Oxidation–Reduction

TOPIC 9

How Scientists Study Oxidation–Reduction

? ***Will we all drive electric cars in the future?*** **?**

It's a re-volt-olution!! After 100 years of using the internal combustion engine to run our cars and trucks, a new era is emerging—the age of the electric car.

Today, we see hybrid cars that make use of both combustion engines and batteries to power vehicles. A large car company is introducing an all-electric car. A smaller car company is already delivering an electric car. The future will see more and more cars using electric motors powered by batteries.

In this topic you will learn the essentials of changing chemical energy into electrical energy.

TOPIC

9 Oxidation–Reduction

Vocabulary

anode	electrolytic cell	redox
cathode	half-reaction	reduction
electrochemical cell	oxidation	salt bridge
electrode	oxidation number (state)	voltaic cell
electrolysis		

Topic Overview

Oxidation and reduction are important chemical reactions. They work both for our benefit, in forms such as batteries, and against us, in ways such as the corrosion of important metals. Originally, the term *oxidation* meant the combination of a substance with oxygen. *Reduction* was the opposite, the loss of oxygen. Today, both terms have a wider interpretation. They are also recognized as interdependent—one cannot occur without the other.

$$\mathrm{Mg{:}} + \cdot\ddot{\mathrm{O}}{:} \longrightarrow \mathrm{Mg}^{2+} + \left[{:}\ddot{\mathrm{O}}{:}\right]^{2-}$$

$$\mathrm{Mg} + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{MgO}$$

Figure 9-1. Chemical reaction between magnesium and oxygen: In the reaction between magnesium and oxygen, a magnesium atom transfers two electrons to an oxygen atom.

Oxidation and Reduction

When magnesium is burned in oxygen, the octet rule allows us to understand the transfer of electrons. Each magnesium atom loses two electrons as each oxygen atom gains two electrons. Both atoms acquire a stable octet, as shown in Figure 9-1.

The same electron transfer occurs as magnesium reacts with chlorine, as shown in Figure 9-2. Again the magnesium atom loses two electrons, while the two chlorine atoms each accept an electron, acquiring a stable octet.

In both of the equations, while the magnesium atom was losing electrons, other atoms were gaining them. **Oxidation** is defined as the loss of electrons by an atom or ion. **Reduction** is the gain of electrons by an atom or ion.

$$\mathrm{Mg{:}} + \begin{matrix}\cdot\ddot{\mathrm{Cl}}{:}\\ \cdot\ddot{\mathrm{Cl}}{:}\end{matrix} \longrightarrow \mathrm{Mg}^{2+} + 2\left[{:}\ddot{\mathrm{Cl}}{:}\right]^{-}$$

$$\mathrm{Mg} + \mathrm{Cl_2} \longrightarrow \mathrm{MgCl_2}$$

Figure 9-2. Chemical reaction between magnesium and chlorine: In the reaction between magnesium and chlorine, a magnesium atom transfers one electron to each of two chlorine atoms.

Redox Whenever one atom loses an electron, there must be another atom available to gain the electron. Neither reduction nor oxidation can ever occur alone. Whenever one occurs, the other must occur at the same time. Because these reactions must accompany each other, the two terms are often combined, and reactions in which both reduction and oxidation occur are called **redox** reactions.

Oxidation Numbers

It is not always possible to simply read an equation and determine whether atoms have exchanged electrons. However, chemists have devised a system that makes it easy to keep track of the number of electrons lost or gained by an atom in a reaction. Positive, negative, or neutral values known as **oxidation numbers (states)** can be assigned to atoms. Changes in oxidation states identify how many electrons are either gained or lost by an atom or ion. The use of these oxidation numbers also provides a more complete way to define oxidation and reduction.

- Oxidation is defined as the loss of electrons and a gain in oxidation number.
- Reduction is defined as the gain of electrons and a loss in oxidation number.

Oxidation numbers are used to identify the path of electrons in redox reactions. A simple device may help in remembering the definitions.

LEO says **GER**
LEO = **L**oss of **E**lectrons is **O**xidation
GER = **G**ain of **E**lectrons is **R**eduction

Oxidation numbers are written differently than ionic charges. The charge on the magnesium ion is 2+, while the oxidation number is written as +2. The periodic table in the *Reference Tables for Physical Setting/Chemistry* supplies some common oxidation numbers for elements in compounds.

It is important to learn the rules for assigning oxidation states to atoms in an equation. These numbers are used to identify what has been oxidized and what has been reduced. Here are some rules for assigning oxidation numbers.

1. Every uncombined element has an oxidation number of zero. In the chemical equation $2Na + Cl_2 \rightarrow 2NaCl$, both the uncombined Na and Cl_2 have oxidation numbers of 0.
2. Monatomic ions have an oxidation number equal to the ionic charge. In the equation $2Na + Cl_2 \rightarrow 2NaCl$, the sodium in the product NaCl has a charge of 1+ and an oxidation number of +1. The chlorine in NaCl has a charge of 1− and an oxidation number of −1.
3. The metals of Group 1 always have an oxidation number of +1 in compounds, and the metals of Group 2 always have an oxidation number of +2 in compounds.
4. Fluorine is always −1 in compounds. The other halogens are also −1 when they are the most electronegative element in the compound.
5. Hydrogen is +1 in compounds unless it is combined with a metal, in which case it is −1. Hydrogen is +1 in HCl but −1 in LiH.
6. Oxygen is usually −2 in compounds. When it is combined with fluorine, which is more electronegative, it is +2. Oxygen is −2 in H_2O, and +2 in OF_2. In the peroxide ion (O_2^{2-}), oxygen is −1.
   These six rules can be used to assign oxidation numbers to many atoms in equations. They can be used with the following two additional rules to calculate oxidation numbers for other elements in compounds or polyatomic ions.
7. The sum of the oxidation numbers in all compounds must be zero.
8. The sum of the oxidation numbers in polyatomic ions must be equal to the charge on the ion.

SAMPLE PROBLEM

What are the oxidation numbers of the atoms in HNO_3?

SOLUTION: Identify the known and unknown values.

