Raffles Institution
Year 5 H2 Chemistry 2022
Lecture Notes 1b – Redox Reactions

Content

- Redox processes: electron transfer and changes in oxidation number (oxidation state)

Learning Outcomes

Candidates should be able to:

(a) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)

(b) construct redox equations using the relevant half-equations

Lecture Outline

1 Redox Reactions

2 Balancing Redox Equations

3 Redox Titrations

References

Similar to those in Lecture Notes 1a

1 Redox Reactions

- The term "redox" is used as an abbreviation for the processes of reduction and oxidation which occur simultaneously. A redox reaction is an oxidation-reduction reaction.

1.1. Definitions of oxidation and reduction

- There are different ways to define oxidation and reduction. *The focus will be on (c) and (d).*

(a)	loss/gain of oxygen	• Oxidation involves gain of oxygen. • Reduction involves loss of oxygen. oxidation • Example: $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$ reduction
(b)	loss/gain of hydrogen	• Oxidation involves loss of hydrogen. • Reduction involves gain of hydrogen. • Oxidation of ethanol to ethanal: $CH_3CH_2OH \longrightarrow CH_3CHO$ • Reduction of ethanal to ethanol: $CH_3CHO \longrightarrow CH_3CH_2OH$
(c)	loss/gain of electrons	• Oxidation involves loss of electron(s). • Reduction involves gain of electron(s). oxidation • Example: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ reduction **OIL RIG** **o**xidation **i**nvolves **l**oss of e^- **r**eduction **i**nvolves **g**ain of e^-
(d)	increase/decrease in oxidation number	• Oxidation involves an increase in oxidation number. • Reduction involves a decrease in oxidation number. oxidation • Example: $\overset{0}{C} + \overset{0}{O_2} \longrightarrow \overset{+4}{C}\overset{-2}{O_2}$ reduction

- An oxidising agent (electron acceptor) oxidises the other reagent while it undergoes reduction by receiving the electrons lost by the oxidised species, i.e. an Oxidising Agent is itself Reduced.

- A reducing agent (electron donor) reduces the other reagent while it undergoes oxidation by giving electrons to cause the reduction, i.e. a Reducing Agent is itself Oxidised.

1.2. Redox processes in terms of electron transfer

- Consider the reaction between zinc metal and copper(II) sulfate solution.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

Or

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

- The overall reaction can be separated into two simpler processes involving electron transfer.

Oxidation half-equation:	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Reduction half-equation:	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Overall equation:	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

- The two separate equations can be termed ion-electron equations, but they are more commonly known as half-equations.

- One half-equation represents the oxidation process while the other represents the reduction process. Addition of the two half-equations gives the overall redox equation.

- In the above redox reaction,
  - Zn acts as a reducing agent. It loses two electrons, and as a result, is itself oxidised to Zn^{2+}.
  - Cu^{2+} acts as an oxidising agent. It gains two electrons, and as a result, is itself reduced to Cu.

Total amount of electrons lost by 1 mol of Zn = Total amount of electrons gained by 1 mol of Cu^{2+}

- In a redox reaction involving electron transfer, the total number of electrons transferred is the same for both half-equations. In other words,

Total number of electrons lost by the reducing agent = Total number of electrons gained by the oxidising agent

- Another example: $2Ag^+(aq) + Fe(s) \rightarrow 2Ag(s) + Fe^{2+}(aq)$

Oxidation half-equation:	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Reduction half-equation:	$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

In this case,

- 1 mol of Fe reacts with 2 mol of Ag^+.
- Total amount of electrons transferred in each half-equation = 2 mol

Note:

Total amount of electrons lost by 1 mol of Fe = Total amount of electrons gained by 2 mol of Ag^+

1.3. Redox processes in terms of change in oxidation number

(a) Oxidation number

- An oxidation number is a number which is assigned to an element in a substance to show its state of oxidation.
  Note: The oxidation number of an element in a substance is related to the number of electrons lost, gained, or shared as a result of chemical bonding.

- An atom is oxidised if its oxidation number increases.
  An atom is reduced if its oxidation number decreases.

- Oxidation occurs when the oxidation number of an atom increases.
  Reduction occurs when the oxidation number of an atom decreases.

(b) Rules for assigning oxidation numbers

- The oxidation number of an atom in the **elemental state** is 0.
  Examples: Oxidation number of oxygen in O_2 is 0.
  Oxidation number of phosphorus in P_4 is 0.

- The oxidation number of **hydrogen** in all compounds, except metal hydrides, is +1.
  In metal hydrides (e.g. NaH, MgH_2), the oxidation number of hydrogen is –1.

- The oxidation number of **fluorine** in all compounds is –1.

- The oxidation number of **oxygen** is –2 in all compounds, except in peroxides, superoxides and OF_2.

  In peroxides (e.g. Na_2O_2), the oxidation number of oxygen is –1.
  In superoxides (e.g. KO_2), the oxidation number of oxygen is –½.
  In OF_2, the oxidation number of oxygen is +2.

