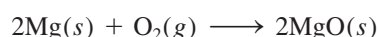


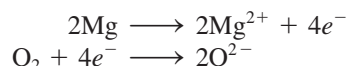
4.4 Oxidation-Reduction Reactions

Whereas acid-base reactions can be characterized as proton-transfer processes, the class of reactions called **oxidation-reduction**, or **redox, reactions** are considered *electron-transfer reactions*. Oxidation-reduction reactions are very much a part of the world around us. They range from the burning of fossil fuels to the action of household bleach. Additionally, most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction.

Many important redox reactions take place in water, but not all redox reactions occur in aqueous solution. We begin our discussion with a reaction in which two elements combine to form a compound. Consider the formation of magnesium oxide (MgO) from magnesium and oxygen (Figure 4.9):

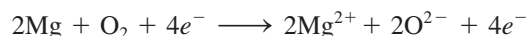


Magnesium oxide (MgO) is an ionic compound made up of Mg^{2+} and O^{2-} ions. In this reaction, two Mg atoms give up or transfer four electrons to two O atoms (in O_2). For convenience, we can think of this process as two separate steps, one involving the loss of four electrons by the two Mg atoms and the other being the gain of four electrons by an O_2 molecule:

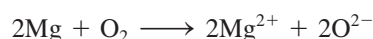


Note that in an oxidation half-reaction, electrons appear as the product; in a reduction half-reaction, electrons appear as the reactant.

Each of these steps is called a **half-reaction**, which *explicitly shows the electrons involved in a redox reaction*. The sum of the half-reactions gives the overall reaction:



or, if we cancel the electrons that appear on both sides of the equation,



Finally, the Mg^{2+} and O^{2-} ions combine to form MgO:

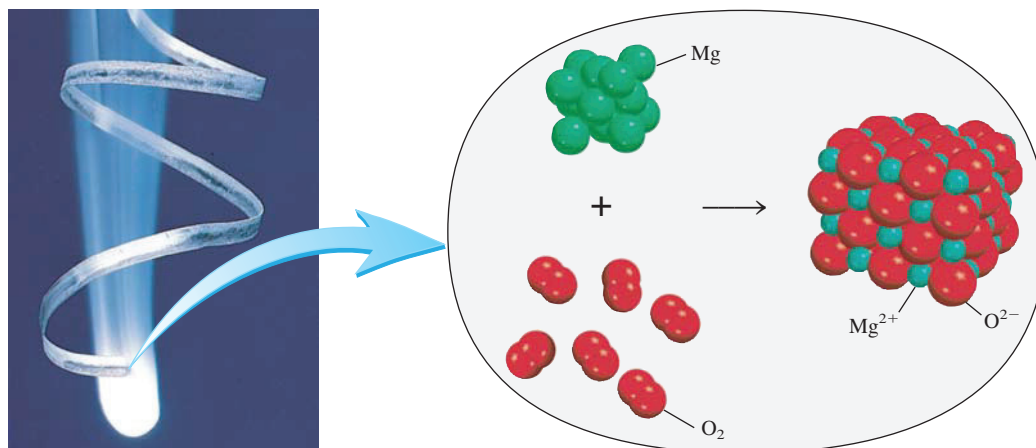
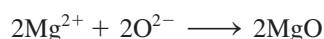


Figure 4.9 Magnesium burns in oxygen to form magnesium oxide.

A useful mnemonic for redox is OILRIG:
Oxidation Is Loss (of electrons) and
Reduction Is Gain (of electrons).

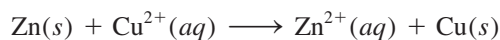
Oxidizing agents are always reduced and
reducing agents are always oxidized. This
statement may be somewhat confusing,
but it is simply a consequence of the
definitions of the two processes.

The term **oxidation reaction** refers to the *half-reaction that involves loss of electrons*. Chemists originally used “oxidation” to denote the combination of elements with oxygen. However, it now has a broader meaning that includes reactions not involving oxygen. A **reduction reaction** is a *half-reaction that involves gain of electrons*. In the formation of magnesium oxide, magnesium is oxidized. It is said to act as a **reducing agent** because it *donates electrons* to oxygen and causes oxygen to be reduced. Oxygen is reduced and acts as an **oxidizing agent** because it *accepts electrons* from magnesium, causing magnesium to be oxidized. Note that the extent of oxidation in a redox reaction must be equal to the extent of reduction; that is, the number of electrons lost by a reducing agent must be equal to the number of electrons gained by an oxidizing agent.

