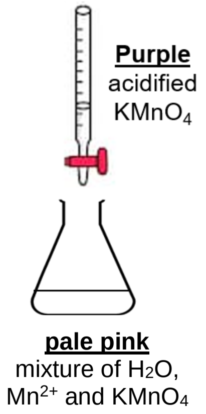
Note:
For a titration result to be accurate, the **end-point** must be close to the **equivalence point**.



No $KMnO_4$ added



At **equivalence point**
($KMnO_4$ added is completely converted to colourless Mn^{2+})



At **end−point**
1 excess drop of purple $KMnO_4$ causes the first permanent pale pink to form

Titration of $C_2O_4^{2-}$ with MnO_4^-

When 2 different ions of the same charge are to react, the reaction tends to be slow and not instantaneous at room temperature due to repulsion between the like charges, hence resulting in the reaction having a high activation energy.

Hence, such titrations are often carried out at higher temperatures, e.g. 60 °C. Otherwise, the end-point will be reached earlier mistakenly, i.e., volume of $KMnO_4$ solution used will be lower than the actual volume required to reach the real end-point.

Worked Example 8 (Redox Titration)

25.0 cm^3 of 0.100 mol dm^{-3} $Fe^{2+}(aq)$ reacted with 26.80 cm^3 of $KMnO_4(aq)$ in excess sulfuric acid. Calculate the concentration of $KMnO_4$ in mol dm^{-3}.

Half-equations: **[R]:** $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

[O]: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

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

$$n_{Fe^{2+}} \text{ in } 25.0\text{ cm}^3 = 0.100 \times \frac{25.0}{1000} = 2.500 \times 10^{-3}\text{ mol (4 s.f.)}$$

$$\therefore\ n_{MnO_4^-} \text{ in } 26.80\text{ cm}^3 = \frac{1}{5} \times n_{Fe^{2+}} = \frac{1}{5} \times 2.500 \times 10^{-3} = 5.000 \times 10^{-4}\text{ mol}$$

$$[KMnO_4] = \frac{5.000 \times 10^{-4}}{(^{26.80}/_{1000})} = 1.866 \times 10^{-2}$$

$$= \underline{1.87 \times 10^{-2}\text{ mol dm}^{-3}}$$

Worked Example 9 (Redox Titration)

50.00 cm^3 of 0.020 mol dm^{-3} acidified Fe^{2+} is oxidised to Fe^{3+} by 25.0 cm^3 of 0.020 mol dm^{-3} of an oxidising agent, **X**O_3^-.
What is the oxidation number of **X** in the resultant solution?

$$\text{Amount of } Fe^{2+} = \frac{50.0}{1000} \times 0.020 = 1.00 \times 10^{-3}\text{ mol}$$

$$\text{Amount of } XO_3^- = \frac{25.0}{1000} \times 0.020 = 5.00 \times 10^{-4}\text{ mol}$$

[O]: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

During oxidation, 1.00×10^{-3} mol of Fe^{2+} lost 1.00×10^{-3} mol of e^-

During reduction, 5.00×10^{-4} mol of XO_3^- gained 1.00×10^{-3} mol of e^-

$\therefore$ 1 mol of XO_3^- gained 2 mol of e^-

O.N. of X in XO_3^- = +5

During reduction, oxidation number of X <u>decreases</u> by <u>2</u> units from <u>+5</u> to <u>+3</u>.

Checkpoint 6 (Redox Titration)

Fe^{2+} reacts with acidified dichromate(VI) according to the half-equations:

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

[R] $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

25.0 cm^3 of iron(II) sulfate solution, acidified with excess dilute sulfuric acid, reacted with 20.00 cm^3 of 0.25 mol dm^{-3} potassium dichromate(VI) solution.

Calculate

(a) the concentration, in g dm^{-3}, of Fe^{2+} in iron(II) sulfate;
*(**Hint: construct balanced overall equation first)*

[67.0]

(b) the number of moles of Cr^{3+} ions produced in the titration.

[0.0100 mol]

4.7 Iodine-thiosulfate Titrations (Iodometric)

Success Criteria:

- Able to understand how iodine-thiosulfate titrations are used to determine the concentrations of other stronger oxidizing agents;
- Able to understand why starch solution is not added at the start of the iodine-thiosulfate titration;
- Able to write balanced equation involving iodine & thiosulfate;
- Able to perform calculations, using mole concept involving volumes and concentrations of solutions; including scaling up when dilution is performed.