Known	*Unknown*
formula HNO_3	oxidation number of H = ?
	oxidation number of N = ?
	oxidation number of O = ?

Use as many of the first six rules as possible.

Hydrogen has an oxidation number of +1 (Rule 5). Each oxygen atom has an oxidation number of −2 (Rule 6), making the total for three oxygen atoms −6.

The sum of all oxidation numbers is zero.

$$\text{oxidation number of N} + (+1) + (-6) = 0$$
$$\text{oxidation number of N} = +5$$

The oxidation number for H is +1; for N, +5; and for O, −2.

SAMPLE PROBLEM

What is the oxidation number of chromium in the dichromate ion ($Cr_2O_7^{2-}$)?

SOLUTION: Identify the known and unknown values.

Known	*Unknown*
formula $Cr_2O_7^{2-}$	oxidation number of Cr = ?

Use as many of the first six rules as possible. O has an oxidation number of −2, producing a total of −14 for the seven O atoms.

The sum of the atoms in a polyatomic ion must equal the charge on the ion.

$$2(\text{oxidation number of Cr}) + (-14) = -2$$
$$\text{oxidation number of Cr} = \frac{+12}{2}$$
$$\text{oxidation number of Cr} = +6$$

Review Questions

1. What is the sum of the oxidation numbers in the compound CO_2?

(1) 0 (2) −2 (3) −4 (4) +4

2. The oxidation number of nitrogen in N_2 is

(1) +1 (2) 0 (3) +3 (4) −3

3. What is the oxidation number of Pt in K_2PtCl_6?

(1) −2 (2) +2 (3) −4 (4) +4

4. In which substance does phosphorus have a +3 oxidation state?

(1) P_4O_{10} (3) $Ca_3(PO_4)_2$
(2) PCl_5 (4) KH_2PO_3

5. What is the oxidation number of sulfur in H_2SO_4?

(1) 0 (2) −2 (3) +6 (4) +4

6. In which substance does sulfur have a negative oxidation number?
   (1) Na_2S (2) $CaSO_4$ (3) S (4) SO_2
7. In which compound is the oxidation number of oxygen −1?
   (1) CO (2) CO_2 (3) H_2O (4) H_2O_2
8. Oxygen has an oxidation number of −2 in
   (1) O_2 (2) NO_2 (3) Na_2O_2 (4) OF_2
9. Oxygen will have a positive oxidation number when combined with
   (1) fluorine (3) bromine
   (2) chlorine (4) iodine
10. In which compound does hydrogen have an oxidation number of −1?
   (1) NH_3 (3) HCl
   (2) KH (4) H_2O

Examining Redox Reactions

Sometimes it's important to know whether a reaction is redox or not. Once it has been determined that a reaction is redox, it is important to know what is oxidized, what is reduced, and what brings about oxidation and reduction.

Recognizing Redox Reactions

Not all reactions are redox reactions. To determine whether or not a reaction is redox, assign oxidation numbers to each atom, both on the reactant and product side. If there is a change in oxidation number for a particular type of atom, the reaction is redox.

Sometimes it is easy to spot a redox reaction. If an uncombined element appears on one side of an equation and is in a compound on the other side, the reaction must be a redox reaction. If you recognize a reaction as a double replacement reaction, it is not redox.

For example:

Redox: $Zn + HCl \rightarrow ZnCl_2 + H_2$

Not Redox: $NaCl + AgNO_3 \Rightarrow AgCl + NaNO_3$

Identifying Oxidation and Reduction

Once oxidation numbers are assigned, the atom that has shown an increase can be identified as the one that has undergone oxidation. The atom that has a decrease in oxidation number has undergone reduction.

Consider the following reaction.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

In the equation, chlorine has an oxidation number of −1 as a reactant in HCl. On the product side, some chlorine ions are still −1, but others have an oxidation state of 0 in Cl_2. Because the chloride ion (Cl^-) changes from a lower oxidation number to a higher one, it has been oxidized. Manganese changes from +4 as a reactant to +2 as a product. Because it changed from a higher oxidation number to a lower one, Mn^{4+} has undergone reduction.

Oxidizing Agents and Reducing Agents

In the previous reaction, Mn^{+4} underwent reduction, having received electrons from the Cl^-. The Cl^- caused the reduction of the Mn^{+4} and is called the <u>reducing agent.</u> By accepting electrons from Cl^-, the Mn^{+4}

caused the Cl^- to be oxidized. The Mn^{+4} is the oxidizing agent. In summary,

- the substance oxidized is the reducing agent.
- the substance reduced is the oxidizing agent.

Review Questions

11. Which equation represents an oxidation-reduction reaction?

(1) $HCl + KOH \rightarrow KCl + H_2O$
(2) $4HCl + MnO_2 \rightarrow MnCl_2 + 2H_2O + Cl_2$
(3) $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$
(4) $2HCl + FeS \rightarrow FeCl_2 + H_2S$

12. Which equation represents an oxidation-reduction reaction?

(1) $Zn + 2HCl \rightarrow ZnCl_2 + H2$
(2) $Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O$
(3) $H_2O + NH_3 \rightarrow NH^{4+} + OH^-$
(4) $H_2O + H_2O \rightarrow H_3O^+ + OH^-$

13. Which equation represents an oxidation-reduction reaction?

(1) $HCl + KOH \rightarrow KCl + H_2O$
(2) $4HCl + MnO_2 \rightarrow MnCl_2 + 2H_2O + Cl_2$
(3) $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$
(4) $2HCl + FeS \rightarrow FeCl_2 + H_2S$

14. Oxidation-reduction reactions occur because of the competition between particles for

(1) neutrons
(2) electrons
(3) protons
(4) positrons

15. Which statement correctly describes a redox reaction?

(1) Oxidation and reduction occur simultaneously.
(2) Oxidation occurs before reduction.
(3) Oxidation occurs after reduction.
(4) Oxidation occurs, but reduction does not.

16. A redox reaction is a reaction in which

(1) only reduction occurs
(2) only oxidation occurs
(3) reduction and oxidation occur at the same time
(4) reduction occurs first and then oxidation occurs

17. All redox reaction involve

(1) the gain of electrons only
(2) the loss of electrons only
(3) both the gain and the loss of electrons
(4) neither the gain nor the loss of electrons

18. Consider the following equation.

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

Which particles must be transferred from one reactant to the other reactant?