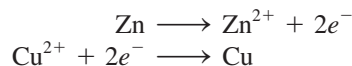
The occurrence of electron transfer is more apparent in some redox reactions than others. When metallic zinc is added to a solution containing copper(II) sulfate (CuSO_4), zinc reduces Cu^{2+} by donating two electrons to it:



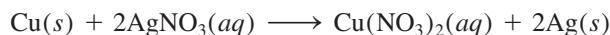
In the process, the solution loses the blue color that characterizes the presence of hydrated Cu^{2+} ions (Figure 4.10):



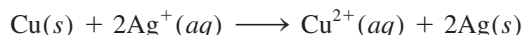
The oxidation and reduction half-reactions are



Similarly, metallic copper reduces silver ions in a solution of silver nitrate (AgNO_3):

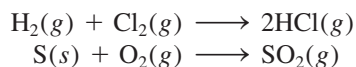


or



Oxidation Number

The definitions of oxidation and reduction in terms of loss and gain of electrons apply to the formation of ionic compounds such as MgO and the reduction of Cu^{2+} ions by Zn . However, these definitions do not accurately characterize the formation of hydrogen chloride (HCl) and sulfur dioxide (SO_2):



Because HCl and SO_2 are not ionic but molecular compounds, no electrons are actually transferred in the formation of these compounds, as they are in the case of MgO . Nevertheless, chemists find it convenient to treat these reactions as redox reactions because experimental measurements show that there is a partial transfer of electrons (from H to Cl in HCl and from S to O in SO_2).

To keep track of electrons in redox reactions, it is useful to assign oxidation numbers to the reactants and products. An atom's **oxidation number**, also called **oxidation state**, signifies the *number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely*. For

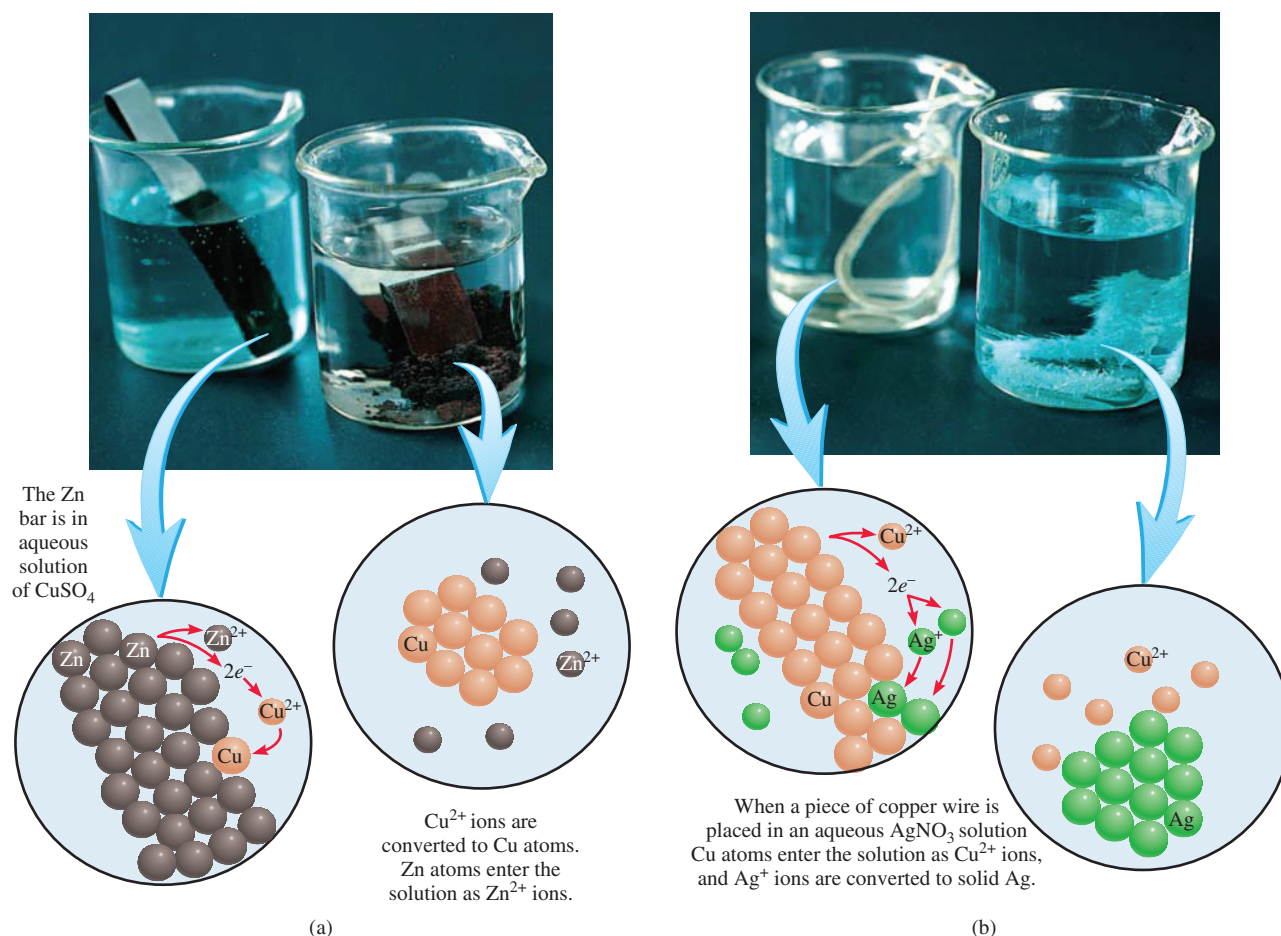
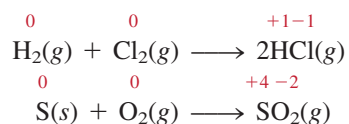


