LEARNERS' ALLEY
Designed by Khow Willard

6 Redox Chemistry

SINGAPORE JUNIOR CHEMISTRY OLYMPIAD



Iron rusts, a match burns, a battery runs down and a breathalyser changes colour. In each of these, electrons move from one substance to another. This chapter shows how to track those electrons with oxidation states, how to write and balance the equations, and how a titration measures an oxidising or reducing agent.

Learning objectives

By the end of this chapter, you can:

Foundation O LEVEL

- define oxidation and reduction in terms of oxygen, hydrogen, electrons and oxidation state
- work out the oxidation state of an element in a compound or ion
- decide whether a reaction is a redox reaction
- identify the oxidising agent and the reducing agent
- describe the tests with aqueous potassium iodide and acidified potassium manganate(VII)

Core A LEVEL

- write and balance half-equations in acidic and alkaline solution
- combine half-equations into a balanced redox equation
- recognise disproportionation
- carry out manganate(VII), dichromate(VI) and iodine–thiosulfate titration calculations
- deduce a change in oxidation state from the amounts that react

Prerequisites

Chapter 2 (electrons in shells), Chapter 3 (ions, formulae and electronegativity), Chapter 4 (equations, ionic equations, moles and gas volumes) and Chapter 5 (reactions of acids, precipitation and titration). Fill in the blanks as the lesson goes.

6.1 Oxidation and reduction

When iron rusts, it reacts with oxygen and water: $4Fe + 3O_2 + 2xH_2O \rightarrow 2Fe_2O_3{\cdot}xH_2O$. The iron gains oxygen, so it is **oxidised**. The reverse happens in a blast furnace, where carbon monoxide takes the oxygen away from iron(III) oxide:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

Iron(III) oxide loses oxygen, so it is **reduced**. At the same moment carbon monoxide gains that oxygen, so it is oxidised. Oxidation and reduction always happen together, and a reaction with both is a **redox** reaction (reduction–oxidation).

The first definitions used oxygen. Later they grew to cover hydrogen, then electrons, then oxidation states (Section 6.2). The last two work for every redox reaction, even one with no oxygen or hydrogen in it.

	oxidation	reduction
oxygen	gain of oxygen	loss of oxygen
hydrogen	loss of hydrogen	gain of hydrogen
electrons	_____	_____
oxidation state	increase	decrease

Methane burning, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, shows the hydrogen definition: the carbon gains oxygen and loses all four of its hydrogen atoms, so methane is oxidised.

6.1.1 Electron transfer

Put a strip of zinc into blue copper(II) sulfate solution. The zinc becomes coated with brown copper and the blue colour fades. Each zinc atom gives two electrons to a copper(II) ion (Figure 6.1):

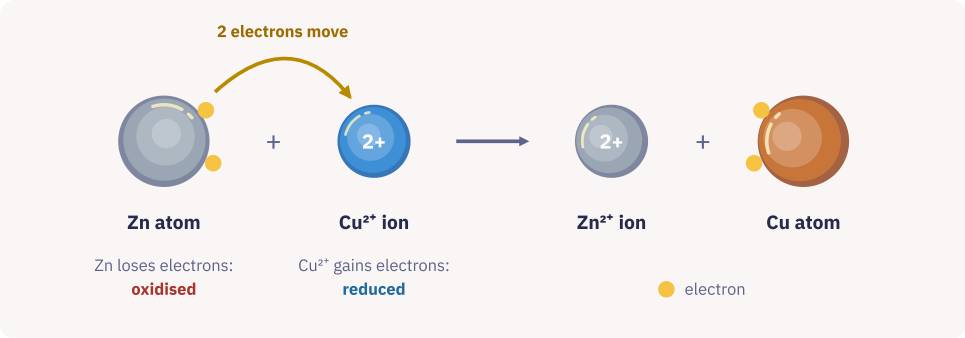


Figure 6.1 Zinc gives two electrons to a copper(II) ion. The sulfate ions are spectators and are not shown.

Each change can be written as a **half-equation**, which shows the electrons:

$$\text{oxidation: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$\text{reduction: } Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

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

The electrons lost by zinc are exactly the electrons gained by copper(II) ions, so they cancel when the half-equations are added.

DEFINITION **Oxidation** is the _____ of electrons. **Reduction** is the _____ of electrons.

NOTE A memory aid: **OIL RIG**, Oxidation Is Loss, Reduction Is Gain (of electrons).