(1) ions
(2) neutrons
(3) protons
(4) electrons

19. What occurs during the reaction below?

$$4HCl + MnO_2 \rightarrow MnCl_2 + 2H_2O + Cl_2$$

(1) The manganese is reduced and its oxidation number changes from +4 to +2.
(2) The manganese is oxidized and its oxidation number changes from +4 to +2.
(3) The manganese is reduced and its oxidation number changes from +2 to +4.
(4) The manganese is oxidized and its oxidation number changes from +2 to +4.

20. What occurs when an atom is oxidized in a chemical reaction?

(1) a loss of electrons and a decrease in oxidation number
(2) a loss of electrons and an increase in oxidation number
(3) a gain of electrons and a decrease in oxidation number
(4) a gain of electrons and an increase in oxidation number

21. When a substance is oxidized, it

(1) loses protons
(2) gains protons
(3) acts as an oxidizing agent
(4) acts as a reducing agent

22. Consider the following redox reaction.

$$Co(s) + PbCl_2(aq) \rightarrow CoCl_2(aq) + Pb(s)$$

Which statement correctly describes the oxidation and reduction that occur?

(1) $Co(s)$ is oxidized and $Cl^-(aq)$ is reduced.
(2) $Co(s)$ is oxidized and $Pb^{2+}(aq)$ is reduced.
(3) $Co(s)$ is reduced and $Cl^-(aq)$ is oxidized.
(4) $Co(s)$ is oxidized and $Pb^{2+}(aq)$ is oxidized.

23. Consider the following equation.

$MnO_2(s) + 4H^+(aq) + 2Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 2Fe^{3+}(aq) + 2H_2O(\ell)$

Which species is oxidized?

(1) $H^+(aq)$
(2) $H_2O(\ell)$
(3) $Fe^{2+}(aq)$
(4) $MnO_2(s)$

24. Consider the following equation.

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

Which substance is oxidized?

(1) $Zn(s)$
(2) $HCl(aq)$
(3) $Cl^-(aq)$
(4) $H^+(aq)$

25. Consider the following redox reaction.

$Ni + Sn^{4+} \rightarrow Ni^{2+} + Sn^{2+}$

Which species has been reduced?

(1) Ni (2) Sn^{4+} (3) Ni^{2+} (4) Sn^{2+}

26. Consider the following equation.

$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$

Which species is the oxidizing agent?

(1) Fe^{3+}
(2) Sn^{2+}
(3) Fe^{2+}
(4) Sn^{4+}

27. Consider the following equation.

$Pb^0(s) + Cu^{2+}(aq) \rightarrow Pb^{2+}(aq) + Cu^0(s)$

What is the reducing agent?

(1) $Pb^{2+}(aq)$
(2) $Cu^{2+}(aq)$
(3) $Pb^0(s)$
(4) $Cu^0(s)$

28. Consider the following equation.

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$

Which species acts as the oxidizing agent?

(1) $Cu(s)$
(2) $Cu^{2+}(aq)$
(3) $Mg(s)$
(4) $Mg^{2+}(aq)$

29. In the reaction $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$, the oxidizing agent is

(1) oxygen
(2) water
(3) sulfur dioxide
(4) hydrogen sulfide

30. In the reaction $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$, the oxidizing agent is

(1) Cu (2) Cu^{2+} (3) Ag^+ (4) Ag

31. In a redox reaction, the reducing agent will

(1) lose electrons and be reduced
(2) lose electrons and be oxidized
(3) gain electrons and be reduced
(4) gain electrons and be oxidized

Half-Reactions

Chemical equations show the formulas of reactants and products, but they do not show the exchange of electrons. A **half-reaction** shows either the oxidation or reduction portion of a redox reaction, including the electrons gained or lost.

A reduction half-reaction shows an atom or ion gaining one or more electrons while its oxidation number decreases.

$$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$$

An oxidation half-reaction shows an atom or an ion losing one or more electrons while its oxidation number increases.

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$$

Like other chemical equations, half-reactions follow the law of conservation of matter; that is, there must be the same number of atoms on both sides of the arrow. Generally, in a half reaction there will only be one type of atom or ion shown on both reactant and product side of the equation.

In addition to conservation of mass, there must also be a conservation of charge. In molecular equations, because no charges are shown, the net charge is zero on both reactant and product side. In half-reactions, the net charge must be the same on both sides of the equation, but it does not necessarily equal zero.

$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	Net charge/side = 0
$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$	Net charge/side = 0
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	Net charge/side = 2+
$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$	Net charge/side = 2+

To write a half-reaction from an equation, first assign an oxidation number to each element.

$$\overset{0}{Cu} + \overset{+1}{Ag}\overset{+5}{N}\overset{-2}{O_3} \rightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{0}{Ag}$$

Then write a partial half-reaction to show the change in oxidation state.

$$\text{Oxidation: } Cu \rightarrow Cu^{2+}$$
$$\text{Reduction: } Ag^+ \rightarrow Ag$$

Then show the number of electrons needed to explain how the oxidation number changed, and to achieve a conservation of charge. Check to see that the net charge is the same on both sides of these equations.

Oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$	Net charge/side = 0
Reduction: $Ag^+ + e^- \rightarrow Ag$	Net charge/side = 0

In all redox reactions, there must be a balance between the number of electrons lost and gained. In the previous example,

$$\text{Oxidation: } Cu \rightarrow Cu^{2+} + 2e^-$$
$$\text{Reduction: } Ag^+ + e^- \rightarrow Ag$$

balance can be achieved by multiplying the reduction equation by two. Thus, there are two electrons lost and two electrons gained. $2Ag^+ + 2e^- \rightarrow 2Ag$. Since the number of electrons lost and gained are equal, we can cancel them and add the two half-reactions:

$$Cu \rightarrow Cu^{2+} + \cancel{2e^-}$$
$$2\,Ag^+ + \cancel{2e^-} \rightarrow 2Ag$$
$$2Ag^+ + Cu \rightarrow Cu^{2+} + 2Ag$$

Redox equations can be balanced by first balancing the number of electrons lost and gained. After balancing the redox portion of the equation, the remainder can be balanced by inspection.

