Chapter 4

Redox Reactions

CHAPTER SUMMARY

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SECTION 1:
OXIDATION AND REDUCTION

SECTION 2:
BALANCING REDOX EQUATIONS

OXIDATION AND REDUCTION

Electron Transfer and Redox Reactions

Oxidation and reduction are **complementary** – as a substance is oxidized, another substance is reduced.

A chemical reaction can usually be classified as one of five types

- synthesis,
- decomposition,
- combustion,
- single-replacement,
- or double-replacement.

A defining characteristic of **combustion** and **single-replacement** reactions is that they always involve the transfer of electrons from one substance to another, as do many synthesis and decomposition reactions.

For example, in the **synthesis** reaction in which **sodium (Na)** and **chlorine (Cl_2)** react to form the ionic compound sodium chloride **(NaCl)**, an electron from each of two sodium atoms is transferred to the Cl_2 molecule to form two Cl^- ions.

Complete chemical equation: $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$
Net ionic equation: $2Na(s) + Cl_2(g) \longrightarrow 2Na^+ + 2Cl^-$ (ions in crystal)

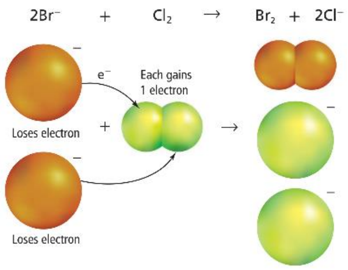
An example of a **combustion** reaction is the burning of magnesium in air, which involves the transfer of electrons. When magnesium reacts with oxygen, each magnesium atom **transfers two electrons** to each oxygen atom. The two magnesium atoms become magnesium ions (Mg^{2+}), and the two oxygen atoms become oxide ions (O^{2-}).

Complete chemical equation: $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$
Net ionic equation: $2Mg(s) + O_2(g) \longrightarrow 2Mg^{2+} + 2O^{2-}$ (ions in crystal)

Oxidation-reduction reaction or **Redox reaction**: is a reaction in which electrons are transferred from one substance to another.

The reaction of magnesium and oxygen involves a transfer of electrons from magnesium to oxygen. Therefore, this reaction is an oxidation-reduction reaction.

The reaction between aqueous bromide ions and chlorine gas is a redox reaction. In this reaction, electrons are transferred from bromide ions to chlorine.



OXIDATION AND REDUCTION

Oxidation and Reduction

Originally, the word oxidation referred only to reactions in which a substance combined with oxygen. Today, **oxidation** is defined as the complete or partial loss of electrons from a reacting substance.

$$\text{Oxidation: } Na \rightarrow Na^{+} + e^{-}$$

In the net ionic equation for the reaction of sodium and chlorine, sodium is **oxidized** because it loses an electron.

For oxidation to occur, the electrons lost by the substance that is oxidized must be accepted by atoms or ions of another substance. **Reduction** is the complete or partial gain of electrons by a reacting substance.

Following the sodium chloride example further, the reduction reaction that accompanies the oxidation of sodium is the reduction of chlorine.

$$\text{Reduction: } Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$$

Oxidation and reduction are **complementary** processes:

oxidation cannot occur unless reduction also occurs.

The phrase **L**oss of **E**lectrons is **O**xidation, and **G**ain of **E**lectrons is **R**eduction is shortened to **LEO GER**.

Oxidation Numbers

Oxidation number is a number assigned to an atom or ion to indicate its degree of oxidation or reduction. For example, the oxidation number of an element in an ionic compound is related to the number of electrons lost or gained by an atom of the element when it becomes an ion.

The reaction of potassium metal with chlorine vapor is a redox reaction.

$$\text{Complete chemical equation: } 2K(s) + Cl_2(g) \rightarrow 2KCl(s)$$
$$\text{Net ionic equation: } 2K(s) + Cl_2(g) \rightarrow 2K^{+}(s) + 2Cl^{-}(s)$$

Potassium, a group 1 element whose atoms tend to lose one electron in reactions because of its **low electronegativity**, is assigned an oxidation number of **+1** in **KCl**.

On the other hand, chlorine, a group 17 element whose atoms tend to gain one electron in reactions because of its **high electronegativity**, is assigned an oxidation number of **-1** in **KCl**.