Check your understanding

1. Sodium burns in chlorine: $2Na + Cl_2 \rightarrow 2NaCl$. Write the two half-equations and state which reactant is oxidised.
2. In $CuO + H_2 \rightarrow Cu + H_2O$, which substance is reduced? Explain in terms of oxygen.

6.2 Oxidation states

In covalent compounds no electrons are fully transferred, so the electron definition is hard to use. Oxidation states solve this. Pretend every bond is ionic: in each bond the more **electronegative** atom (Chapter 3) takes both shared electrons. The charge each atom would then carry is its oxidation state.

The **oxidation state** (or oxidation number) of an atom is the _____ if the compound were made of ions.

An oxidation state is written with its sign first, as +2 or −1. A charge is written with the sign last, as 2+ or 1−. Work it out with these rules. An earlier rule wins over a later one.

1. An uncombined element is _____: Mg, O_2, P_4.
2. A simple ion has its charge: Na^+ is +1, O^{2-} is −2.
3. The oxidation states in a compound add up to _____. In an ion they add up to the ion's charge.
4. In compounds, Group 1 metals are +1, Group 2 metals are +2 and aluminium is +3.
5. Fluorine is always −1.
6. Hydrogen is +1, except in metal hydrides such as NaH, where it is −1.
7. Oxygen is −2, except in peroxides such as H_2O_2 (−1) and in OF_2 (+2).
8. Chlorine is −1, except when it is bonded to oxygen or fluorine.

Elements that can have several oxidation states show it in the name with Roman numerals: iron(III) chloride contains iron in the +3 state, and potassium manganate(VII), $KMnO_4$, contains manganese in the +7 state.

WORKED EXAMPLE Find the oxidation state of (a) carbon in Na_2CO_3, (b) each nitrogen in NH_4NO_3, (c) manganese in MnO_4^-.

(a) $2(+1) + x + 3(-2) = 0$, so $x =$ _____ — *Na is +1, O is −2, the compound totals 0.*

(b) NH_4^+: $p + 4(+1) = +1$, so $p = -3$. NO_3^-: $q + 3(-2) = -1$, so $q = +5$ — *Treat each ion on its own. The two nitrogen atoms differ.*

(c) $x + 4(-2) = -1$, so $x =$ _____ — *The ion totals its charge, −1.*

One element can take many oxidation states. Nitrogen runs from −3 to +5 (Figure 6.2). Moving up the scale is oxidation and moving down is reduction.

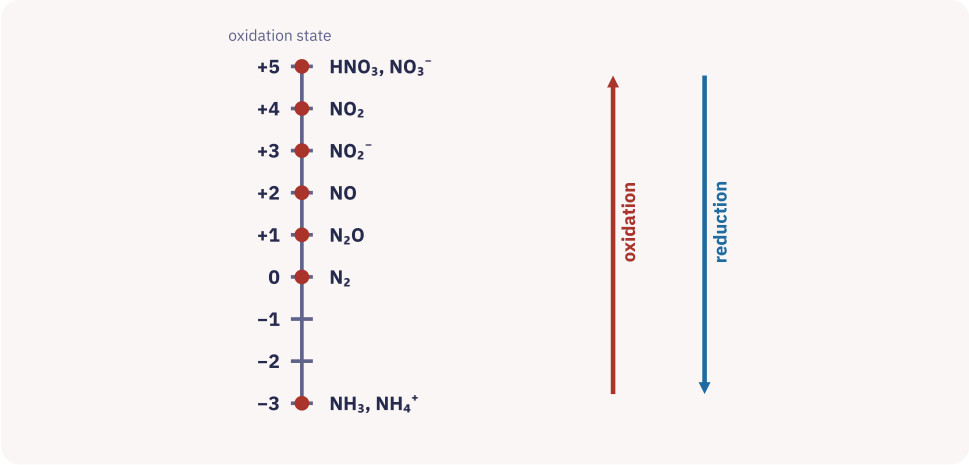


Figure 6.2 The oxidation states of nitrogen.

GOING FURTHER A calculated oxidation state can be a fraction. In the tetrathionate ion, $S_4O_6^{2-}$, $4x + 6(-2) = -2$ gives $x = +2.5$. This is an average: the four sulfur atoms are bonded differently and do not all have the same oxidation state.

