O

10 Oxidation and Reduction

Study Station ▸▸

A What Are Oxidation and Reduction?

Learning Outcomes

- Define *oxidation* and *reduction* in terms of:
  - gain and loss of oxygen;
  - gain and loss of hydrogen;
  - gain and loss of electrons; and
  - increase and decrease in oxidation state.

1. Some reactions involve **oxidation** and **reduction**, which can be seen as opposites.
2. A substance is **oxidised** if it undergoes oxidation, and **reduced** if it undergoes reduction.

Gain and Loss of Oxygen

1. Oxidation can be defined as the gain of oxygen, while reduction can be defined as the loss of oxygen.
2. For example, sodium reacts with water to form sodium oxide and hydrogen.

reduction (loss of oxygen)

$$2Na + H_2O \longrightarrow Na_2O + H_2$$

oxidation (gain of oxygen)

- Sodium gains oxygen and is oxidised to sodium oxide.
- Water loses oxygen and is reduced to hydrogen.

Gain and Loss of Hydrogen

1. Oxidation can also be defined as the loss of hydrogen, while reduction can also be defined as the gain of hydrogen.
2. For example, ammonia reacts with bromine to form nitrogen and hydrogen bromide.

reduction (gain of hydrogen)

$$2NH_3 + 3Br_2 \longrightarrow N_2 + 6HBr$$

oxidation (loss of hydrogen)

- Ammonia loses hydrogen and is oxidised to nitrogen.
- Bromine gains hydrogen and is reduced to hydrogen bromide.

Worked Example 10.1

When ammonia is passed over heated lead(II) oxide, lead is obtained.

$$2NH_3 + 3PbO \longrightarrow N_2 + 3Pb + 3H_2O$$

Identify the compound that is

(a) oxidised,

(b) reduced.

Explain your answer.

Strategy

To identify the compound that is oxidised, check which reactant has gained oxygen or lost hydrogen. To identify the compound that is reduced, check which reactant has lost oxygen or gained hydrogen.

Solution

(a) Ammonia (NH_3) is oxidised because it loses hydrogen to form nitrogen (N_2).

(b) Lead(II) oxide (PbO) is reduced because it loses oxygen to form lead (Pb).

Gain and Loss of Electrons

1. Oxidation can also be defined as the loss of electrons, while reduction can also be defined as the gain of electrons.
2. For example, zinc reacts with copper(II) sulfate to form copper and zinc sulfate.

reduction (gain of electrons)

$$Zn \quad + \quad Cu^{2+} \longrightarrow Zn^{2+} \quad + \quad Cu$$

oxidation (loss of electrons)

- Zn loses electrons and is oxidised to Zn^{2+}.
- Cu^{2+} gains electrons and is reduced to Cu.

3. To show the electron transfer in the above reaction more clearly, we can write the ionic equation as two half-equations.
   - Oxidation: $Zn \longrightarrow Zn^{2+} + 2e^-$
   - Reduction: $Cu^{2+} + 2e^- \longrightarrow Cu$
   - Electrons are included as e^- on the right-hand side and left-hand side of the half-equations to show the loss and gain of electrons respectively.

Determining Oxidation State

1. The **oxidation state** is the charge an atom of an element would have if the atom exists as an ion in a substance, regardless whether the substance is ionic or covalent.
2. The oxidation state is a number used to indicate the degree of oxidation or reduction. It can be a positive number (e.g. +1), zero or a negative number (e.g. –1).
3. The oxidation state is also known as **oxidation number**.

4. The oxidation state of an atom of an element can be determined using the rules listed below.

Rule	Examples
• The oxidation state of atoms of an element in the uncombined state is zero.	In K, oxidation state of K = 0 In Fe, oxidation state of Fe = 0 In H_2, oxidation state of H = 0 In O_2, oxidation state of O = 0 In Cl_2, oxidation state of Cl = 0
• The oxidation state of a monoatomic ion is equal to its charge.	In K^+, oxidation state of K = +1 In Fe^{2+}, oxidation state of Fe = +2 In H^+, oxidation state of H = +1 In O^{2-}, oxidation state of O = −2 In Cl^-, oxidation state of Cl = −1
• The oxidation state of a Group 1 element (e.g. lithium, sodium) in a compound is always +1. • The oxidation state of a Group 2 element (e.g. beryllium, magnesium) in a compound is always +2.	In $LiCl$, oxidation state of Li = +1 In $NaNO_3$, oxidation state of Na = +1 In $BeCl_2$, oxidation state of Be = +2 In $MgSO_4$, oxidation state of Mg = +2
• The oxidation state of fluorine in a compound is always −1. • The oxidation state of oxygen in a compound is usually −2, except in peroxides. • The oxidation state of hydrogen in a compound is usually +1, except in hydrides.	In HF, oxidation state of F = −1 In AlF_3, oxidation state of F = −1 In H_2O, oxidation state of O = −2 In Al_2O_3, oxidation state of O = −2 In H_2O_2, oxidation state of O = −1 In HF, oxidation state of H = +1 In H_2O, oxidation state of H = +1 In AlH_3, oxidation state of H = −1
• The sum of the oxidation states of all the atoms present in a compound is zero.	Sum of the oxidation states of all atoms in $NaCl = 0$ $H_2O = 0$ $Fe_2O_3 = 0$ $NH_3 = 0$ $CH_4 = 0$
• The sum of the oxidation states of all the atoms present in a polyatomic ion is equal to the charge of the ion.	Sum of the oxidation states of all atoms in $NH_4^+ = +1$ $NO_3^- = -1$ $SO_4^{2-} = -2$