OXIDATION AND REDUCTION

In redox terms, you would say that **potassium** atoms are **oxidized** from **0** to the **+1** state because each atom loses an electron, and **chlorine** atoms are **reduced** from **0** to the **-1** state because each atom gains an electron.

- When an atom or ion is **oxidized**, its oxidation number **increases**.
- When an atom or ion is **reduced**, its oxidation number **decreases**.

Oxidation numbers are tools that scientists use in written chemical equations to help them keep track of the movement of electrons in a redox reaction.

Oxidation numbers have a specific notation. **Oxidation numbers** are written with the positive or negative sign **before** the number **(+3, +2)**, whereas **ionic charge** is written with the sign **after** the number **(3+, 2+)**.

Oxidation number: +3　　　Ionic charge: 3+

Oxidizing and Reducing Agents

The potassium-chlorine reaction in can also be described by saying that **"potassium is oxidized by chlorine."**. This description is useful because it clearly identifies both the substance that is oxidized and the substance that does the oxidizing.

An **oxidizing agent** is the substance that oxidizes another substance by accepting its electrons. This term describes the substance that is **reduced**.

A **reducing agent** is the substance that reduces another substance by losing electrons. A reducing agent supplies electrons to the substance being reduced (gaining electrons).

The reducing agent is oxidized because it loses electrons. The reducing agent in the potassium-chlorine reaction is potassium – the substance that is oxidized.

$$\overbrace{2K(s) + Cl_2}^{\text{oxidized}}(g) \rightarrow 2KCl(s)$$

$$2K(s) + \underbrace{Cl_2(g) \rightarrow 2KCl}_{\text{reduced}}(s)$$

Oxidizing agent: Cl_2
Reducing agent: K

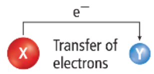
OXIDATION AND REDUCTION

A common application of redox chemistry is to remove tarnish from metal objects (تنظيف أسطح الفلزات).

When you add chlorine bleach to your laundry to whiten clothes, you are using an aqueous solution of sodium hypochlorite ($NaClO$), an oxidizing agent. It oxidizes dyes, stains, and other materials that discolor clothes.

Table 1 summarizes the different ways to describe oxidation-reduction reactions.

Table 1 Summary of Redox Reactions

Process	
Oxidation • A reactant loses an electron. • Reducing agent is oxidized. • Oxidation number increases.	• X loses an electron. • X is the reducing agent and becomes oxidized. • The oxidation number of X increases.
Reduction • Other reactant gains an electron. • Oxidizing agent is reduced. • Oxidation number decreases.	• Y gains an electron. • Y is the oxidizing agent and becomes reduced. • The oxidation number of Y decreases.

Redox and Electronegativity

The chemistry of oxidation-reduction reactions is **not limited** to atoms of an element changing to ions or the reverse. Some redox reactions involve changes in molecular substances or polyatomic ions in which atoms are covalently bonded to other atoms.

For example, the redox reaction used to manufacture ammonia **(NH_3)**.

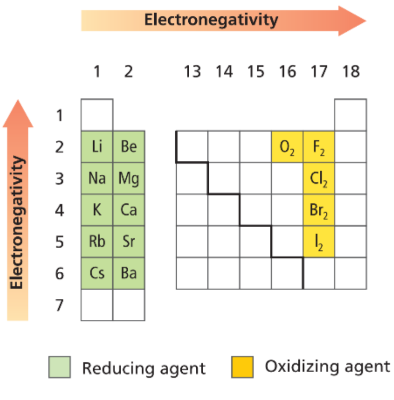
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

This process involves **neither** ions nor any obvious transfer of electrons. The reactants and products are all molecular compounds. Yet, it is still a redox reaction in which nitrogen is the oxidizing agent and hydrogen is the reducing agent.

In situations such as the formation of ammonia, where two atoms share electrons, you need to know which atom **attracts** electrons more strongly, or, in other words, which atom is more **electronegative**.

The electronegativity of elements **increases** from **left to right** across the periodic table, and it **decreases** going **down** a group.