Check your understanding

1. Find the oxidation state of (a) chromium in $Cr_2O_7^{2-}$, (b) sulfur in $Na_2S_2O_3$, (c) hydrogen in NaH.
2. Vanadium forms the ions VO^{2+} and VO_2^{+}. Find the oxidation state of vanadium in each.

6.3 Is it a redox reaction?

Write the oxidation state of each element on both sides of the equation (Figure 6.3). If an element's oxidation state **increases**, it is oxidised. If it **decreases**, it is reduced. If no oxidation state changes, the reaction is not a redox reaction.

WORKED EXAMPLE Chlorine is bubbled into potassium iodide solution: $Cl_2(g) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$. What is oxidised and what is reduced?

1. Cl_2: 0. KI: K +1, I −1. KCl: K +1, Cl −1. I_2: 0	*Elements are 0. K is in Group 1.*
2. Iodine: −1 to 0, an increase	*Iodide ions are oxidised.*
3. Chlorine: 0 to −1, a decrease. Potassium does not change.	*Chlorine is reduced. K^+ is a spectator.*

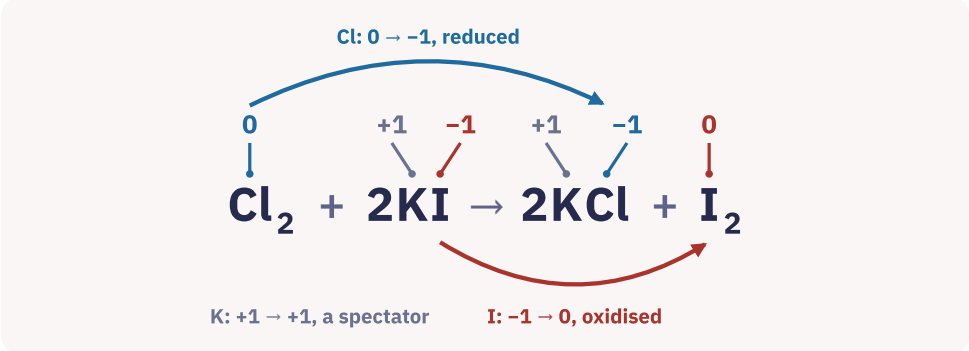


Figure 6.3 The oxidation state of each atom, before and after. Potassium does not change.

Respiration, $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$, is redox: carbon rises from 0 to +4 and oxygen falls from 0 to −2. In the Haber process, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, nitrogen falls from 0 to −3 and hydrogen rises from 0 to +1.

Two common kinds of reaction are **not** redox, because every ion keeps its charge:

- **Acid–base reactions** (Chapter 5): $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$. Hydrogen stays +1 and oxygen stays −2.
- **Precipitation** (Chapter 5): $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. Silver stays +1 and chlorine stays −1.

EXAM TIP If an element appears uncombined on one side of an equation and in a compound on the other, its oxidation state has changed from 0, so the reaction is redox.

Check your understanding

1. Which of these are redox reactions? Explain using oxidation states. (a) $NH_3 + HNO_3 \rightarrow NH_4NO_3$ (b) $CuCO_3 \rightarrow CuO + CO_2$ (c) $2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$

6.4 Oxidising and reducing agents

In a redox reaction one substance gives electrons and the other takes them (Figure 6.4).

DEFINITION An **oxidising agent** oxidises another substance by taking its electrons, so it is itself _____. A **reducing agent** reduces another substance by giving it electrons, so it is itself _____.