Review Questions

32. Which half-reaction correctly represents reduction?

(1) $Fe^{2+} + 2e^- \rightarrow Fe$
(2) $Fe^{2+} + e^- \rightarrow Fe^{3+}$
(3) $Fe + 2e^- \rightarrow Fe^{2+}$
(4) $Fe + e^- \rightarrow Fe^{3+}$

33. Consider the following oxidation reduction equation.

$$Hg^{2+} + 2I^- \rightarrow Hg + I_2$$

Which equation correctly represents the half-reaction for the oxidation that occurs?

(1) $Hg^{2+} \rightarrow Hg + 2e^-$
(2) $Hg^{2+} + 2e^- \rightarrow Hg$
(3) $2I^- \rightarrow I_2 + 2e^-$
(4) $2I^- + 2e^- \rightarrow I_2$

34. Which statement describes what occurs in the following redox reaction?

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

(1) Only mass is conserved.
(2) Only charge is conserved.
(3) Both mass and charge are conserved.
(4) Neither mass nor charge is conserved.

35. Which equation is correctly balanced?
(1) $Fe^{3+} + 2Ni \rightarrow Fe^{2+} + 2Ni^{2+}$
(2) $2Fe^{3+} + Ni \rightarrow 2Fe^{2+} + Ni^{2+}$
(3) $Fe^{3+} + Ni \rightarrow Fe^{2+} + Ni^{2+}$
(4) $2Fe^{2+} + 2Ni \rightarrow 2Fe^{2+} + 2Ni^{2+}$

36. Which equation is correctly balanced?
(1) $Cr^{3+} + Mg \rightarrow Cr + Mg^{2+}$
(2) $Al^{3+} + K \rightarrow Al + K^{+}$
(3) $Sn^{4+} + H_2 \rightarrow Sn + 2H^{+}$
(4) $Br_2 + Hg \rightarrow Hg^{2+} + 2Br^{-}$

Electrochemical Cells

In redox reactions there is a chemical reaction and an exchange of electrons between the particles being oxidized and reduced. One practical use of such a reaction is in an electrochemical cell. An **electrochemical cell** involves a chemical reaction and a flow of electrons.

There are two common types of electrochemical cells. A **voltaic cell** is an electrochemical cell in which a spontaneous chemical reaction produces a flow of electrons. An **electrolytic cell** requires an electric current to force a nonspontaneous chemical reaction to occur.

Memory Jogger

A metal will react with the ion of another metal found below it on the table. For example, zinc metal will react with lead nitrate, but not with aluminum nitrate.

$Zn + Pb(NO_3)_2 \rightarrow Pb + Zn(NO_3)_2$
$Zn + Al(NO_3)_3 \rightarrow$ no reaction

Electrochemical cells have two surfaces called electrodes that can conduct electricity. An **electrode** is the site at which oxidation or reduction occurs. The electrode at which oxidation occurs is called the **anode.** The electrode at which reduction occurs is called the **cathode.**

Spontaneous Reactions—Voltaic Cells

If a strip of zinc is placed into a solution of lead nitrate, the zinc will be oxidized and the copper ions will be reduced according to the following equation.

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

The exchange of electrons takes place on the surface of the zinc, as shown by equations for the two half-reactions.

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

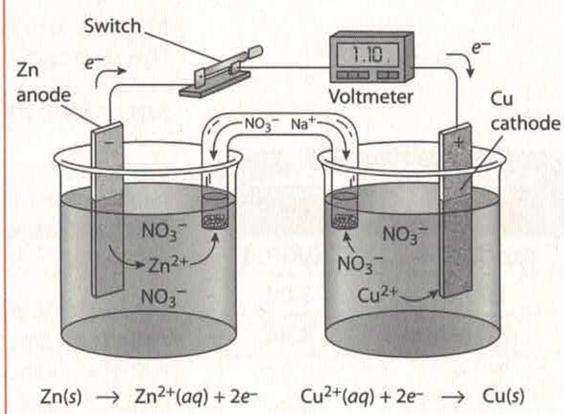


Figure 9-3. A typical voltaic cell

It is also possible to have these materials separated into two containers, so the electrons travel through a wire connecting them. In a voltaic cell, a **salt bridge** connects the two containers and provides a path for a flow of ions between the two beakers. This makes a complete circuit and allows the reaction to proceed. The diagram in Figure 9-3 shows a voltaic cell. In a voltaic cell, chemical energy is spontaneously converted to electrical energy.

In such a voltaic cell, when a strip of zinc metal is located in one beaker and copper ions are in solution in another beaker, the reaction can occur as if the solutions were in the same beaker. An electrical current is produced by separating the solutions into two beakers and forcing electrons to flow through the wire to complete the circuit.

When electrons are lost during oxidation at the anode, they travel through the wire to the cathode. At this electrode, the material being reduced gains electrons. As with all redox reactions, the substance being oxidized loses electrons, and the substance being reduced gains them. The number of electrons lost must be equal to the number of electrons gained.

(R) The Activity series in *Reference Tables for Physical Setting/Chemistry* can be used to identify the anode and cathode in a voltaic cell. Identify the two metals shown in the cell, and locate them on the table. The metal that is higher on the chart will be oxidized, and is thus the anode. The lower metal is the site of reduction and will be the cathode. Notice that the cathode itself is not reduced; it is the place where the reduction occurs. Ions in solution are reduced. To help you identify the anode and cathode, remember **RED CAT** and **AN OX.**

REDuction occurs at the **CAT**hode.
ANode is the site of **OX**idation.

SAMPLE PROBLEM

Consider the following equation.

$$Zn^0(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb^0(s)$$

Identify the anode and the cathode, and give the direction of electron flow.

SOLUTION: Identify the known and unknown values.