- In any compound, the more electronegative atom has the negative oxidation number while the less electronegative atom has the positive oxidation number.
  Example: For $BrCl$, the oxidation number of Br is +1 and the oxidation number of Cl is –1.
    - The **electronegativity** of an atom is the ability of the atom in a molecule to attract shared electrons in a bond.
    - Electronegativity *generally* increases across a period and decreases down a group.
    - To search for electronegativity values, visit: *http://www.rsc.org/periodic-table/trends*

- In **monatomic ions**, the oxidation number is simply the charge on the ion.
  Examples: Oxidation number of Na in Na^+ is +1
  Oxidation number of Cl in Cl^- is –1

- In **polyatomic ions**, the algebraic sum of the oxidation numbers equals the charge on the ion.
  Example: For MnO_4^-, $(+7) + (4)(-2) = -1$

- In a **compound** (e.g. CO_2, $NaCl$, $AlCl_3$), the algebraic sum of the oxidation numbers of the atoms is 0.
  Examples: For CO_2, $(+4) + (2)(-2) = 0$
  For $NaCl$, $(+1) + (-1) = 0$

Note: Oxidation number of Mg in Mg^{2+} = +2 (the "+" sign precedes the number "2")
Charge on Mg^{2+} ion = 2+ (the "+" sign is written after the number "2")

The oxidation number of Mg in $MgSO_4$ is +2.
Mg exists in an oxidation state of +2 or displays an oxidation state of +2 in $MgSO_4$.

Worked Example 1

What is the oxidation number of uranium (symbol: U) in K_3UF_6?

Solution

Let the oxidation number of U in K_3UF_6 be n.

$$(3)(+1) + n + (6)(-1) = 0$$
$$n = +3$$

Hence oxidation number of U is +3.

Worked Example 2

An element can exhibit different oxidation states in different compounds. Determine the oxidation number of

(a) nitrogen in

NH_3	N_2H_4	N_2O	NO	NF_3	NO_2	N_2O_5
−3	−2	+1	+2	+3	+4	+5

(b) chlorine in

Cl_2O_7	ClO_3	$NaClO_3$	ClO_2	$KClO_2$	Cl_2O	Cl_2	$NaCl$
+7	+6	+5	+4	+3	+1	0	−1

Exercise

(this question is part of Redox Reactions Quiz 1 on IVY)

An element can exhibit different oxidation states in different compounds. Determine the oxidation number of sulfur in:

H_2S	SO_3	SO_3^{2-}	SCl_2	H_2SO_3	H_2SO_4
−2	+6	+4	+2	+4	+6

(c) Oxidation numbers of atoms in complicated structures

- In complicated molecules or ions, it is helpful to deduce the oxidation states of the elements based on the structures. We will revisit this method in topic on 'Introduction to Organic Chemistry'.

(d) Examples of redox reactions

- In general, to decide whether a reaction is a redox reaction, assign oxidation numbers to the atoms in the reactants and products, and check for any changes in oxidation numbers.

  The following are examples of redox reactions.

$$2\overset{+1}{H}Cl(aq) + \overset{0}{Mg}(s) \rightarrow \overset{+2}{Mg}Cl_2(aq) + \overset{0}{H_2}(g)$$

$$2\overset{0}{Fe}(s) + 3\overset{0}{Cl_2}(g) \rightarrow 2\overset{+3}{Fe}\overset{-1}{Cl_3}(s)$$

$$\overset{0}{Ca}(s) + 2\overset{+1}{H_2}O(l) \rightarrow \overset{+2}{Ca}(OH)_2(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Cl_2}(aq) + 2\overset{-1}{Br^-}(aq) \rightarrow \overset{0}{Br_2}(aq) + 2\overset{-1}{Cl^-}(aq)$$

Note: In a redox reaction, $\boxed{\text{total increase in oxidation number}} = \boxed{\text{total decrease in oxidation number}}$

(e) Disproportionation reactions

- Definition:

  > A disproportionation reaction is a redox reaction in which the <u>same element in a substance is simultaneously oxidised and reduced</u>.

- Examples: $3\overset{0}{Cl_2}(g) + 6OH^-(aq) \rightarrow 5\overset{-1}{Cl^-}(aq) + \overset{+5}{Cl}O_3^-(aq) + 3H_2O(l)$

  $2H_2\overset{-1}{O_2}(aq) \rightarrow 2H_2\overset{-2}{O}(l) + \overset{0}{O_2}(g)$

(f) Non-redox reactions

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	**Note:** There is no change in oxidation number of any atom during such reactions.

- All balanced equations must satisfy two criteria:
  1. There must be mass balance.
     ⇒ The same number of atoms of each kind must be shown as reactants and products.
  2. There must be charge balance.
     ⇒ The sums of actual charges on the left and right sides of the equation must be equal.

- The half-reaction method will be used to balance redox equations.