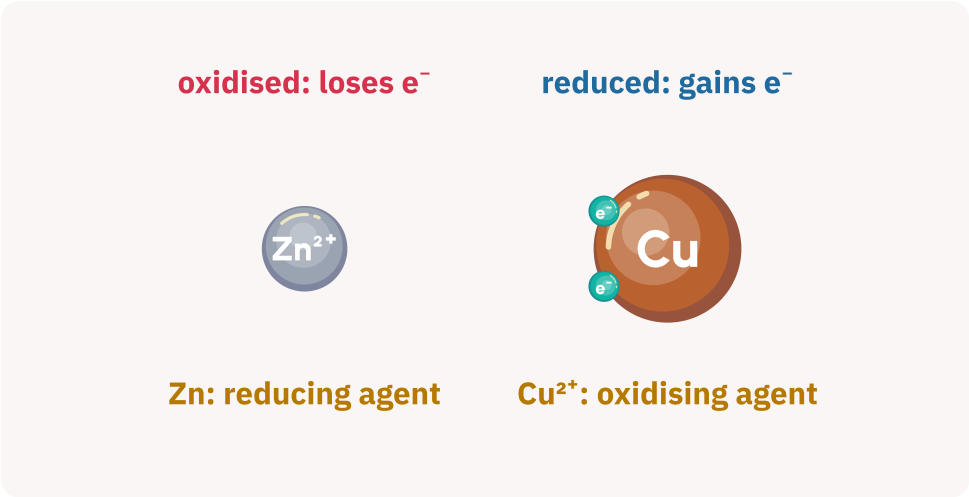


Figure 6.4 Electrons move from the reducing agent to the oxidising agent.

In $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, zinc is the reducing agent and Cu^{2+} is the oxidising agent. Common agents, with the colours that show they have reacted:

oxidising agent	becomes	reducing agent	becomes
O_2, Cl_2	O^{2-}, Cl^-	H_2, C, CO, reactive metals	H^+, CO_2, metal ions
MnO_4^- in acid (purple)	Mn^{2+} (very pale pink, looks colourless)	I^- (colourless)	I_2 (yellow-brown in water)
$Cr_2O_7^{2-}$ in acid (orange)	Cr^{3+} (green)	Fe^{2+} (pale green)	Fe^{3+} (yellow)
H_2O_2 in acid	H_2O	SO_2, SO_3^{2-}	SO_4^{2-}

6.4.1 Testing for oxidising and reducing agents

An unknown that reacts with a known reducing agent must be an oxidising agent, and the other way round. Two tests use this (Figure 6.5).

1 Test for an oxidising agent: aqueous potassium iodide

Add a few drops of colourless KI(aq) to the unknown.

$$2I^-(aq) \rightarrow I_2(aq) + 2e^-$$

- **Positive**: colourless to _____, as iodide ions are oxidised to iodine.
- A lot of iodine may form a black solid. If the colour is too pale to judge, add starch: it turns **dark blue** with iodine.
- For a gas, hold a strip of filter paper spotted with KI(aq) in it.

2 Test for a reducing agent: acidified potassium manganate(VII)

Add a few drops of purple $KMnO_4(aq)$, acidified with dilute sulfuric acid, to the unknown.

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

- **Positive**: purple to _____, as manganate(VII) ions are reduced to manganese(II) ions.
- Acidified potassium dichromate(VI) works in the same way: orange to **green**.
- For a gas, use filter paper spotted with the acidified solution.

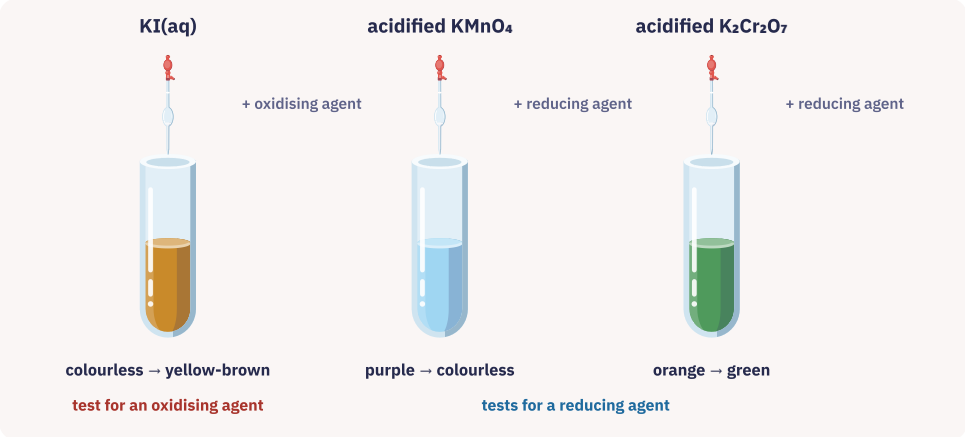


Figure 6.5 Positive tests for oxidising and reducing agents.

EXAM TIP Some substances can act either way. Hydrogen peroxide oxidises iodide ions, but it reduces acidified manganate(VII) and is oxidised to oxygen. Iron(II) ions reduce manganate(VII), yet in $FeSO_4 + Mg \rightarrow Fe + MgSO_4$ they are the oxidising agent. Decide the role from the reaction in front of you, not from a label.