Known	*Unknown*
reaction equation	anode = ?
Data in Table J	cathode = ?
	direction of electron flow

Locate zinc and lead on Table J. Zinc is higher on the table. Thus, it is more reactive. Zinc will undergo oxidation and is the anode. The Pb^{2+} ions are not the cathode, but they will be reduced at the cathode. If the cell has a strip of lead metal in the beaker with the Pb^{2+} ions, the lead metal will be the cathode.

The zinc is oxidized and is losing electrons. The electrons will flow from the zinc to the lead, which is from anode to cathode. Electrons always flow from the anode to the cathode.

Table 9-1. Reduction Potentials

Ion/Metal	E^0 (Volts)
Li^+/Li	−3.04
Rb^+/Rb	−2.98
K^+/K	−2.93
Cs^+/Cs	−2.92
Ba^{2+}/Ba	−2.91
Sr^{2+}/Sr	−2.89
Ca^{2+}/Ca	−2.87
Na^+/Na	−2.71
Mg^{2+}/Mg	−2.37
Al^{3+}/Al	−1.66
Mn^{2+}/Mn	−1.19
Zn^{2+}/Zn	−0.76
Cr^{3+}/Cr	−0.74
Co^{2+}/Co	−0.28
Ni^{2+}/Ni	−0.26
Pb^{2+}/Pb	−0.13
H^+/H_2	0.00
Cu^{2+}/Cu	+0.34
Ag^+/Ag	+0.80
Au^{3+}/Au	+1.50

When a voltaic cell begins to react, the electrons flow from the anode to the cathode. A voltmeter placed in the circuit measures the electric potential between the metals in the electrodes in units of volts. Table 9-1 shows a series of reduction pairs as ions are reduced to the atomic state. The voltage for each pair is the voltage obtained when the given pair is compared to the standard hydrogen cell, which is assigned a value of 0.00 V.

The reductions at the top of the table are the least likely to occur. The more positive the E^0 value, the more likely the reduction. Thus, when Zn^{2+}/Zn and Cu^{2+}/Cu are in a voltaic cell, the reduction of Cu^{2+} to Cu will occur, while the oxidation of Zn to Zn^{2+} will supply the electrons. The voltage between the two can be calculated using the following relationship.

$$\begin{aligned} E^0_{cell} &= E^0_{reduction} - E^0_{oxidation} \\ &= E^0_{Cu^{2+}} - E^0_{Zn^{2+}} \\ &= +0.34V - (-0.76V) \\ &= +1.10V \end{aligned}$$

Nonspontaneous Reactions—Electrolytic Cells

In a voltaic cell, the electrons flow spontaneously from the anode to the cathode. In the example given, electrons from the oxidation of zinc travel through the wire to reduce lead ions. Can the reverse take place? Can the electrons travel from the lead to the zinc causing the lead metal to be oxidized and the zinc ions to be reduced? The answer is yes, but the reaction cannot occur spontaneously. There must be some electrical generator placed into the circuit to force the electrons to flow from the anode to the cathode. When electricity is used to force a chemical reaction to occur, the process is called **electrolysis.** In an automobile, both spontaneous and nonspontaneous redox reactions occur. When the car is started, a spontaneous chemical reaction occurs in the battery, providing electricity to start the car. Once the car has been started, the alternator, in a nonspontaneous reaction, recharges the battery.

Electrolysis can be used to obtain active elements such as sodium and chlorine by the electrolysis of fused (molten) salts.

$$2NaCl(\ell) \rightarrow 2Na(s) + Cl_2(g)$$

Electrolysis can also be used to electroplate metals onto a surface. The material to be plated with a metal is the cathode. The anode is made of the metal used for the plating. The electrolyte contains ions of the desired metal. Figure 9-4 shows the diagram of an apparatus used to plate silver. The anode is itself a piece of silver. As silver ions are produced by oxidation, they travel through the solution to the cathode. At the cathode, they are reduced back to silver atoms and adhere to the metal being plated.

Notice that the positive silver ions migrate away from the anode. Because like charges repel, the anode is positive in an electrolytic cell. The positive silver ions migrate through the solution toward the cathode, which must have a negative charge. The external power source forces the electrons in the wire to travel from the anode to the cathode.

Although there are distinct differences in voltaic and electrolytic cells, they also have several things in common.

- Both use redox reactions.
- The anode is the site of oxidation.
- The cathode is the site of reduction.
- The electrons flow through the wire from anode to cathode.

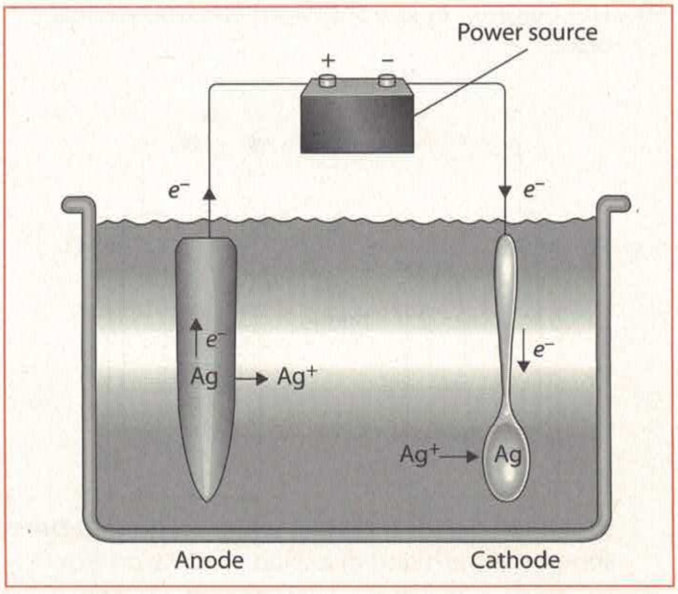


Figure 9-4. **An electroplating apparatus**

Differences between voltaic and electrolytic cells include the following.

- The redox reaction in a voltaic cell is spontaneous, but it is nonspontaneous in an electrolytic cell.
- In a voltaic cell the anode is negative and the cathode is positive. In an electrolytic cell, the anode is positive and the cathode is negative.