Note:
The redox half equations for $S_2O_3^{2-}$ and I_2 can be obtained from the *Data Booklet*.

Iodine, I_2 is often used to oxidise thiosulfate ion, $S_2O_3^{2-}$, to tetrathionate ion, $S_4O_6^{2-}$, according to the following equation, forming colourless products:

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

This reaction is used to analyse the concentrations of other **stronger** oxidising agents (O.A.) that cannot undergo direct titration.

It involves the following 2 steps:

Step 1: Add excess KI solution to the O.A. to ensure all O.A. has reacted, oxidizing iodide ions into iodine:

$$\text{O.A.} + 2I^- \longrightarrow I_2 + \ldots$$

Step 2: Titrate the I_2 formed with $Na_2S_2O_3$(aq), using starch as indicator.

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

Since amount of O.A. is directly proportional to the amount of I_2, the amount of I_2 can then be used to calculate the amount of O.A.

This table shows some common oxidising agents where their concentrations can be determined through iodometric titration.

Oxidising Agent	Reaction with I^-
Cl_2	$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$
Br_2	$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$
IO_3^-	$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$
MnO_4^-	$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 5I_2 + 8H_2O + 2Mn^{2+}$
Cu^{2+}	$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$

Note:
Some time after the titration is completed, the blue-black colour may be observed again due to oxidation of iodide to iodine in the reaction mixture, which combines with starch to form the blue-black complex. This should be ignored.

Indicator and end-point

- Starch solution is used as the indicator for the titration of I_2 with $Na_2S_2O_3$.
- Starch indicator reacts with I_2 molecules to form a blue-black coloured iodine-starch complex. When the *end-point is reached,* the blue-black colour is discharged as all the iodine has reacted with $Na_2S_2O_3$.
- Unlike typical titrations where indicator is added at the start, starch indicator is **only added when the solution turns pale yellow** (low concentration of iodine). This is to prevent the formation of an insoluble starch-iodine complex (when in high concentration of iodine), which could lead to an inaccurate titre value.

Worked Example 10 (Redox Titration)

25.0 cm^3 of aqueous potassium iodate(V), KIO_3, reacts with excess acidified potassium iodide, KI, according to the following equation.

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

The iodine produced required 18.00 cm^3 of sodium thiosulfate solution for complete reaction. The sodium thiosulfate solution contains 24.82 g $Na_2S_2O_3{\cdot}5H_2O$ per dm^3 of solution.

Calculate the concentration of aqueous KIO_3 in mol dm^{-3}.

M_r of $Na_2S_2O_3{\cdot}5H_2O$ = 248.2

$[S_2O_3^{2-}] = \dfrac{24.82}{248.2} = 0.100$ mol dm^{-3}

Amount of $S_2O_3^{2-}$ reacted with $I_2 = \dfrac{18.00}{1000} \times 0.100 = 1.800 \times 10^{-3}$ mol

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

$n_{I_2} = \dfrac{1}{2} \times n_{S_2O_3^{2-}} = \dfrac{1}{2} \times 1.800 \times 10^{-3} = 9.000 \times 10^{-4}$ mol (4 s.f.)

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

$\therefore n_{IO_3^-} = \dfrac{1}{3} \times n_{I_2} = \dfrac{1}{3} \times 9.000 \times 10^{-4} = 3.000 \times 10^{-4}$ mol (4 s.f.)

$[IO_3^-] = [KIO_3] = \dfrac{3.000 \times 10^{-4}}{(^{25.0}/_{1000})} = 1.20 \times 10^{-2}$ mol dm^{-3}

Alternative method:

Equations for reactions involved:

Reaction 1 : $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

Reaction 2 : $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

$IO_3^- \equiv 3I_2 \equiv 6S_2O_3^{2-}$

Amount of IO_3^- used $= \dfrac{1}{6} \times$ amount of $S_2O_3^{2-}$

$= \dfrac{1}{6} \times 0.100 \times \dfrac{18.00}{1000}$

$= 3.000 \times 10^{-4}$ mol

$[IO_3^-] = [KIO_3] = \dfrac{3.000 \times 10^{-4}}{(^{25.0}/_{1000})} = 1.20 \times 10^{-2}$ mol dm^{-3}