Check your understanding

1. Sulfur dioxide decolourises acidified potassium manganate(VII) and turns acidified potassium dichromate(VI) green. State whether each of the three substances is acting as an oxidising agent or a reducing agent.
2. Iron(III) chloride solution oxidises iodide ions, and is reduced to iron(II). Write the ionic equation.

6.5 Half-equations

CORE · A LEVEL

A balanced redox equation must balance two things: the **atoms** and the **charge**. The surest way is to write the two half-equations, balance each, then add them.

WORKED EXAMPLE Write the equation for acidified manganate(VII) ions oxidising iodide ions: $MnO_4^- + I^- \rightarrow Mn^{2+} + I_2$.

1. Reduction: $MnO_4^- \rightarrow Mn^{2+}$ (Mn +7 to +2). Oxidation: $I^- \rightarrow I_2$ (I −1 to 0).	*Split by the oxidation states that change.*
2. $MnO_4^- \rightarrow Mn^{2+}$ and $2I^- \rightarrow I_2$	*Balance atoms other than O and H.*
3. $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$	*Add H_2O to balance O.*
4. $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$	*Add H^+ to balance H.*
5. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ and $2I^- \rightarrow I_2 + 2e^-$	*Add electrons to balance charge: 7+ on the left becomes 2+.*
6. Multiply the first by 2 and the second by 5: 10 electrons each.	*Electrons lost must equal electrons gained.*
7. _____	*Add, and cancel the electrons.*

Check: the electrons in each half-equation equal the change in oxidation state. Mn changes by 5 and gains 5 electrons. Each I changes by 1, and two I atoms lose 2 electrons.

In alkaline solution, balance as if in acid, then add as many OH^- ions as there are H^+ ions to **both** sides. Each $H^+ + OH^-$ becomes H_2O, and spare water molecules cancel. In alkali, manganate(VII) is reduced only to MnO_2:

$$2MnO_4^- + 6I^- + 8H^+ \rightarrow 2MnO_2 + 3I_2 + 4H_2O$$

add $8OH^-$ to both sides: $\mathbf{2MnO_4^- + 6I^- + 4H_2O \rightarrow 2MnO_2 + 3I_2 + 8OH^-}$

These half-equations come up again and again. Learn them:

change	half-equation
manganate(VII) in acid	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
dichromate(VI) in acid	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
iron(II) to iron(III)	$Fe^{2+} \rightarrow Fe^{3+} + e^-$
iodide to iodine	$2I^- \rightarrow I_2 + 2e^-$
thiosulfate to tetrathionate	$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$
hydrogen peroxide as oxidising agent	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$
hydrogen peroxide as reducing agent	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
ethanedioate to carbon dioxide	$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

6.5.1 Finding an oxidation state from the amounts that react

Electrons lost always equal electrons gained. So for the atoms that change:

amount oxidised × rise in oxidation state = amount reduced × fall in oxidation state

WORKED EXAMPLE 30.0 cm^3 of 0.0500 mol dm^{-3} iron(II) sulfate reacts exactly with 15.0 cm^3 of 0.0250 mol dm^{-3} potassium manganate(VII). Iron ends as Fe^{3+}. What is the final oxidation state of manganese?

1. $n_{Fe^{2+}} = 0.0500 \times 0.0300 = 1.500 \times 10^{-3}$ mol. $n_{MnO_4^-} = 0.0250 \times 0.0150 = 3.750 \times 10^{-4}$ mol — *$n = c \times V$, volumes in dm^3.*
2. Each Fe^{2+} loses 1 electron: 1.500×10^{-3} mol of electrons — *Fe +2 to +3.*
3. Each Mn gains $1.500 \times 10^{-3} \div 3.750 \times 10^{-4} = 4$ electrons — *Electrons gained = electrons lost.*
4. +7 − 4 = _____ — *Gaining electrons lowers the oxidation state.*

Check your understanding

1. Write the balanced equation for acidified dichromate(VI) ions oxidising iron(II) ions.
2. 25.0 cm^3 of 0.100 mol dm^{-3} NH_2OH reacts exactly with 25.0 cm^3 of 0.200 mol dm^{-3} Mn^{3+}, which is reduced to Mn^{2+}. Nitrogen in NH_2OH is −1. What is its final oxidation state?

6.6 Disproportionation

CORE · A LEVEL

DEFINITION **Disproportionation** is a redox reaction in which the _____ is oxidised and reduced at the same time.