Review Questions

37. The type of reaction in a voltaic cell is best described as

(1) spontaneous oxidation reaction only
(2) nonspontaneous oxidation reaction only
(3) spontaneous oxidation-reduction reaction
(4) nonspontaneous oxidation-reduction reaction

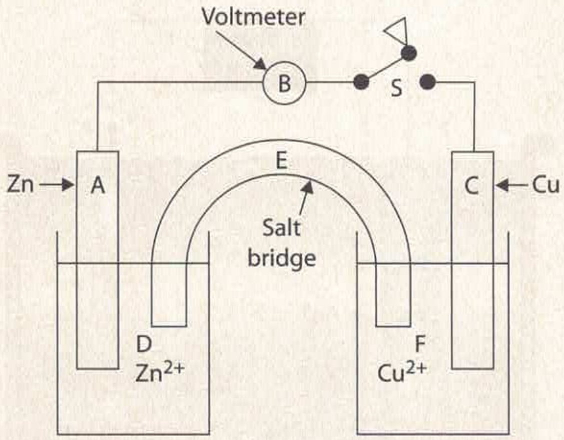
38. An electrochemical cell is made up of two half-cells connected by a salt bridge and an external conductor. What is the function of the salt bridge?

(1) to permit the migration of ions
(2) to prevent the migration of ions
(3) to permit the mixing of solutions
(4) to prevent the flow of electrons

39. Compared to the total mass and total charge at the beginning of a redox reaction, the total mass and total charge upon completion of the reaction is

(1) less
(2) greater
(3) the same
(4) dependent on what the reaction is

40. The diagram below shows an electrochemical cell.



When the switch is closed, which series of letters shows the path and direction of electron flow?

(1) ABC (2) CBA (3) DEF (4) FED

41. Consider the following equation.

$$2H_2O + \text{electricity} \rightarrow 2H_2 + O_2$$

In which type of cell would this reaction most likely occur?

(1) a voltaic cell, because it releases energy
(2) an electrolytic cell, because it releases energy
(3) a voltaic cell, because it absorbs energy
(4) an electrolytic cell, because it absorbs energy

42. In an electrolytic cell, which ion would migrate through the solution to the positive electrode?

(1) a hydrogen ion
(2) a chloride ion
(3) an ammonium ion
(4) a hydronium ion

43. The overall reaction in a chemical cell is

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

As the reaction takes place the

(1) mass of the Zn(*s*) electrode decreases
(2) mass of the Cu(*s*) electrode decreases
(3) Cu^{2+} (*aq*) concentration stays the same
(4) Zn^{2+} (*aq*) concentration stays the same

44. An electrolytic cell differs from an electrochemical cell in that the electrolytic cell

(1) involves redox
(2) is exothermic
(3) produces an electric current
(4) uses an applied electric current

45. In the electrolysis of fused (molten) silver chloride, the Ag+ ions are

(1) reduced at the negative electrode
(2) reduced at the positive electrode
(3) oxidized at the negative electrode
(4) oxidized at the positive electrode

46. In an electrolytic cell, to which electrode will a positive ion migrate and undergo reduction?

(1) The anode, which is negatively charged
(2) The anode, which is positively charged
(3) The cathode, which is negatively charged
(4) The cathode, which is positively charged

Practice Questions for the New York Regents Exam

Directions

Review the Test-Taking Strategies section of this book. Then answer the following questions. Read each question carefully and answer with a correct choice or response.

Part A

1 The oxidation number of an uncombined Group 2 metal is
(1) +1 (2) +2 (3) −2 (4) 0

2 In all oxidation-reduction reactions there is conservation of
(1) charge, but not mass
(2) mass, but not charge
(3) neither mass nor charge
(4) both mass and charge

3 During a reduction reaction there is a
(1) loss of electrons and a loss of oxidation number
(2) loss of electrons and a gain of oxidation number
(3) gain of electrons and a loss of oxidation number
(4) gain of electrons and a gain of oxidation number

4 As an atom is oxidized, the number of protons in the nucleus
(1) decreases
(2) increases
(3) remains the same
(4) depends on the atom

5 In a redox reaction, the species reduced
(1) gains electrons
(2) gains oxidation number
(3) loses electrons and is the oxidizing agent
(4) loses electrons and is the reducing agent

6 A redox reaction always involves
(1) a change in oxidation number
(2) a change of phase
(3) a transfer of protons
(4) the formation of ions

7 The function of a salt bridge in a voltaic cell is to
(1) allow the flow of electrons
(2) allow the flow of protons
(3) allow the flow of ions
(4) provide a site for electron transfer

8 Which of the following occurs in an electrolytic cell?
(1) A chemical reaction produces an electric current.
(2) An electric current produces a chemical reaction.
(3) An oxidation reaction takes place at the cathode.
(4) A reduction reaction takes place at the anode.

9 Hydrogen has an oxidation number of
(1) 0 only (3) −1 only
(2) +1 only (4) 0, +1, or −1

10 Voltaic cells differ from electrolytic cells because in a voltaic cell
(1) the cathode is positively charged
(2) the anode is positively charged
(3) electrons flow from anode to cathode
(4) electrons flow from cathode to anode

11 In a half-reaction
(1) mass only is conserved
(2) charge only is conserved
(3) both mass and charge are conserved
(4) neither mass nor charge is conserved

12 Which reaction occurs at the anode in voltaic and electrolytic cells?
(1) reduction only
(2) oxidation only
(3) both reduction and oxidation
(4) neither reduction nor oxidation

Part B

13 What is the oxidation number of carbon in $NaHCO_3$?
(1) −2 (2) +2 (3) −4 (4) +4

14 Chlorine has an oxidation state of +3 in the compound
(1) $HClO$ (2) $HClO_2$ (3) $HClO_3$ (4) $HClO_4$

15 What are the two oxidation states of nitrogen in the compound NH_4NO_3?
(1) −3 and +5 (3) +3 and +5
(2) −3 and −5 (4) +3 and −5

16 Which equation represents a redox reaction?
(1) $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$
(2) $HCl + KOH \rightarrow H_2O + KCl$
(3) $2KClO_3 \rightarrow 2KCl + 3O_2$
(4) $H_2CO_3 \rightarrow H_2O + CO_2$