- Elements with **low electronegativity** (Groups 1 and 2) are **strong reducing agents**.
- Elements with **high electronegativity** (Group 17 and oxygen) are **strong oxidizing agents**.



The more-electronegative element (nitrogen) is treated as if it had been reduced by gaining electrons from the other element (hydrogen). Conversely, the less-electronegative element (hydrogen) is treated as if it had been oxidized by losing electrons to the other element (nitrogen).

$$\overbrace{N_2(g) + 3}^{\text{reduced (partial gain of } e^-)}\underbrace{H_2(g) \rightarrow 2NH_3(g)}_{\text{oxidized (partial loss of } e^-)}$$

Determining Oxidation Numbers

In order to understand all types of redox reactions, you must have a way to determine the **oxidation number** ($n_{element}$) of each element involved in a reaction. **Table 2** outlines the rules chemists use to make this determination easier.

Table 2 Rules for Determining Oxidation Numbers

Rule	Example	$n_{element}$
1. The oxidation number of an atom of an uncombined element is zero.	Na, O_2, Cl_2, H_2	0
2. The oxidation number of a monatomic ion is equal to the charge of the ion.	Ca^{2+}	+2
	Br^-	−1
3. The oxidation number of the more-electronegative atom in a molecule or a complex ion is the same as the charge it would have if it were an ion.	N in NH_3	−3
	O in NO	−2
4. The oxidation number of the most-electronegative element, fluorine, is always −1 when it is bonded to another element.	F in LiF	−1
5. The oxidation number of oxygen in compounds is always −2 except in peroxides, such as hydrogen peroxide (H_2O_2), where it is −1. When it is bonded to fluorine, the only element more electro-negative than oxygen, the oxidation number of oxygen is positive.	O in NO_2	−2
	O in H_2O_2	−1
6. The oxidation number of hydrogen in most of its compounds is +1, except in metal hydrides; then, the oxidation number is −1.	H in NaH	−1
7. The oxidation numbers of group 1 and 2 metals and aluminum are positive and equal to their number of valence electrons.	K	+1
	Ca	+2
	Al	+3

8. The sum of the oxidation numbers in a neutral compound is zero.	$CaBr_2$	$(+2) + 2(-1) = 0$
9. The sum of the oxidation numbers of the atoms in a polyatomic ion is equal to the charge of the ion.	SO_3^{2-}	$(+4) + 3(-2) = -2$

Oxidation Numbers in Redox Reactions

The equation for the replacement of **bromine** in aqueous **potassium bromide** (**KBr**) by chlorine (**Cl_2**) is shown below.

$$2KBr(aq) + Cl_2(aq) \longrightarrow 2KCl(aq) + Br_2(aq)$$

To learn how oxidation numbers change, start by assigning numbers, using **Table 3**, to all elements in the balanced equation. Then, review the changes, as shown in the equation below.

change: −1 reduction

change: +1 oxidation

$$\overset{+1\,-1}{2KBr(aq)} + \overset{0}{Cl_2(aq)} \longrightarrow \overset{+1\,-1}{2KCl(aq)} + \overset{0}{Br_2(aq)}$$

no change in oxidation number

Table 3 Various Oxidation Numbers

Oxidation Number	+1	+2	+3	−1	−2
Aluminum			X		
Barium		X			
Bromine				X	
Cadmium		X			
Calcium		X			
Cesium	X				
Chlorine				X	
Fluoride				X	
Hydrogen	X			X	
Iodine				X	
Lithium	X				
Magnesium		X			
Oxygen					X
Potassium	X				
Sodium	X				
Silver	X				
Strontium		X			

You should notice that the oxidation number of bromine changed from **−1** to **0**, an increase of **1**.

At the same time, the oxidation number of chlorine changed from **0** to **−1**, a decrease of **1**.

Therefore, chlorine is reduced and bromine is oxidized.

All redox reactions follow the same pattern. When an atom is oxidized, its oxidation number increases. When an atom is reduced, its oxidation number decreases.

Note that there is no change in the oxidation number of potassium. The potassium ion takes no part in the reaction and is therefore a **spectator ion**

BALANCING REDOX EQUATIONS

Balancing Net Ionic Redox Equations

Sometimes, chemists prefer to express redox reactions in the **simplest** possible terms – *as an equation showing only the oxidation and reduction processes*. Refer again to the balanced equation for the oxidation of copper by nitric acid.