Figure 4.10 Metal displacement reactions in solution. (a) First beaker: A zinc strip is placed in a blue CuSO_4 solution. Immediately Cu^{2+} ions are reduced to metallic Cu in the form of a dark layer. Second beaker: In time, most of the Cu^{2+} ions are reduced and the solution becomes colorless. (b) First beaker: A piece of Cu wire is placed in a colorless AgNO_3 solution. Ag^+ ions are reduced to metallic Ag. Second beaker: As time progresses, most of the Ag^+ ions are reduced and the solution acquires the characteristic blue color due to the presence of hydrated Cu^{2+} ions.

example, we can rewrite the previous equations for the formation of HCl and SO_2 as follows:



The numbers above the element symbols are the oxidation numbers. In both of the reactions shown, there is no charge on the atoms in the reactant molecules. Thus, their oxidation number is zero. For the product molecules, however, it is assumed that complete electron transfer has taken place and that atoms have gained or lost electrons. The oxidation numbers reflect the number of electrons “transferred.”

Oxidation numbers enable us to identify elements that are oxidized and reduced at a glance. The elements that show an increase in oxidation number—hydrogen and sulfur in the preceding examples—are oxidized. Chlorine and oxygen are reduced, so their oxidation numbers show a decrease from their initial values. Note that the sum

of the oxidation numbers of H and Cl in HCl (+1 and -1) is zero. Likewise, if we add the charges on S (+4) and two atoms of O [$2 \times (-2)$], the total is zero. The reason is that the HCl and SO_2 molecules are neutral, so the charges must cancel.

We use the following rules to assign oxidation numbers:

1. In free elements (that is, in the uncombined state), each atom has an oxidation number of zero. Thus, each atom in H_2 , Br_2 , Na, Be, K, O_2 , and P_4 has the same oxidation number: zero.
2. For ions composed of only one atom (that is, monatomic ions), the oxidation number is equal to the charge on the ion. Thus, Li^+ ion has an oxidation number of +1; Ba^{2+} ion, +2; Fe^{3+} ion, +3; I^- ion, -1 ; O^{2-} ion, -2 ; and so on. All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.
3. The oxidation number of oxygen in most compounds (for example, MgO and H_2O) is -2 , but in hydrogen peroxide (H_2O_2) and peroxide ion (O_2^{2-}), it is -1 .
4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds. In these cases (for example, LiH , NaH , CaH_2), its oxidation number is -1 .
5. Fluorine has an oxidation number of -1 in *all* its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen—for example in oxoacids and oxoanions (see Section 2.7)—they have positive oxidation numbers.
6. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion, NH_4^+ , the oxidation number of N is -3 and that of H is +1. Thus the sum of the oxidation numbers is $-3 + 4(+1) = +1$, which is equal to the net charge of the ion.
7. Oxidation numbers do not have to be integers. For example, the oxidation number of O in the superoxide ion, O_2^- , is $-\frac{1}{2}$.