2 Balancing Redox Equations

2.1. Balancing redox equation in acidic medium

- The steps involved are:

1	Construct unbalanced oxidation and reduction half-equations by writing the reagent and product involved in each half-equation.	
	To each half-equation,	
2	Balance the **element reduced or oxidised** in each half-equation.	
3	Balance **oxygen atoms** by adding **H_2O** molecules.	Only H_2O, H^+ or e^- can be added, either as 'reactant' or 'product'.
4	Balance **hydrogen atoms** by adding **H^+** ions.	
5	Balance **overall charges** by adding **e^-**. (Check that oxidation half-eqns have e^- on RHS and reduction half-eqns have e^- on LHS.)	
6	Multiply each balanced half-equation by appropriate integers so that no. of electrons gained = no. of electrons lost.	
7	Add the 2 balanced half-equations and eliminate any common terms to obtain the overall balanced equation (with no e^-).	

Worked Example 3

Write a balanced equation for the reaction between MnO_4^- and $C_2O_4^{2-}$ in acidic medium. The products include Mn^{2+} and CO_2.

Solution

1	Construct **unbalanced half-equations.**	Oxidation half-equation: $C_2O_4^{2-} \rightarrow CO_2$ Reduction half-equation: $MnO_4^- \rightarrow Mn^{2+}$
2	Balance the **element reduced or oxidised.**	Oxidation: $C_2O_4^{2-} \rightarrow 2CO_2$ Reduction: $MnO_4^- \rightarrow Mn^{2+}$
3	Balance **O atoms** by adding H_2O molecules.	Oxidation: $C_2O_4^{2-} \rightarrow 2CO_2$ Reduction: $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
4	Balance **H atoms** by adding H^+ ions.	Oxidation: $C_2O_4^{2-} \rightarrow 2CO_2$ Reduction: $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
5	Balance **overall charges** by adding e^-.	Oxidation: $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
6	Multiply each balanced half-equation so that no. of e^- gained = no. of e^- lost.	Oxidation: $5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$ Reduction: $2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$
7	Add the 2 balanced half-equations and eliminate any common terms to obtain the overall balanced equation (Note: There should be no e^- left).	$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

2.2. Balancing redox equation in basic medium

- The steps involved are:

1 2 3 4 5	Use steps 1 – 5 to get **balanced half-equations** in acidic medium.
	Convert the already balanced half-equations to basic medium
A	"Neutralise" the H^+ ions by adding the required number of OH^- ions to **both** sides of a half-equation.
B	Combine the H^+ and OH^- ions on the same side of the equation to form H_2O.
C	Re-balance the half-equation by eliminating any common terms, such as H_2O.
6 7	Use steps 6 – 7 to combine the balanced half-equations to obtain the overall balanced equation.

Worked Example 4

Balance the following reaction: $I_2(aq) + OH^-(aq) \rightarrow IO_3^-(aq) + I^-(aq)$

Solution

	Use steps 1 – 5 to get **balanced half-equations** in acidic medium.	Oxidation half-equation: $I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$ Reduction half-equation: $I_2 + 2e^- \rightarrow 2I^-$
A	"Neutralise" the H^+ ions by adding the required number of OH^- ions to both sides of a half-equation.	Oxidation: $I_2 + 6H_2O + 12OH^- \rightarrow 2IO_3^- + 12H^+ + 10e^- + 12OH^-$ Reduction: $I_2 + 2e^- \rightarrow 2I^-$
B	Combine the H^+ and OH^- ions on the same side of the equation to form H_2O.	Oxidation: $I_2 + 6H_2O + 12OH^- \rightarrow 2IO_3^- + 12H_2O + 10e^-$ Reduction: $I_2 + 2e^- \rightarrow 2I^-$
C	Re-balance the half-equation by eliminating any common terms, such as H_2O.	Oxidation: $I_2 + 12OH^- \rightarrow 2IO_3^- + 6H_2O + 10e^-$ Reduction: $I_2 + 2e^- \rightarrow 2I^-$
6	Multiply each balanced half-equation so that no. of e^- gained = no. of e^- lost.	Oxidation: $I_2 + 12OH^- \rightarrow 2IO_3^- + 6H_2O + 10e^-$ Reduction: $5I_2 + 10e^- \rightarrow 10I^-$
7	Add the 2 balanced half-equations and eliminate any common terms to obtain the overall balanced equation (Note: There should be no e^- left).	$6I_2 + 12OH^- \rightarrow 2IO_3^- + 6H_2O + 10I^-$ or $3I_2 + 6OH^- \rightarrow IO_3^- + 3H_2O + 5I^-$

Worked Example 5

Consider the following reaction: $Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+}$

(a) Write down the balanced oxidation and reduction half-equations.

(b) Write down the overall balanced equation.

Solution

(a) Oxidation half-equation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

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

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

Worked Example 6

Consider the following reaction in basic medium: $Zn + NO_3^- \longrightarrow [Zn(OH)_4]^{2-} + NH_3$

(a) Write down the balanced oxidation and reduction half-equations.

(b) Write down the overall balanced equation.