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

Note that the reaction takes place in aqueous solution, so HNO_3, which is a strong acid, will be ionized. Likewise, copper(II) nitrate ($Cu(NO_3)_2$) will be dissociated into ions. Therefore, the equation can also be written in ionic form.

$$Cu(s) + 4H^+(aq) + 4NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2NO_3^-(aq) + 2NO_2(g) + 2H_2O(l)$$

There are **four** nitrate ions among the reactants, but only **two** of them undergo change to form two nitrogen dioxide molecules. The other two nitrate ions are only **spectator ions** and can be eliminated from the equation.

To simplify things when writing redox equations in ionic form, chemists usually indicate hydrogen ions by $\mathbf{H^+}$ with the understanding that they exist in hydrated form as **hydronium ions** ($\mathbf{H_3O^+}$). The equation can then be rewritten showing only the substances that undergo change.

$$Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$$

Now look at the equation in unbalanced form.

$$Cu(s) + H^+(aq) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO_2(g) + H_2O(l)$$

You might also see this same reaction expressed in a way that shows only the substances that are oxidized and reduced.

$$Cu(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO_2(g) \text{ (in acidic solution)}$$

In this case, the **hydrogen ion** and the **water molecule** are **eliminated** because neither is oxidized nor reduced. In acidic solution, hydrogen ions ($\mathbf{H^+}$) and water molecules are abundant and free to participate in redox reactions as either reactants or products.

Some redox reactions can occur only in basic solution. When you balance equations for these reactions, you can add hydroxide ions ($\mathbf{OH^-}$) and water molecules to either side of the equation.

BALANCING REDOX EQUATIONS

Bioluminescence is the conversion of potential energy in chemical bonds into light during a redox reaction. Depending on the species, bioluminescence is produced by different chemicals and by different means. In fireflies, light results from the oxidation of the molecule luciferin.

Scientists are still unravelling the mystery of bioluminescence. Some luminescent organisms emit light constantly, whereas others emit light when they are disturbed.

Deep-sea fishes and some jellyfish appear to be able to control the light they emit, and one species of mushroom is known to emit light of two different colors.

Zoologists have also determined that some light-emitting organisms do not produce light themselves; they produce light by harboring bioluminescent bacteria.

Balancing Redox Equations Using Half-Reactions

In chemistry, a **species** is any kind of chemical unit involved in a process. In the equilibrium equation $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$, there are four species: the two molecules NH_3 and H_2O and the two ions NH_4^+ and OH^-.

Oxidation-reduction reactions occur whenever a species that can give up electrons (reducing agent) comes in contact with another species that can accept them (oxidizing agent). For example, iron can reduce many species that are oxidizing agents, including chlorine.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

In this reaction, each iron atom is oxidized by losing three electrons to become an $\mathbf{Fe^{3+}}$ ion. At the same time, each chlorine atom in Cl_2 is reduced by accepting one electron to become a $\mathbf{Cl^-}$ ion.

$$\text{Oxidation: } Fe \longrightarrow Fe^{3+} + 3e^-$$
$$\text{Reduction: } Cl_2 + 2e^- \longrightarrow 2Cl^-$$

The reaction between aqueous bromide ions and chlorine gas is a redox reaction. In this reaction, electrons are transferred from bromide ions to chlorine.

Equations such as these represent half-reactions. A **half-reaction** is one of the two parts of a redox reaction – the oxidation half or the reduction half.