5. In the chemical names of some metal compounds, the roman numeral after the name of the metal indicates the oxidation state of the metal. Such oxidation states are positive.

Examples:

(a) Oxidation state of iron in iron(II) hydroxide = +2

(b) Oxidation state of iron in iron(III) hydroxide = +3

6. The oxidation state of an element which cannot be determined directly can be calculated.
7. For example, the oxidation states of sulfur in the compound MgS and in the ion SO_4^{2-} are calculated as shown below.
   (a) Let the oxidation state of S in MgS be x.
   Oxidation state of Mg = +2
   Sum of the oxidation states of all atoms in MgS = 0
   $(+2) + x = 0$
   $x = -2$
   Oxidation state of S in MgS = −2
   (b) Let the oxidation state of S in SO_4^{2-} be y.
   Oxidation state of O = −2
   Sum of the oxidation states of all atoms in $SO_4^{2-} = -2$
   $y + [4 \times (-2)] = -2$
   $y = -2 + 8$
   $y = +6$
   Oxidation state of S in $SO_4^{2-} = +6$

Common Error

✗ In magnesium oxide, the oxidation state of both magnesium and oxygen is 2.

✓ In magnesium oxide, the oxidation state of magnesium is +2 and the oxidation state of oxygen is −2.

Explanation
When writing oxidation states, it is necessary to include the "+" and "−" signs.

Worked Example 10.2

In which substance does chlorine have the highest oxidation state?

A $BaCl_2$
B Cl_2
C ClO_2
D $KClO_3$

Solution

D

Explanation

Let the oxidation state of Cl be x.
Oxidation state of Ba = +2
Sum of the oxidation states of all atoms in $BaCl_2 = 0$
$(+2) + 2x = 0$
$2x = -2$
$x = -1$
In Cl_2, $x = 0$
Oxidation state of O = −2
Sum of the oxidation states of all atoms in $ClO_2 = 0$
$x + [2 \times (-2)] = 0$
$x = +4$

Oxidation state of K = +1

Sum of the oxidation states of all atoms in $KClO_3 = 0$

$(+1) + x + [3 \times (-2)] = 0$

$x = +5$

Thus, the oxidation state of Cl is highest in $KClO_3$.

Increase and Decrease in Oxidation State

1. Oxidation can be defined as an increase in oxidation state, while reduction can be defined as a decrease in oxidation state.
2. To determine which element is oxidised and which element is reduced in a reaction, write the chemical equation, followed by the oxidation states of all the elements in the reactants and products in the reaction.
3. For example, nitrogen and hydrogen react to form ammonia.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Oxidation state of N in $N_2 = 0$

Oxidation state of H in $H_2 = 0$

Let the oxidation state of N in NH_3 be z.

Oxidation state of H in $NH_3 = +1$

Sum of oxidation states of all atoms present in $NH_3 = 0$

$z + [3 \times (+1)] = 0$

$z = -3$

Oxidation state of N in $NH_3 = -3$

reduction (decrease in oxidation number)

$$\underset{0}{N_2} + \underset{0}{3H_2} \longrightarrow 2NH_3 \quad (N: -3,\ H: +1)$$

oxidation (increase in oxidation number)

Hydrogen is oxidised as its oxidation state increases from 0 in H_2 to +1 in NH_3.

Nitrogen is reduced as its oxidation state decreases from 0 in N_2 to −3 in NH_3.

4. Using oxidation states to determine whether oxidation or reduction has occurred can be applied to most reactions.

Worked Example 10.3

Methane, the main component of natural gas, reacts with excess oxygen to form carbon dioxide and water.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Identify, in terms of oxidation states, the element that is oxidised and reduced in this reaction.

Strategy

Determine the oxidation states of all the elements in the reactants and products. To identify the element that is oxidised, check for an increase in oxidation state of any element in the reaction. To identify the element that is reduced, check for a decrease in oxidation state of any element in the reaction.