Checkpoint 7 (Redox Titration)

A solution contained 15.60 g dm^{-3} of a metal chromate(VI), **M**CrO_4. 10.0 cm^3 of this solution was added to excess acidified potassium iodide. Chromate(VI) ions react with iodide ions according to the equation:

$$2CrO_4^{2-} + 16H^+ + 6I^- \longrightarrow 3I_2 + 8H_2O + 2Cr^{3+}$$

The iodine produced was titrated with a thiosulfate solution. 30.00 cm^3 of the thiosulfate solution containing 11.2 g of $S_2O_3^{2-}$ per dm^3 was used.
Calculate the relative atomic mass of **M** and identify **M**.

[40.3 , Ca]

	Success Criteria	Relevant Tutorial Qns	What do you still struggle with? Write your queries here.
	I am able to:		
(a)	State the observations (colour changes at end-point) when performing titrations using 1) common indicators; namely methyl orange & phenolphthalein 2) starch indicator 3) manganate(VII)		
(b)	Define the terms *oxidation, reduction* & *disproportionation* in terms of - loss / gain of electrons - increase / decrease in oxidation number		
(c)	Determine the oxidation number of an atom 1) in its elemental form 2) in a neutral molecule 3) in a monoatomic / polyatomic ion	**DQ11**	
(d)	Construct balanced half-equations, by balancing element, oxygen, hydrogen & charge on both sides of the equation, in both acidic & alkaline medium.	**DQ14, 15**	
(e)	Use half-equations to construct a full balanced equation, ensuring that it is electronically balanced.	**DQ8, 10, 12, 16**	
(f)	Read & analyse the given information in a question & hence be able to: 1) write relevant equations for the reactions involved 2) perform relevant calculations using mole concept, taking into account mole ratio of species & dilution factor (if any) 3) present the answers for intermediate steps correct to 4 significant figures 4) present the final answer to 3 significant figures unless instructed otherwise 5) include relevant units	**DQ1 - 13**	

(A) Discussion Questions (Volumetric Analysis)

Acid-Base Titration

1. 45 cm^3 of concentrated aqueous NH_3 was diluted to 250 cm^3 solution labelled as **FA 1**. Given that 10.0 cm^3 of **FA 1** required 23.20 cm^3 of 0.18 mol dm^{-3} of HNO_3 for complete neutralisation, calculate the concentration of the concentrated aqueous NH_3.

[2.32 mol dm^{-3}]

2. A solution of a dibasic acid contains 7.30 g dm^{-3} of $HOOC–(CH_2)_n–COOH$. 20.0 cm^3 of this acid solution was titrated with 25.00 cm^3 of NaOH(aq) containing 1.36 g of hydroxide ion per dm^3. Calculate

(a) the relative molecular mass of the acid; [146.0]

(b) the value of ***n*** in the formula. [4]

3. **FA 8** solution contains 20.2 g of the acid $H\mathbf{Z}O_4$ per dm^3 of solution.
FA 9 is a 0.100 mol dm^{-3} NaOH solution. In a titration, 20.0 cm^3 of **FA 8** solution reacted with 21.05 cm^3 of **FA 9** solution. Calculate the relative atomic mass of element **Z** and identify **Z**.

[126.9; I]

4. Washing soda has the formula $Na_2CO_3{\cdot}nH_2O$. 1.43 g of washing soda was made up to 250 cm^3 with water. 25.0 cm^3 of this solution was neutralised by 20.00 cm^3 of 0.050 mol dm^{-3} dilute hydrochloric acid. The equation for the reaction is:

$$Na_2CO_3(aq) + 2HCl\,(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Find the value of *n*, and hence the chemical formula of the washing soda.
[The dissolution of washing soda in water: $Na_2CO_3{\cdot}nH_2O(s) \longrightarrow Na_2CO_3(aq) + nH_2O(l)$]

[$n = 10$]

Back Titration

5. 3.92 g of an oxide of formula **M**O was completely dissolved in 30.0 cm^3 of 2.00 mol dm^{-3} sulfuric acid. The resulting solution was made up to 100 cm^3. 25.0 cm^3 of this solution was neutralised by 27.50 cm^3 of 0.10 mol dm^{-3} NaOH(aq).
What is the relative atomic mass of **M**? Identify the metal.