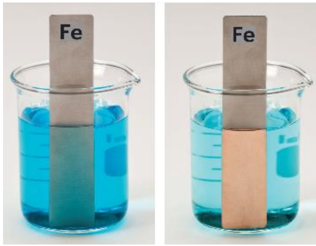
BALANCING REDOX EQUATIONS

Table 5 Redox Reactions that Oxidize Iron

Overall Reaction (unbalanced)	Oxidation Half-Reaction	Reduction Half-Reaction
$Fe + O_2 \rightarrow Fe_2O_3$	$Fe \rightarrow Fe^{3+} + 3e^-$	$O_2 + 4e^- \rightarrow 2O^{2-}$
$Fe + F_2 \rightarrow FeF_3$		$F_2 + 2e^- \rightarrow 2F^-$
$Fe + HBr \rightarrow H_2 + FeBr_3$		$2H^+ + 2e^- \rightarrow H_2$
$Fe + AgNO_3 \rightarrow Ag + Fe(NO_3)_3$		$Ag^+ + e^- \rightarrow Ag$
$Fe + CuSO_4 \rightarrow Cu + Fe_2(SO_4)_3$		$Cu^{2+} + 2e^- \rightarrow Cu$

You will learn more about the importance of half-reactions when you study electrochemistry. For now, however, you can learn to use half-reactions to balance a redox equation.

For example, the following unbalanced equation represents the reaction that occurs when you put an **iron nail** into a solution of **copper(II) sulfate**, as shown in the figure.



$$Fe(s) + CuSO_4(aq) \rightarrow Cu(s) + Fe_2(SO_4)_3(aq)$$

Iron atoms are **oxidized** as they lose electrons to the copper(II) ions. The steps for balancing redox equations by using half-reactions are shown in **Table 6**.

Table 6 The Half-Reaction Method

1. Write the unbalanced, net ionic equation for the reaction, omitting spectator ions. $Fe + Cu^{2+} + SO_4^{2-} \rightarrow Cu + 2Fe^{3+} + 3SO_4^{2-}$ $Fe + Cu^{2+} \rightarrow Cu + 2Fe^{3+}$
2. Write separate, incomplete equations for the oxidation and reduction half-reactions, including oxidation numbers. $\overset{0}{Fe} \rightarrow \overset{+3}{2Fe^{3+}}$ (oxidation) $\quad \overset{+2}{Cu^{2+}} \rightarrow \overset{0}{Cu}$ (reduction)
3. Balance the atoms in the half-reactions. Balance the charges in each half-reaction by adding electrons as reactants or products. $2Fe \rightarrow 2Fe^{3+} + 6e^-$ $\quad Cu^{2+} + 2e^- \rightarrow Cu$
4. Adjust the coefficients so that the number of electrons lost in oxidation equals the number of electrons gained in reduction. $2Fe \rightarrow 2Fe^{3+} + 6e^-$ $\quad 3Cu^{2+} + 6e^- \rightarrow 3Cu$
5. Add the half-reactions and cancel or reduce like terms on both sides of the equation. $2Fe + 3Cu^{2+} \rightarrow 3Cu + 2Fe^{3+}$
6. Return spectator ions, if desired. Restore state descriptions. $2Fe(s) + 3CuSO_4(aq) \rightarrow 3Cu(s) + Fe_2(SO_4)_3(aq)$

BALANCING REDOX EQUATIONS

PROBLEM-SOLVING STRATEGY

Balancing Redox Equations

Determine which species is oxidized, which species is reduced, which species is the oxidizing agent, and which species is the reducing agent.

Do the oxidized and reduced species appear more than once on either side of the equation, or does the reaction occur in an acidic or basic solution?

No — **Oxidation-Number Method of Balancing Redox Equations**

1. Assign oxidation numbers to all of the elements.
2. Adjust the coefficients in the equation so that the oxidation numbers are equal in magnitude.
3. Balance the rest of the equation by the conventional method.

Yes — **Half-Reaction Method of Balancing Redox Equations**

1. Write the unbalanced, net ionic equation for the reaction, omitting the spectator ions.
2. Determine the oxidation and the reduction half-reactions.
3. Balance the atoms and the charges in each half-reaction.
4. Adjust the coefficients so that the number of electrons lost and the number of electrons gained is equal.
5. Combine the balanced half-reactions and return spectator ions.

Apply the Strategy

Balance the following equation using this flowchart.

$$P_4(s) + H_2O(l) \rightarrow PH_3(g) + H_2PO_2(aq)$$

The Oxidation-Number Method and its applications are not required for the EOT2 exam this year.

CHAPTER 4

REDOX REACTIONS

CHAPTER SUMMARY

Resources

- *Redox Reactions, from Glencoe Chemistry: Matter and Change ©2017*

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