Chlorine reacts with aqueous sodium hydroxide: $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$. Half of the chlorine atoms rise from 0 to +1 in ClO^-, and the other half fall from 0 to −1 in Cl^- (Figure 6.6).

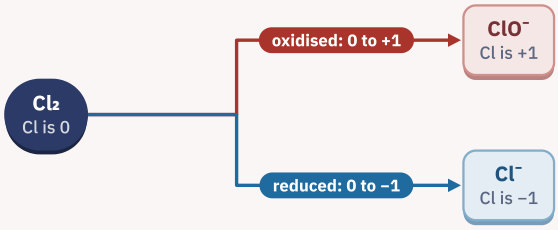


Figure 6.6 Chlorine disproportionates in aqueous sodium hydroxide.

Two more examples:

- $2H_2O_2 \rightarrow 2H_2O + O_2$: oxygen goes from −1 to −2 and to 0.
- $Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$: copper goes from +1 to +2 and to 0.

EXAM TIP Two different elements changing, as in $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$ (nitrogen reduced, oxygen oxidised), is ordinary redox, not disproportionation.

Check your understanding

1. Is $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$ a disproportionation? Give the oxidation states of nitrogen.

6.7 Redox titrations

CORE · A LEVEL

A redox titration uses the same apparatus and method as an acid–base titration (Chapter 5). The difference is the reaction: electrons pass from the reducing agent to the oxidising agent, and the mole ratio comes from the balanced redox equation. Three kinds are common.

1 Manganate(VII) titrations

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

- $KMnO_4$ goes in the burette. It is a strong oxidising agent, used with Fe^{2+}, H_2O_2 or ethanedioate.
- **No indicator** is needed. Purple MnO_4^- is decolourised until all the reducing agent has reacted. The end-point is the first _____ from one excess drop.
- The acid is **dilute sulfuric acid**. Hydrochloric acid is not used, because MnO_4^- would oxidise Cl^- to Cl_2. Nitric acid is not used, because it is itself an oxidising agent.

2 Dichromate(VI) titrations

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

- Orange to green, but the green appears long before the end-point, so an **indicator** is needed.
- Dichromate(VI) is a weaker oxidising agent than manganate(VII). It does not oxidise Cl^-, so hydrochloric or sulfuric acid can be used.

3 Iodine–thiosulfate titrations

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

- An oxidising agent is first added to **excess KI**. It forms an equal amount of iodine every time, which is then titrated with standard sodium thiosulfate (Figure 6.7).
- Excess KI makes sure all the oxidising agent reacts, and keeps the iodine dissolved.
- The titre gives the amount of iodine present, and so the original amount of oxidising agent (e.g. 1 mol $IO_3^- \equiv 3$ mol $I_2 \equiv 6$ mol $S_2O_3^{2-}$).
- The brown iodine fades to pale yellow. **Starch** is then added, giving dark blue, and the end-point is when the blue just disappears. Starch is added only near the end-point, because at high iodine concentration the starch–iodine complex can come out as a solid.

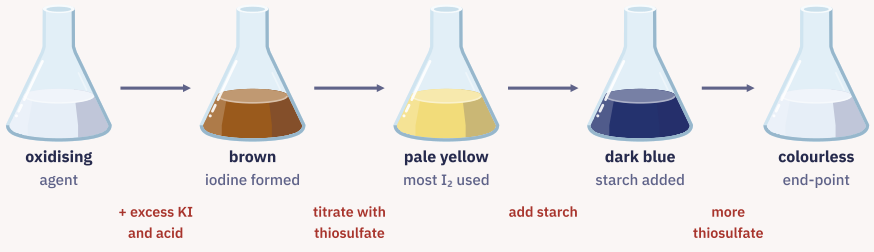


Figure 6.7 The colours in an iodine–thiosulfate titration.

WORKED EXAMPLE 10.0 cm^3 of hydrogen peroxide solution is diluted to 250 cm^3. 25.0 cm^3 of the diluted solution needs 14.60 cm^3 of 0.0200 mol dm^{-3} acidified $KMnO_4$. Find the concentration of the original hydrogen peroxide in g dm^{-3}.