[55.9; Fe]

6. 5.00 g of ammonium chloride contaminated with sodium chloride was boiled with 100.0 cm^3 of 2 mol dm^{-3} NaOH solution until no ammonia was evolved. The residual solution was made up to 250 cm^3 with water. 25.0 cm^3 of this solution required 22.40 cm^3 of 0.50 mol dm^{-3} HC*l* for neutralisation.

(a) What was the mass of sodium chloride in the ammonium chloride sample? [0.292 g]

(b) Hence, calculate the percentage by mass of sodium chloride in the ammonium chloride sample.
[5.84%]

Redox Titration

7. **FA 4** contains 10.0 g of Fe^{2+} and Fe^{3+}, dissolved in 500 cm^3 of solution. **FA 5** contains 0.015 mol dm^{-3} $KMnO_4$.

In an experiment, 10.0 cm^3 of solution of **FA 4** was pipetted into a titration flask. Excess dilute sulfuric acid was added and the mixture titrated with **FA 5**. 26.65 cm^3 of **FA 5** was required to reach end-point.

(a) Calculate the mass of Fe^{2+} in 500 cm^3 of **FA 4**. [5.58 g]

(b) Calculate the percentage by mass of Fe^{3+} ions in **FA 4**. [44.2 %]

8. Chlorate(V) ions, ClO_3^-, act as an oxidising agent according to the following half-equation:

$$ClO_3^- + 6H^+ + 6e^- \longrightarrow Cl^- + 3H_2O$$

(a) Chlorate(V) ions are reduced by Fe^{2+} ions. Write a balanced equation for the reaction between Fe^{2+} and ClO_3^-.
[Hint: Write the half equation for Fe^{2+} oxidized to Fe^{3+} before combining the 2 half-equations]

(b) In an experiment, 25.0 cm^3 of a solution of $KClO_3$ was titrated with a solution of iron(II) sulfate containing 6.72 g dm^{-3} of Fe^{2+}. In the titration, 20.0 cm^3 of iron(II) sulfate was used for the reaction.

(i) What other chemical is required for the titration? Suggest a reactant that can be added to the reaction mixture for the titration.

(ii) Calculate the concentration of $KClO_3$ in mol dm^{-3}. [0.0161 mol dm^{-3}]

(iii) Calculate the mass of potassium in 1 dm^3 of the $KClO_3$ solution. [0.630 g]

9. **FA 2** is a solution containing 6.70 g dm^{-3} of a metal ethanedioate, $\mathbf{M}_2C_2O_4$.
FA 3 is a solution containing 0.010 mol dm^{-3} of manganate(VII) ions, MnO_4^-.
10.0 cm^3 of **FA 2** was pipetted into a conical flask and dilute sulfuric acid was added in excess. The mixture was then titrated with **FA 3** and the end-point was reached when 20.00 cm^3 of **FA 3** had been added.

(a) **(i)** How do you know when the end-point was reached?

(ii) What other condition was required for the titration to be successful?

(b) Calculate the relative formula mass of $\mathbf{M}_2C_2O_4$ and the relative atomic mass of **M**.
[134.0; 23.0]

10. Hydroxylamine, NH_2OH, can be oxidised to nitrogen according to the following half-equation:

$$2NH_2OH \longrightarrow N_2 + 2H_2O + 2H^+ + 2e^-$$

Hydroxylamine can also be oxidised to dinitrogen oxide, N_2O, according to the following half-equation:

$$2NH_2OH \longrightarrow N_2O + H_2O + 4H^+ + 4e^-$$

(a) In an experiment, 40.00 cm^3 of 0.05 mol dm^{-3} NH_2OH(aq) was reacted with 10.0 cm^3 of 0.40 mol dm^{-3} Fe^{3+}(aq). In the reaction, the Fe^{3+} was reduced to Fe^{2+}. Calculate the amount of Fe^{3+} that reacted with 1 mole of NH_2OH.

[2 mol]

(b) Hence deduce whether the NH_2OH is oxidised to N_2 or N_2O by the Fe^{3+} and write a balanced ionic equation for the reaction.