17 Consider the equations A, B, C, and D.
(A) $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$
(B) $Cl_2 + H_2O \rightarrow HClO + HCl$
(C) $CuO + CO \rightarrow CO_2 + Cu$
(D) $NaOH + HCl \rightarrow NaCl + H_2O$
Which two reactions are redox equations?
(1) A and C
(2) B and C
(3) C and D
(4) A and D

18 In the reaction $AgNO_3(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + AgCl(s)$, the reactants
(1) gain electrons only
(2) lose electrons only
(3) both gain and lose electrons
(4) neither gain nor lose electrons

19 In the reaction $Cl_2 + H_2O \rightarrow HClO + HCl$, hydrogen is
(1) oxidized only
(2) reduced only
(3) both oxidized and reduced
(4) neither oxidized nor reduced

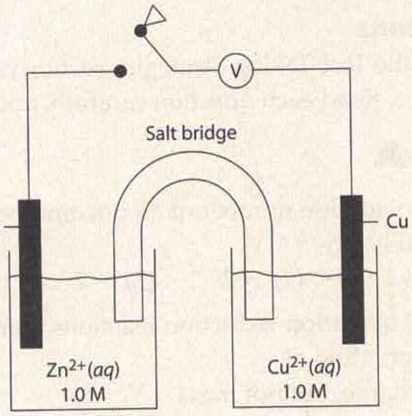
20 In the reaction $2KCl(\ell) \rightarrow 2K(s) + Cl_2(g)$, the K^+ ions are
(1) reduced by losing electrons
(2) reduced by gaining electrons
(3) oxidized by losing electrons
(4) oxidized by gaining electrons

21 Which equation correctly represents a reduction half-reaction?
(1) $Sn^0 + 2e^- \rightarrow Sn^{2+}$
(2) $Na^0 + e^- \rightarrow Na^+$
(3) $Li^0 + e^- \rightarrow Li^+$
(4) $Br_2{}^0 + 2e^- \rightarrow 2Br^-$

22 In the reaction $Mg + Cl_2 \rightarrow MgCl_2$, the correct half-reaction for the oxidation that occurs is
(1) $Mg + 2e^- \rightarrow Mg^{2+}$
(2) $Cl_2 + 2e^- \rightarrow 2Cl^-$
(3) $Mg \rightarrow Mg^{2+} + 2e^-$
(4) $Cl_2 \rightarrow 2Cl^- + 2e^-$

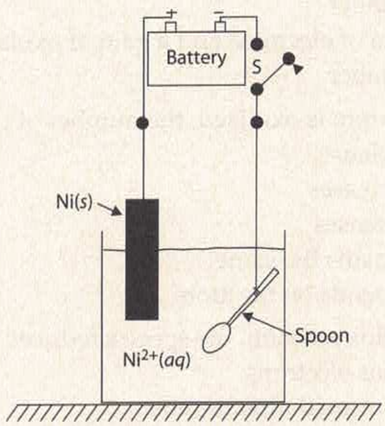
23 In an electrolytic cell, which ion would migrate through the solution to the positive electrode?
(1) a hydrogen ion
(2) a chloride ion
(3) an ammonium ion
(4) a hydronium ion

24 The diagram below represents a voltaic cell.



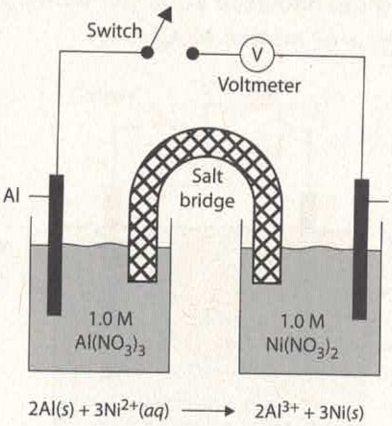
What occurs when the switch is closed?
(1) Zn is reduced.
(2) Cu is oxidized.
(3) Electrons flow from Cu to Zn.
(4) Electrons flow from Zn to Cu.

25 The diagram below shows a spoon that will be electroplated with nickel metal. What will occur when switch S is closed?



(1) The spoon will lose mass, and the Ni(s) will be reduced.
(2) The spoon will lose mass, and the Ni(s) will be oxidized.
(3) The spoon will gain mass, and the Ni(s) will be reduced.
(4) The spoon will gain mass, and the Ni(s) will be oxidized.

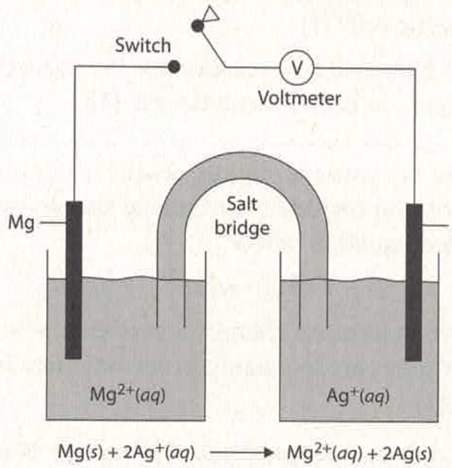
26 The diagram below represents a chemical cell.



When the switch is closed, electrons flow from

(1) $Al(s)$ to $Ni(s)$
(2) $Ni(s)$ to $Al(s)$
(3) $Al^{3+}(aq)$ to $Ni^{2+}(aq)$
(4) $Ni^{2+}(aq)$ to $Al^{3+}(aq)$

27 The diagram below represents a voltaic cell.



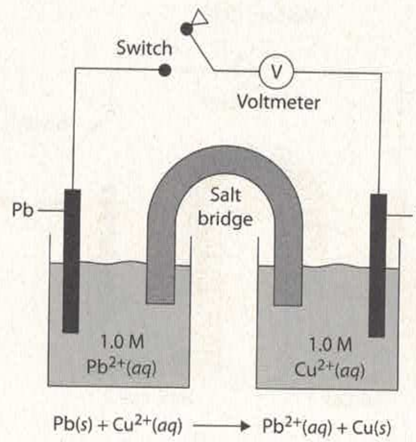
Which species is oxidized when the switch is closed?