Solution

(a) Oxidation half-equation: $Zn + 4OH^- \rightarrow [Zn(OH)_4]^{2-} + 2e^-$

Reduction half-equation: $NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$

(b) Overall equation: $4Zn + NO_3^- + 7OH^- + 6H_2O \rightarrow 4[Zn(OH)_4]^{2-} + NH_3$

2.3. Determination of oxidation number using half-equation

- In a redox reaction which involves transfer of electrons, the number of electrons transferred is related to the change in oxidation number of the atom oxidised or reduced.

- Example: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu^{2+}$

Oxidation half-equation:	$\overset{0}{Zn(s)} \rightarrow \overset{+2}{Zn^{2+}(aq)} + \overset{-2}{2e^-}$
oxidation no. of Zn in reactant = oxidation no. of Zn in Zn^{2+} + (–2)	

Reduction half-equation:	$\overset{+2}{Cu^{2+}(aq)} + \overset{-2}{2e^-} \rightarrow \overset{0}{Cu(s)}$
oxidation no. of Cu in Cu^{2+} + (–2) = oxidation no. of Cu in product	

Worked Example 7

(a) Consider the following unbalanced reduction half-equation: $MnO_4^- + 5e^- \rightarrow$ product **X**
What is the oxidation number of Mn in the manganese-containing product **X**?

(b) Consider the following unbalanced oxidation half-equation: reactant **Y** $\rightarrow PbO_2 + 2e^-$
What is the oxidation number of Pb in the lead-containing reactant **Y**?

Solution

(a) oxidation number of Mn in product **X** = oxidation number of Mn in MnO_4^- + (–5) = +7 + (–5) = +2	**(b)** oxidation number of Pb in reactant **Y** = oxidation number of Pb in PbO_2 + (–2) = +4 + (-2) = +2

Worked Example 8

In an experimental investigation of the reduction of chlorate(VII) ion (ClO_4^-) in aqueous solution, it was found that 25.0 cm³ of 0.0500 mol dm⁻³ potassium chlorate(VII) solution required 50.0 cm³ of 0.200 mol dm⁻³ aqueous titanium(III) chloride ($TiCl_3$) for complete reaction. The titanium(III) ion is oxidised to the titanium(IV) ion in this reaction.

Which of the following formulae could correctly represent the reduction product of the chlorate(VII) ion?

A Cl_2 **B** Cl^- **C** OCl^- **D** ClO_2^- **E** ClO_3^-

Solution

1	Calculate the amount of each reactant.	Amount of $ClO_4^- = (\frac{25.0}{1000})(0.0500) = 1.25 \times 10^{-3}$ mol Amount of $Ti^{3+} = (\frac{50.0}{1000})(0.200) = 1.00 \times 10^{-2}$ mol
2	Determine the molar ratio of the two reactants.	Molar ratio of ClO_4^- to Ti^{3+} = 1 : 8
3	Construct a balanced half-equation to find the total amount of electrons transferred.	$Ti^{3+} \rightarrow Ti^{4+} + e^-$ Oxidation half-equation: $8Ti^{3+} \rightarrow 8Ti^{4+} + 8e^-$ Amount of e^- lost by 8 mol of Ti^{3+} = 8 mol
4	Construct the unbalanced half-equation.	Amount of e^- gained by 1 mol of ClO_4^- = 8 mol Reduction half-equation (unbalanced): $ClO_4^- + 8e^- \rightarrow$ product
5	Calculate the unknown oxidation number.	Oxidation number of Cl in chlorine-containing product = oxidation number of Cl in ClO_4^- + (–8) = +7 – 8 = –1
6	Conclude accordingly.	**A** $\overset{0}{Cl_2}$ **B** $\overset{-1}{Cl^-}$ **C** $\overset{+1}{OCl^-}$ **D** $\overset{+3}{ClO_2^-}$ **E** $\overset{+5}{ClO_3^-}$ Hence, the reduction product is Cl^-.

Worked Example 9

In an experiment, H_2S was reacted with 24.00 cm^3 of 0.150 mol dm^{-3} of a bromine-containing ion, BrO_x^-, in acidic medium. The products formed included Br_2 and 0.289 g of sulfur, S.

What is the value of x in BrO_x^-?

Solution

$$\text{Amount of } H_2S = \text{Amount of S} = \frac{0.289}{32.1} = 9.00 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } BrO_x^- = \frac{24.00}{1000} \times 0.150 = 3.60 \times 10^{-3} \text{ mol}$$

n_{H_2S}	:	n_{e^-}	:	$n_{BrO_x^-}$
9.00×10^{-3}	:		:	3.60×10^{-3}
5	:	10	:	2
5	:	10	:	2
		5	:	1

Since

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

or $5H_2S \rightarrow 5S + 10H^+ + 10e^-$

Reduction (unbalanced): $2BrO_x^- + 10e^- \rightarrow Br_2$

or $BrO_x^- + 5e^- \rightarrow \frac{1}{2}Br_2$

Let the oxidation number of Br in BrO_x^- be n.