11. A solution of vanadium ions, VO_2^+(aq) is blue. The VO_2^+(aq) are reduced by zinc powder and acid to violet V^{z+}(aq) ions.

(a) What is the oxidation number of the vanadium in VO_2^+? [+5]

(b) The V^{z+}(aq) can be oxidised quantitatively to VO_2^+(aq) by acidified MnO_4^-(aq). It was found experimentally that 20.0 cm^3 of 0.10 mol dm^{-3} V^{z+}(aq) reacted with 24.00 cm^3 of 0.050 mol dm^{-3} MnO_4^-(aq).

(i) Calculate the number of moles of V^{z+}(aq) that react with 1 mol of acidified MnO_4^-(aq).

[$\frac{5}{3}$ mol]

(ii) Hence deduce the number of moles of electrons transferred per mole of V^{z+}(aq) in the reaction and value of **z** on V^{z+}. [z = 2]

12. A 25.0 cm^3 sample of 0.0210 mol dm^{-3} potassium peroxodisulfate(VI),$K_2S_2O_8$, was treated with an excess of potassium iodide. The iodine liberated reacted with 21.00 cm^3 of 0.0500 mol dm^{-3} thiosulfate.

(a) Calculate the amount of $S_2O_8^{2-}$ used. [5.25×10^{-4} mol]

(b) Calculate the amount of I^- that reacted with 1 mol of $S_2O_8^{2-}$. [2 mol]

(c) Suggest a likely equation for the reaction between $K_2S_2O_8$ and KI, given that $S_2O_8^{2-}$ is reduced to SO_4^{2-}.

13. A solution contained 5.53 g dm^{-3} of a metal iodate(VII), **M**IO_4. 25.0 cm^3 of the solution was added to excess acidified potassium iodide. The iodate(VII) ions reacted with the iodide according to the following equation:

$$IO_4^- + 7I^- + 8H^+ \longrightarrow 4I_2 + 4H_2O$$

The iodine liberated was then titrated with 0.120 mol dm^{-3} $S_2O_3^{2-}$, where starch was added only when the solution turned pale yellow. It was found that 33.30 cm^3 of $S_2O_3^{2-}$ was required for the dark-blue colour to be discharged.

(a) Explain why it is necessary for the potassium iodide to be added in excess.

(b) Why was the starch indicator not added at the beginning of the titration of iodine with thiosulfate?

(c) Calculate the relative atomic mass of element **M**. Suggest the identity of **M**. [85.9; Rb]

(B) Discussion Questions (Redox Practice)

14. Nitrogen dioxide reacts with iodine under acidic conditions according to the equation shown.

$$NO_2 + 2I^- + 2H^+ \longrightarrow NO + I_2 + H_2O$$

How many moles of electrons are gained by one mole of the nitrogen dioxide?

A 1 **B** 2 **C** 3 **D** 4

15. Write the half–equations and balance them in the respective mediums.

(a) $As_2O_3(s) + VO_2^+(aq) \longrightarrow As_2O_5(s) + VO^{2+}(aq)$ (in acidic medium)

(b) $H_2O_2(aq) + Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + H_2O(l)$ (in acidic medium)

(c) $Cl_2(aq) \longrightarrow Cl^-(aq) + ClO_3^-(aq)$ (in alkaline medium)

(d) $MnO_4^{2-}(aq) \longrightarrow MnO_2(s) + MnO_4^-(aq)$ (in alkaline medium)

16. Write the half–equations and hence the full balanced equation for each reaction below.

(a) Sodium sulfite, Na_2SO_3, reduces an orange acidified solution of dichromate(VI) ions, $Cr_2O_7^{2-}$, to green solution containing Cr^{3+} ions. Sulfate ions are formed in the reaction.

(b) When copper is added to concentrated nitric acid, the solution becomes pale blue due to $Cu^{2+}(aq)$, and brown fumes of nitrogen dioxide are produced.

(c) When potassium iodide (KI) is added to acidified hydrogen peroxide, brown I_2 solution is formed.

(d) When heated, phosphorus acid, H_3PO_3, gives phosphoric acid, H_3PO_4, and phosphine gas, PH_3.

(e) When zinc is added to silver nitrate solution, $AgNO_3(aq)$, silver solid forms on the surface of zinc. Zn^{2+} ions are formed.