Solution

Oxidation state of H = +1

Let the oxidation state of C in CH_4 be x.

$x + [4 \times (+1)] = 0$

$x = -4$

Oxidation state of O = −2

Let the oxidation state of C in CO_2 be y.

$y + [2 \times (-2)] = 0$

$y = +4$

$$\underset{-4\quad +1}{CH_4} + \underset{0}{2O_2} \longrightarrow \underset{+4\quad -2}{CO_2} + \underset{+1\quad -2}{2H_2O}$$

Carbon is oxidised as its oxidation state increases from −4 in CH_4 to +4 in CO_2.

Oxygen is reduced as its oxidation state decreases from 0 in O_2 to −2 in CO_2 and H_2O.

Link — Discover Chemistry (3rd Edition) Textbook — Section 10.1

B How Do We Test for Redox Reactions?

Learning Outcome

- Describe how aqueous potassium iodide and acidified potassium manganate(VII) are used to test for oxidising and reducing agents based on the resulting colour changes.

1. Reduction and oxidation usually take place at the same time in a reaction. Such a reaction is known as a **redox** (reduction-oxidation) reaction.
2. We can describe redox reactions based on the oxidising agent and reducing agent in a reaction.
3. An **oxidising agent** is a substance that oxidises other reactants in the same reaction.
   - It causes oxidation while being reduced itself.
   - It gains electrons from another reactant.

4. A **reducing agent** is a substance that reduces other reactants in the same reaction.
   - It causes reduction while being oxidised itself.
   - It loses electrons to another reactant.
5. For example, iron reacts with fluorine to form iron(III) fluoride.

$$\underset{\text{reducing agent}}{2Fe} + \underset{\text{oxidising agent}}{3F_2} \longrightarrow 2FeF_3$$

   - Iron is the reducing agent. It loses electrons to fluorine and causes reduction of fluorine. Iron itself is oxidised. Its oxidation state increases from 0 in Fe to +3 in FeF_3.
   - Fluorine is the oxidising agent. It gains electrons from iron and causes oxidation of iron. Fluorine itself is reduced. Its oxidation state decreases from 0 in F_2 to −1 in FeF_3.
6. In the identification of unknown compounds, it can be useful to test whether the unknown compound is an oxidising agent or a reducing agent.
7. Aqueous potassium iodide is often used to test for oxidising agents.
   - An oxidising agent causes iodide ions to be oxidised to iodine. The oxidation state of iodine increases from −1 in I^- to 0 in I_2.

$$\underset{\text{colourless}}{2I^-} \longrightarrow \underset{\text{yellow-brown}}{I_2} + 2e^-$$

   - Small portions of an unknown solution can be added to aqueous potassium iodide. If the unknown is a gas, a strip of filter paper with a spot of aqueous potassium iodide, or moist potassium iodide starch paper can be used.
   - If the unknown solution is an oxidising agent, it will turn colourless potassium iodide solution yellow-brown. If the test result is too pale, a few drops of starch can be added to the iodine formed. Iodine reacts with starch to give a blue colour.
   - If the unknown is a gas, it will turn white potassium iodide starch paper blue.
8. Acidified potassium manganate(VII) solution, $KMnO_4$, is often used to test for reducing agents.
   - A reducing agent causes manganate(VII) ions to be reduced to manganese(II) ions. The oxidation state of manganese decreases from +7 in MnO_4^- to +2 in Mn^{2+}.

$$\underset{\text{purple}}{MnO_4^-} + 8H^+ + 5e^- \longrightarrow \underset{\text{colourless}}{Mn^{2+}} + 4H_2O$$

   - Small portions of an unknown solution can be added to acidified potassium manganate(VII) solution. If the unknown is a gas, a strip of filter paper with a spot of acidified potassium manganate(VII) solution can be used.
   - If the unknown solution is a reducing agent, the purple acidified potassium manganate(VII) solution will turn colourless.
   - If the unknown is a gas, it will turn the purple acidified potassium manganate(VII) solution in the strip of filter paper colourless.

Common Misconception

✗ A substance can only act an oxidising agent or a reducing agent in all reactions.

✓ Some substances can act as an oxidising agent in one reaction and a reducing agent in another reaction. For example, hydrogen peroxide, H_2O_2, acts as an oxidising agent when it reacts with aqueous potassium iodide. It acts as an reducing agent when it reacts with acidified potassium manganate(VII) solution.

Worked Example 10.4

In which of the following reactions does SO_2 act as an oxidising agent?

A $SO_2 + H_2O \longrightarrow H_2SO_3$

B $SO_2 + 3Mg \longrightarrow 2MgO + MgS$

C $SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$

D $5SO_2 + 2KMnO_4 + 2H_2O \longrightarrow 2H_2SO_4 + 2MnSO_4 + K_2SO_4$

Solution

B

Explanation

An oxidising agent is a substance that causes oxidation while being reduced itself.