Then $n + (-5) = 0 \Rightarrow n = +5$

Consider the BrO_x^- ion,
balancing the oxidation numbers, $+5 + (x)(-2) = -1$

$\Rightarrow x = 3$

3 Redox Titrations

- In redox titrations, the chemical reaction involves the transfer of electrons from a reducing agent (electron donor) to an oxidising agent (electron acceptor).

- Important half-equations to take note:

Reduction

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$I_2 + 2e^- \rightarrow 2I^-$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$
$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

Oxidation

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$
$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$
$$2I^- \rightarrow I_2 + 2e^-$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

- The following types of redox titrations will be discussed:

  1. Manganate(VII) titrations
  2. Iodine-thiosulfate titrations

3.1 Manganate(VII) titrations

- Potassium manganate(VII), $KMnO_4$, is a powerful oxidising agent and is used for the estimation of a wide range of reducing agents (e.g. iron(II) salts, ethanedioates and hydrogen peroxide).

1	Reaction with Fe(II) ion	$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$
2	Reaction with ethanedioate ion	$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$
3	Reaction with H_2O_2	$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$

- In **acidic** medium, the manganate(VII) ion is reduced to **Mn^{2+}**.

$$\underset{\text{purple}}{MnO_4^-(aq) + 8H^+(aq) + 5e^-} \rightarrow \underset{\text{faint pink/colourless in dilute solutions}}{Mn^{2+}(aq) + 4H_2O(l)}$$

- H_2SO_4 is the mineral acid used to provide the acidic medium.
  - HCl is not used for such titrations as Cl^- can be oxidised by the acidified $KMnO_4$ to Cl_2;
  - HNO_3 is also not used as it is an oxidising agent.

- In **neutral or alkaline** medium, MnO_4^- ion is reduced to solid **MnO_2**.

$$\underset{\text{purple}}{MnO_4^-(aq) + 4H^+(aq) + 3e^-} \rightarrow \underset{\text{brown/black solid}}{MnO_2(s) + 2H_2O(l)}$$

- When using $KMnO_4$ for volumetric analysis, it is often difficult to read the meniscus of the solution in a burette. It is therefore recommended that the surface of the solution be used as the reference point in these titrations.

- Colour change at the end-point when performing a redox titration with acidified $KMnO_4$ placed in the burette.

Manganate(VII) titration	**Colour change at the end-point**
$KMnO_4(aq)$ and $H_2O_2(aq)$	from colourless to pale pink
$KMnO_4(aq)$ and $Fe^{2+}(aq)$	from yellow to pale orange/pink *(video of this titration is available accompanying the lecture video on IVY)*

Note: Elaboration of species responsible for the colour change will be covered in VA planning.

Worked Example 10

12.5 cm^3 of a given solution of hydrogen peroxide were diluted to 500 cm^3 with deionised water. 25.0 cm^3 of this diluted solution then required 22.50 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) solution for titration in acidic conditions.

(a) Calculate the concentration of the hydrogen peroxide solution.

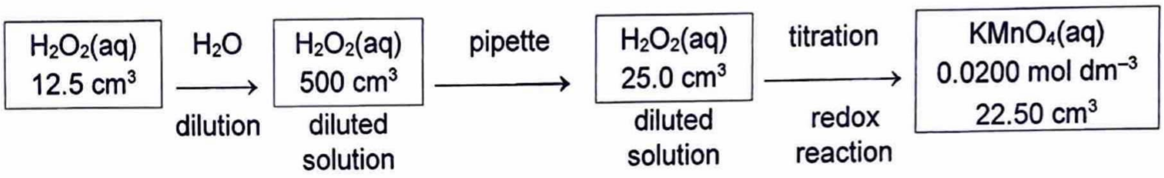
The "volume strength" of hydrogen peroxide is the number of volumes of O_2 obtained from one volume of H_2O_2 at s.t.p. based on the following disproportionation reaction:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

For example, a "20 volume" hydrogen peroxide means 1 dm^3 of H_2O_2 on decomposition produces 20 dm^3 of oxygen.

(b) Calculate the volume strength of the given hydrogen peroxide solution.

Solution



(a) $$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

Amount of MnO_4^- reacted $= \frac{22.50}{1000} \times 0.0200 = 4.50 \times 10^{-4}$ mol

Amount of H_2O_2 reacted $= \frac{5}{2} \times 4.50 \times 10^{-4} = 1.125 \times 10^{-3}$ mol

Amount of H_2O_2 in 25.0 cm^3 of diluted solution $= 1.125 \times 10^{-3}$ mol

Amount of H_2O_2 in 500 cm^3 of diluted solution $= \frac{1.125 \times 10^{-3}}{25.0} \times 500 = 0.0225$ mol

Amount of H_2O_2 in 12.5 cm^3 of original solution $= 0.0225$ mol

Hence concentration of H_2O_2 solution $= \frac{0.0225}{12.5 \times 10^{-3}} = \underline{1.80 \text{ mol dm}^{-3}}$

(b) Consider a 1 dm^3 solution of H_2O_2.