(1) $Mg(s)$
(2) $Mg^{2+}(aq)$
(3) $Ag(s)$
(4) $Ag^{+}(aq)$

28 The overall reaction in an electrochemical cell is $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}$. As the reaction in this cell takes place,

(1) oxidation occurs at the cathode
(2) the Cu^{2+} is oxidized
(3) the concentration of Zn^{2+} increases
(4) the concentration of Cu^{2+} increases

29 The diagram below represents an electrochemical cell.



Which change occurs when the switch is closed?

(1) Pb is oxidized, and electrons flow to the Cu electrode.
(2) Pb is reduced, and electrons flow to the Cu electrode.
(3) Cu is oxidized, and electrons flow to the Pb electrode.
(4) Cu is reduced, and electrons flow to the Pb electrode.

30 Consider the following equation.

$$2Cr(s) + 3Cu^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cu(s)$$

Which reaction occurs at the cathode in this voltaic cell?

(1) reduction of $Cu^{2+}(aq)$
(2) reduction of $Cu(s)$
(3) oxidation of $Cr^{3+}(aq)$
(4) oxidation of $Cr(s)$

Part C

Use the following balanced equation for questions 31 and 32.

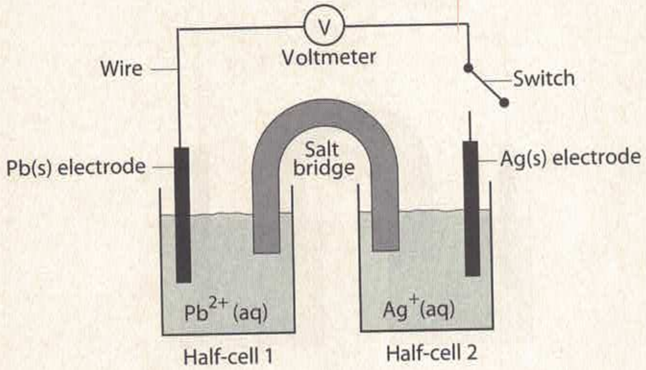
Given the reaction: $4\,Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

31 Write the balanced oxidation half-reaction for this oxidation-reduction reaction.

32 What is the oxidation number of oxygen in Al_2O_3?

Base your answers to questions 33 through 37 on the diagram of the voltaic cell below.

Voltaic Cell



$$2\,Ag^{+}(aq) + Pb(s) \longrightarrow Pb^{2+}(aq) + 2\,Ag(s)$$

33 What is the direction of the electron flow through the wire? [1]

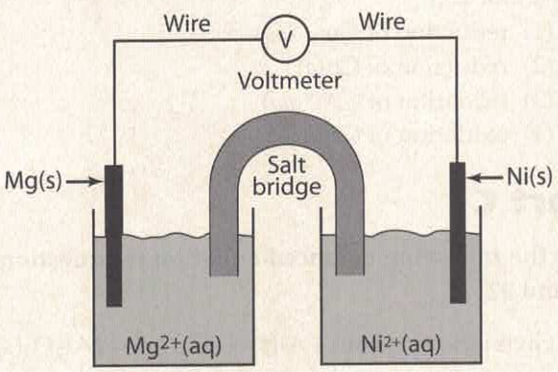
34 Write an equation for the half-reaction that occurs at the silver electrode. [1]

35 Explain the function of the salt bridge. [1]

36 When the switch is closed, in which half-cell does oxidation occur? [1]

37 Write the half-reaction that occurs in half-cell 1. [1]

Base your answers to questions 38 through 40 on the diagram of a voltaic cell below.



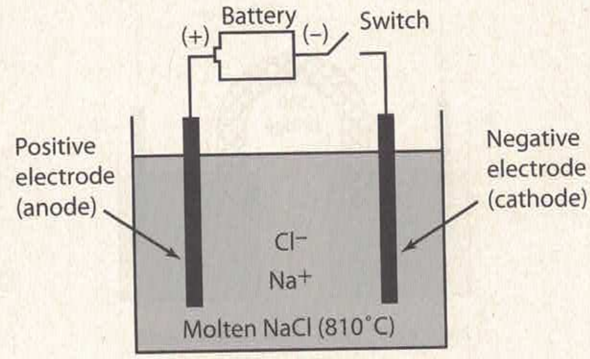
$$Mg(s) + Ni^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Ni(s)$$

38 What is the total number of moles of electrons needed to completely reduce 6.0 moles of Ni^{2+}(*aq*) ions? [1]

39 Identify one metal from Reference Table J that is more easily oxidized than Mg(*s*). [1]

40 As the cell operates, the mass of the Mg(*s*) decreases. Explain, in terms of particles, why this decrease occurs. [1]

Base your answers to questions 41 through 43 on the diagram and the balanced equation which represent the electrolysis of molten NaCl.



$$2NaCl \longrightarrow Cl_2 + 2Na$$

41 When the switch is closed, which electrode will attract the sodium ion? [1]

42 What is the purpose of the battery in this electrolytic cell? [1]

43 Write a balanced half-reaction for the reduction that occurs in this electrolytic cell. [1]

---

44 Because tap water is slightly acidic, water pipes made of iron corrode over time, as shown by the balanced equation below:

$$2Fe + 6H^{+} \rightarrow 2Fe^{3+} + 3H_2$$

Explain, in terms of chemical reactivity, why copper pipes are less likely to corrode than iron pipes. [1]

Base your answers to questions 45 through 47 on the information below.

A flashlight can be powered by a rechargeable nickel-cadmium battery. In the battery, the anode is Cd(*s*) and the cathode is NiO_2(*s*). The unbalanced equation below represents the reaction that occurs as the battery produces electricity. When a nickel-cadmium battery is recharged, the reverse reaction takes place.

$$Cd(s) + NiO_2(s) + H_2O(l) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

45 Balance the equation for the reaction that produces electricity using the smallest whole-number coefficients. [1]

46 Determine the change in oxidation number for the element that makes up the anode in the reaction that produces electricity. [1]

47 Explain why Cd would be above Ni if placed on Table J. [1]