In option **B**, SO_2 causes Mg to be oxidised as the oxidation state of magnesium increases from 0 in Mg to +2 in MgO and MgS. Thus, SO_2 acts as an oxidising agent.

In options **A** and **C**, the oxidation state of S is +4 in both the reactant SO_2 and the products H_2SO_3 and Na_2SO_3. Thus, SO_2 does not act as an oxidising agent.

In option **D**, SO_2 causes $KMnO_4$ to be reduced as the oxidation state of Mn decreases from +7 in $KMnO_4$ to +2 in $MnSO_4$. Thus, SO_2 acts as a reducing agent.

Link Discover Chemistry (3rd Edition) Textbook — Section 10.2

Checkpoint 10.1

1. Fluorine reacts with moisture in air to form oxygen and hydrogen fluoride.

$$2F_2(g) + 2H_2O(g) \longrightarrow O_2(g) + 4HF(g)$$

State whether fluorine is oxidised or reduced in the reaction above. Explain your answer.

Tip

Determining whether a reactant is oxidised or reduced has been tested in examinations, e.g. GCE 'O' Level Science Chemistry Oct/Nov 2020, Paper 3, Q7(b)(ii).

2. Reactive metals react with dilute acids to form salts.
   (a) Write a balanced chemical equation for the reaction between magnesium and dilute sulfuric acid.
   (b) State whether magnesium is oxidised or reduced in the reaction in **(a)**. Explain your answer.

3. In each of the following redox reactions, identify the oxidising agent and reducing agent.
   (a) $2P + 3Br_2 \longrightarrow 2PBr_3$
   (b) $SiO_2 + 2C \longrightarrow Si + 2CO$
   (c) $Al^{3+} + 3Li \longrightarrow 3Li^+ + Al$

Tip

The identification of oxidising and reducing agents has been tested in examinations, e.g. GCE 'O' Level Science Chemistry Oct/Nov 2012, Paper 3, Q5.

Test Station ▸▸

1. In which of the following reactions is the element Cl oxidised?
   A $Cl_2 + 2NaI \longrightarrow 2NaCl + I_2$
   B $2KCl + F_2 \longrightarrow 2KF + Cl_2$
   C $2KClO_3 \longrightarrow 2KCl + 3O_2$
   D $2Na + 2HCl \longrightarrow 2NaCl + H_2$
2. Iron reacts with iron(III) chloride to form iron(II) chloride.

$$Fe + 2FeCl_3 \longrightarrow 3FeCl_2$$

   Which statement about the reaction is **correct**?
   A Iron(III) chloride is a reducing agent and is oxidised.
   B Iron(III) chloride is a reducing agent and is reduced.
   C Iron(III) chloride is an oxidising agent and is oxidised.
   D Iron(III) chloride is an oxidising agent and is reduced.
3. Coal contains a small amount of sulfur. Sulfur dioxide is released into the atmosphere when coal is burnt.

   The conversion of sulfur dioxide into sulfur trioxide occurs via a two-step process involving oxides of nitrogen.

   Step 1: $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

   Step 2: $NO_2(g) + SO_2(g) \longrightarrow NO(g) + SO_3(g)$

   (a) Determine the oxidation states of nitrogen in NO and NO_2. [2]
   (b) In terms of gain and loss of oxygen, explain which reactant in step 2 is oxidised and which reactant is reduced. [2]
   (c) Write the overall chemical equation, including state symbols, for the conversion of sulfur dioxide to sulfur trioxide. [1]

4. When aqueous copper(II) sulfate was added to aqueous potassium iodide, a yellow-brown solution and an off-white precipitate of copper(I) iodide were formed.

$$2CuSO_4(aq) + 4KI(aq) \longrightarrow 2CuI(s) + I_2(aq) + 2K_2SO_4(aq)$$

(a) Explain why a yellow-brown solution was formed in the reaction above. [1]

(b) Complete Table 10.1 to show the oxidation states of all the elements in the reactants and products in the chemical equation above. [5]

Table 10.1

Element	Oxidation State in Reactant	Oxidation State in Product(s)
copper		
sulfur		
oxygen		
potassium		
iodine		

(c) Which element is oxidised and which element is reduced in the reaction? Explain why. [2]

5. Disproportionation occurs when an element is both oxidised and reduced in a reaction.

For each reaction below, identify the element that undergoes disproportionation. State the changes in oxidation state of the element during the reaction.

(a) $4FeO \longrightarrow Fe + Fe_3O_4$ [2]

(b) $H_2O + 2NO_2 \longrightarrow HNO_3 + HNO_2$ [2]

(c) $H_2C_2O_4 \longrightarrow H_2O + CO + CO_2$ [2]