Amount of H_2O_2 in 1 dm^3 $= (1 \text{ dm}^3)(1.80 \text{ mol dm}^{-3}) = 1.80$ mol

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Amount of O_2 produced $= \frac{1}{2} \times 1.80 = 0.900$ mol

Molar volume of O_2 at s.t.p. = 22.7 dm^3 mol^{-1}

Volume of O_2 produced at s.t.p = $0.900 \times 22.7 = 20.4$ dm^3

Hence, the volume strength of hydroxide peroxide is 20.4.

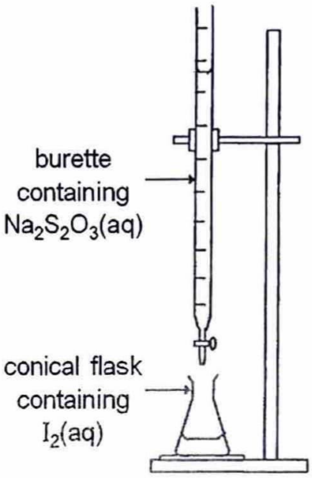
3.2 Iodine-thiosulfate titrations

- Thiosulfate acts as a reducing agent and reduces iodine to iodide as represented by the equation

Oxidation half-equation:	$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$
Reduction half-equation:	$I_2 + 2e^- \rightarrow 2I^-$
Overall equation:	$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$ colourless brown colourless colourless

- The above reaction is used for the estimation of iodine or for substances which will liberate iodine from potassium iodide. Most iodometric titrations involve two steps:

  1. A substance is normally added to acidified potassium iodide solution to liberate iodine.
  2. The liberated iodine is then estimated using standard thiosulfate solution.



- Colour change at the end-point of an iodometric titration

Iodometric titration	Colour change at the end-point with **iodine** in the conical flask	Colour change at the end-point with **iodine** and **starch indicator** placed in the conical flask
$I_2(aq)$ and $Na_2S_2O_3(aq)$	from pale yellow to colourless	from blue-black to colourless

- Starch solution is used as an indicator and is normally added when the solution is pale yellow in colour, i.e. when majority of the iodine has been reacted away. Starch solution is not added at the beginning of the titration as the iodine molecules tend to be trapped in the spiral starch molecules, leading to inaccurate results.
- Iodine in the conical flask forms a blue-black solution (starch-iodine complex) with the starch added. The titration is then continued until one drop of thiosulfate solution changes the colour of the reaction mixture from blue-black to colourless. This gives a distinct colour change and is hence preferred that starch indicator is used for iodometric titrations. The same amount of starch should be used in each titration.
- When left aside, the titrated solution may slowly become blue again. This should be ignored, as it is due to atmospheric oxidation of the iodide in the reaction mixture to give iodine, which combines with the starch to reform the blue colour.

Worked Example 11

(video of this titration is available accompanying the lecture video on IVY)

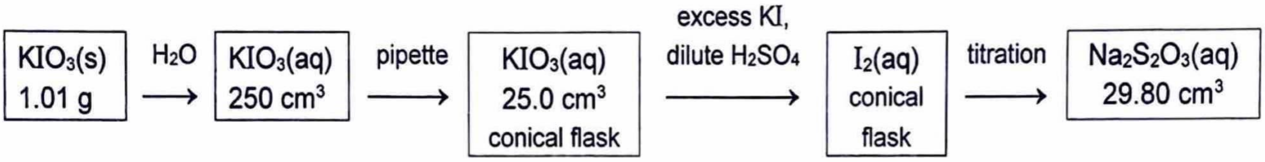
Iodate(V) ions react with iodide ions in the presence of an acid to produce iodine:

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

1.01 g of potassium iodate(V) were dissolved and made up to 250 cm³. To a 25.0 cm³ portion, an excess of potassium iodide and dilute sulfuric acid was added. The resultant solution was titrated with a solution of sodium thiosulfate, starch solution being added near the end-point. 29.80 cm³ of the sodium thiosulfate solution were required.

Calculate the concentration of the thiosulfate solution.

Solution



$$\text{Amount of } KIO_3 \text{ in 250 cm}^3 = \frac{1.01}{39.1 + 126.9 + 3 \times 16.0} = 4.720 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } IO_3^- \text{ in 25.0 cm}^3 = \frac{25.0}{250} \times 4.720 \times 10^{-3} = 4.720 \times 10^{-4} \text{ mol}$$

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

$$\text{Amount of } I_2 \text{ produced} = 3 \times \text{Amount of } IO_3^- \text{ reacted} = 3 \times 4.720 \times 10^{-4} = 1.416 \times 10^{-3} \text{ mol}$$

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

$$\text{Amount of } S_2O_3^{2-} \text{ reacted} = 2 \times \text{Amount of } I_2 \text{ produced} = 2 \times 1.416 \times 10^{-3} = 2.832 \times 10^{-3} \text{ mol}$$

Volume of $S_2O_3^{2-}$ reacted = 29.80 cm³

$$\text{Hence, } \left[S_2O_3^{2-}\right] = \frac{2.832 \times 10^{-3}}{29.80 \times 10^{-3}} = 0.0950 \text{ mol dm}^{-3}$$