1. $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ *5 electrons × 2 and 2 electrons × 5.*

2. $n_{MnO_4^-} = 0.0200 \times 0.01460 = 2.920 \times 10^{-4}$ mol, so $n_{H_2O_2} = 5/2 \times 2.920 \times 10^{-4} = 7.300 \times 10^{-4}$ mol — *Ratio MnO_4^- : H_2O_2 = 2 : 5.*

3. In 250 cm^3: 7.300×10^{-3} mol, all from the 10.0 cm^3 sample, so $c = 7.300 \times 10^{-3} \div 0.0100 = 0.7300$ mol dm^{-3} — *Scale up, then divide by the original volume.*

4. $0.7300 \times 34.0 =$ _____ — *$M_r(H_2O_2) = 34.0$*

WORKED EXAMPLE 0.875 g of potassium iodate(V), KIO_3, is made up to 250 cm^3. 25.0 cm^3 is added to excess KI and dilute sulfuric acid: $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$. The iodine needs 22.70 cm^3 of sodium thiosulfate. Find the concentration of the thiosulfate.

1. $n_{KIO_3} = 0.875 \div 214.0 = 4.089 \times 10^{-3}$ mol in 250 cm^3, so 4.089×10^{-4} mol in 25.0 cm^3 — *$M_r(KIO_3) = 214.0$*

2. $n_{I_2} = 3 \times 4.089 \times 10^{-4} = 1.227 \times 10^{-3}$ mol — *1 IO_3^- gives 3 I_2.*

3. $n_{S_2O_3^{2-}} = 2 \times 1.227 \times 10^{-3} = 2.453 \times 10^{-3}$ mol — *1 I_2 reacts with 2 $S_2O_3^{2-}$.*

4. $c = 2.453 \times 10^{-3} \div 0.02270 =$ _____ — *Each IO_3^- needs 6 $S_2O_3^{2-}$ in all.*

Check your understanding

1. 25.0 cm^3 of an acidified iron(II) solution needs 20.00 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$. Find the concentration of the iron(II) ions.
2. 12.0 g of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot xH_2O$ is made up to 250 cm^3. 25.0 cm^3 needs 25.50 cm^3 of 0.0200 mol dm^{-3} $K_2Cr_2O_7$. Find x.
3. Why is no indicator needed in a manganate(VII) titration?

Answers to Check your understanding

6.1

1. $Na \rightarrow Na^+ + e^-$ and $Cl_2 + 2e^- \rightarrow 2Cl^-$. Sodium is oxidised, because it loses electrons.
2. Copper(II) oxide, because it loses oxygen.

6.2

1. (a) $2x + 7(-2) = -2$, so +6 (b) $2(+1) + 2x + 3(-2) = 0$, so +2 (c) −1, because NaH is a metal hydride.
2. VO^{2+}: $x - 2 = +2$, so +4. VO_2^+: $x - 4 = +1$, so +5.

6.3

1. (a) Not redox: nitrogen stays −3 and +5, hydrogen +1 and oxygen −2. (b) Not redox: copper stays +2, carbon +4 and oxygen −2. (c) Redox: nitrogen falls from +5 to +4, and some oxygen rises from −2 to 0.

6.4

1. Sulfur dioxide is a reducing agent. Acidified potassium manganate(VII) and acidified potassium dichromate(VI) are oxidising agents, and both are reduced.
2. $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

6.5

1. $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
2. $n_{NH_2OH} = 2.50 \times 10^{-3}$ mol and $n_{Mn^{3+}} = 5.00 \times 10^{-3}$ mol, each gaining 1 electron. So each N loses 2 electrons: $-1 + 2 = +1$.

6.6

1. Yes. Nitrogen is +4 in NO_2, and goes up to +5 in HNO_3 and down to +3 in HNO_2.

6.7

1. $n_{MnO_4^-} = 4.000 \times 10^{-4}$ mol. $MnO_4^- + 5Fe^{2+}$, so $n_{Fe^{2+}} = 2.000 \times 10^{-3}$ mol and $c = 2.000 \times 10^{-3} \div 0.0250 = 0.0800$ mol dm^{-3}.
2. $n_{Cr_2O_7^{2-}} = 5.100 \times 10^{-4}$ mol, so $n_{Fe^{2+}} = 3.060 \times 10^{-3}$ mol in 25.0 cm^3 and 0.03060 mol in 250 cm^3. $M_r = 12.0 \div 0.03060 = 392.2$. $284.0 + 18.0x = 392.2$, so $x = 6$.
3. Purple manganate(VII) is decolourised as it reacts. The first excess drop leaves the solution pale pink, which marks the end-point.