Raffles Institution
Year 5 H2 Chemistry 2022
Tutorial 1b – Redox Reactions

Self-Check Questions

1 Determine the oxidation number of the underlined element in the following species:

(a) $Ba\underline{S}O_4$ **(c)** $\underline{Ti}O^{2+}$ **(e)** $H_2\underline{O}_2$ **(g)** $\underline{Br}F$

(b) $Na_3\underline{V}O_4$ **(d)** $\underline{C}_2O_4^{2-}$ **(f)** $\underline{N}_2O_4$ **(h)** $\underline{I}F_7$

2 A Level N2010/III/4(f)

Ozone is usually made by passing oxygen gas through a tube between two highly charged electrical plates.

$$3O_2(g) \rightarrow 2O_3(g)$$

The reaction does not go to completion, so a mixture of the two gases results.
The concentration of O_3 in the mixture can be determined by its reaction with aqueous KI.

$$O_3 + 2KI + H_2O \rightarrow I_2 + O_2 + 2KOH$$

The iodine formed can be estimated by its reaction with sodium thiosulfate.

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

When 500 cm^3 of an oxygen/ozone gaseous mixture at s.t.p. was passed into an excess of aqueous KI, and iodine titrated, 15.0 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$ was required to discharge the iodine colour.

(a) Calculate the amount in moles of iodine produced.

(b) Hence calculate the percentage of O_3 in the gaseous mixture.

3 A Level N2009/III/3(c)

When sodium is burned in air, a mixture of sodium oxide, Na_2O, and sodium peroxide, Na_2O_2, is formed. The mixture reacts with water according to the following equations.

$$Na_2O + H_2O \rightarrow 2NaOH$$
$$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$$

The following information will allow you to calculate the relative amounts of the two oxides produced when sodium is burned.

- The mixture obtained by burning a sample of sodium was dissolved in distilled water and made up to 100 cm^3 to give solution **H**.
- A 25.0 cm^3 portion of solution **H** was titrated with 0.100 mol dm^{-3} HCl. 22.50 cm^3 of acid was required to reach the end-point.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

- The H_2O_2 content of solution **H** was found by titration of another 25.0 cm^3 portion with 0.0200 mol dm^{-3} $KMnO_4$ in acidic medium. 10.0 cm^3 of $KMnO_4$ solution was required to reach the end-point.

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

(a) Using the results of the HCl titration, calculate the total amount of $NaOH$ in 100 cm^3 of solution **H**.

(b) Using the results of the $KMnO_4$ titration, calculate the amount of H_2O_2 in 100 cm^3 of solution **H**.

(c) Hence, calculate the amount of Na_2O and Na_2O_2 formed during the burning of the sodium sample.

Suggested solutions to the self-check questions can be found on Ivy. Please use these solutions to check through your working and your final answers. Consult your tutor if you have any questions.

Practice Questions

4 Identify if the following equations represent a redox or non-redox reaction. Determine the change in oxidation number for the relevant element to support your answer.

(a) $2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$

(b) $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

(c) $3Mg(s) + 2NH_3(g) \rightarrow Mg_3N_2(s) + 3H_2(g)$

(d) $2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$

(e) $Cu_2O(s) + H_2SO_4(aq) \rightarrow Cu(s) + CuSO_4(aq) + H_2O(l)$

(f) $2CH_4(g) + 2NH_3(g) + 3O_2(g) \rightarrow 2HCN(g) + 6H_2O(g)$

[In (f), the oxidation numbers of hydrogen and nitrogen remain unchanged after reaction.]

5 Write balanced half-equations and the overall equation for each of the following reactions in **acidic** solution:

(a) $I^-(aq) + H_2SO_4(aq) \rightarrow I_2(g) + H_2S(g)$

(b) $MnO_4^{2-}(aq) \rightarrow MnO_2(s) + MnO_4^-(aq)$

(c) $FeC_2O_4(aq) + Ce^{3+}(aq) \rightarrow Ce^{2+}(aq) + Fe^{3+}(aq) + CO_2(g)$

[Note: FeC_2O_4 contains Fe^{2+} and $C_2O_4^{2-}$. Determine the oxidation number of each element and find out which element(s) underwent oxidation or reduction.]

6 Write balanced half-equations and the overall equation for each of the following reactions in **basic** solution:

(a) $ClO^-(aq) + Mn(OH)_2(s) \rightarrow Cl^-(aq) + MnO_2(s)$

(b) $MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow MnO_2(s) + CO_3^{2-}(aq)$

(c) $ClO^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$

7 RI 2014 Y5 CT Qn B1(c)

Sodium metabisulfite, $Na_2S_2O_5$, is often used as a food preservative.

100 g of preserved meat was boiled with hydrochloric acid.

$$Na_2S_2O_5 + 2HCl \rightarrow 2NaCl + 2SO_2 + H_2O$$

The sulfur dioxide gas produced reacted completely with 14.20 cm^3 of 0.0100 mol dm^{-3} acidified potassium dichromate(VI).

(a) Chromium (III) sulfate was formed in the reaction between sulfur dioxide and acidified potassium dichromate(VI). Write a balanced ionic equation for this reaction.

(b) Calculate the concentration of sodium metabisulfite in the preserved meat in ppm (parts per million). [1 ppm = 1 g in 10^6 g of meat]

8 RI 2014 Y5 CT Qn A3

An aqueous solution containing 1 mole of Cl_2O_7 oxidises 4 moles of H_2O_2 to form O_2 and a chlorine–containing product.

What is the chlorine–containing product of this reaction?

A Cl^- **C** ClO_2^-

B ClO^- **D** ClO_3^-

9 RI 2014 Y5 Promo Qn A2

An aqueous solution containing 0.010 mol of $NaNO_2$ oxidises 0.005 mol of acidified $(NH_4)_2SO_4$ to form a single nitrogen-containing product.

What is the nitrogen-containing product?

A N_2 **C** N_2O

B NO **D** NH_2OH

10 Hydroxylamine, NH_2OH, can be oxidised to nitrogen, N_2, or nitrogen oxide, N_2O, depending on the oxidising agent.

(a) Write a half-equation for each of the oxidation reactions in an acidic medium.

(b) In an experiment, 50 cm^3 of 0.050 mol dm^{-3} NH_2OH was found to reduce 10 cm^3 of 0.50 mol dm^{-3} Fe^{3+} to Fe^{2+}. Determine whether the NH_2OH is oxidised to N_2 or N_2O by Fe^{3+} and write a balanced ionic equation for the reaction.

11 Solution **FA1** contains 12.1 g dm^{-3} of sodium thiosulfate(VI) pentahydrate, $Na_2S_2O_3.5H_2O$.

Solution **FA2** contains 7.95 x 10^{-3} mol dm^{-3} of a compound MXO_3. M is a univalent metal and X is the symbol of an unknown element.

25.0 cm^3 of **FA2** was mixed with about equal volumes of potassium iodide solution and dilute sulfuric acid. The iodine liberated required 24.40 cm^3 of **FA1** for reaction.

(a) Calculate the number of moles of iodine liberated by 1 mole of XO_3^- when iodide ions are oxidised by XO_3^-. M^+ does not react with iodide ions.

(b) Using the answer obtained in **(a)**, decide which of the following species could be the product obtained from the reduction of XO_3^-: XO_2^-, X^+, X^- or X_2.

(c) Hence, write a balanced equation for the reaction between XO_3^- ions and iodide ions using the half-equation method.

12 RI Prelim 2018/4/1 (modified)

Copper(II) ions react with iodide ions according to the following equation.

$$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow \underset{\text{cream ppt}}{2CuI(s)} + \underset{\text{brown solution}}{I_2\,(aq)}$$

The iodine produced in this reaction may be titrated against thiosulfate ions, $S_2O_3^{2-}$, using starch solution as indicator. Thiosulfate ions react with iodine according to the following equation:

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

41.00 cm^3 of a solution containing $CuSO_4$ was placed in a 250 cm^3 volumetric flask. Deionised water was added to make a total volume of 250.0 cm^3 of the diluted solution. 25.0 cm^3 of this diluted solution was transferred to a conical flask. Excess KI was added, and the resultant solution titrated against 0.0500 mol dm^{-3} $Na_2S_2O_3$, using starch solution as an indicator. It was found that 24.80 cm^3 of $Na_2S_2O_3$ was required for the dark blue colour to decolourise.

Calculate the concentration of $CuSO_4$ in the initial undiluted solution.

13 Solution **X** contains a mixture of a dibasic acid, ethanedioic acid ($H_2C_2O_4$), and a salt, sodium ethanedioate ($Na_2C_2O_4$). A student performed two titrations to determine the concentrations of ethanedioic acid and sodium ethanedioate in solution **X**.

In the first titration, 25.0 cm^3 of solution **X** required 14.75 cm^3 of 0.100 mol dm^{-3} sodium hydroxide solution for neutralisation.

In the second titration, 25.0 cm^3 of solution **X** required 32.00 cm^3 of 0.0205 mol dm^{-3} potassium manganate(VII) solution for complete oxidation. In the oxidation reaction, all the $C_2O_4^{2-}$ ions are oxidised to CO_2 in acidic conditions.

(a) Write the equation for the reaction between ethanedioic acid, $H_2C_2O_4$, and sodium hydroxide solution to form sodium ethanedioate, $Na_2C_2O_4$, and water.

Use this equation and the results of the first titration to calculate the concentration of ethanedioic acid in solution X.

(b) **(i)** Construct a balanced ionic equation for the reaction between ethanedioate ions ($C_2O_4^{2-}$) and manganate(VII) ions (MnO_4^-).

(ii) Using the balanced equation in **(b)(i)** and the results of the second titration, calculate the total amount of $C_2O_4^{2-}$ ions present in 25 cm^3 of solution **X**.

(c) Hence, calculate the concentration of sodium ethanedioate in solution **X**.