We apply the preceding rules to assign oxidation numbers in Example 4.4.

EXAMPLE 4.4

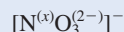
Assign oxidation numbers to all the elements in the following compounds and ion: (a) Li_2O , (b) HNO_3 , (c) $\text{Cr}_2\text{O}_7^{2-}$.

Strategy In general, we follow the rules just listed for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1, and in most cases hydrogen has an oxidation number of +1 and oxygen has an oxidation number of -2 in their compounds.

Solution (a) By rule 2 we see that lithium has an oxidation number of +1 (Li^+) and oxygen's oxidation number is -2 (O^{2-}).
(b) This is the formula for nitric acid, which yields a H^+ ion and a NO_3^- ion in solution. From rule 4 we see that H has an oxidation number of +1. Thus the other group (the nitrate ion) must have a net oxidation number of -1 . Oxygen has an

(Continued)

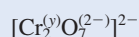
oxidation number of -2 , and if we use x to represent the oxidation number of nitrogen, then the nitrate ion can be written as



so that $x + 3(-2) = -1$

or $x = +5$

- (c) From rule 6 we see that the sum of the oxidation numbers in the dichromate ion $\text{Cr}_2\text{O}_7^{2-}$ must be -2 . We know that the oxidation number of O is -2 , so all that remains is to determine the oxidation number of Cr, which we call y . The dichromate ion can be written as



so that $2(y) + 7(-2) = -2$

or $y = +6$

Check In each case, does the sum of the oxidation numbers of all the atoms equal the net charge on the species?

Figure 4.11 shows the known oxidation numbers of the familiar elements, arranged according to their positions in the periodic table. We can summarize the content of this figure as follows:

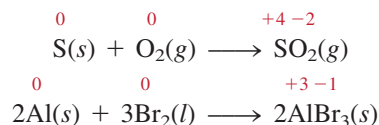
- Metallic elements have only positive oxidation numbers, whereas nonmetallic elements may have either positive or negative oxidation numbers.
- The highest oxidation number an element in Groups 1A–7A can have is its group number. For example, the halogens are in Group 7A, so their highest possible oxidation number is $+7$.
- The transition metals (Groups 1B, 3B–8B) usually have several possible oxidation numbers.

Types of Redox Reactions

Among the most common oxidation-reduction reactions are combination, decomposition, combustion, and displacement reactions. A more involved type is called disproportionation reactions, which will also be discussed in this section.

Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single product. Figure 4.12 shows some combination reactions. For example,



Not all combination reactions are redox in nature. The same holds for decomposition reactions.

1 1A																18 8A	
1 H $+1$ -1																2 He	
2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	
3 Li $+1$	4 Be $+2$											5 B $+3$	6 C $+4$ $+2$ -4	7 N $+5$ $+4$ $+3$ $+2$ $+1$ -3	8 O $+2$ -1 -2	9 F -1	10 Ne
11 Na $+1$	12 Mg $+2$											13 Al $+3$	14 Si $+4$ -4	15 P $+5$ $+3$ -3	16 S $+6$ $+4$ $+2$ -2	17 Cl $+7$ $+6$ $+5$ $+4$ $+3$ $+1$ -1	18 Ar
		3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B						
19 K $+1$	20 Ca $+2$	21 Sc $+3$	22 Ti $+4$ $+3$ $+2$	23 V $+5$ $+4$ $+3$ $+2$	24 Cr $+6$ $+5$ $+4$ $+3$ $+2$	25 Mn $+7$ $+6$ $+4$ $+3$ $+2$	26 Fe $+3$ $+2$	27 Co $+3$ $+2$	28 Ni $+2$	29 Cu $+2$ $+1$	30 Zn $+2$	31 Ga $+3$	32 Ge $+4$ -4	33 As $+5$ $+3$ -3	34 Se $+6$ $+4$ -2	35 Br $+5$ $+3$ $+1$ -1	36 Kr $+4$ $+2$
37 Rb $+1$	38 Sr $+2$	39 Y $+3$	40 Zr $+4$	41 Nb $+5$ $+4$	42 Mo $+6$ $+4$ $+3$	43 Tc $+7$ $+6$ $+4$	44 Ru $+8$ $+6$ $+4$ $+3$	45 Rh $+4$ $+3$ $+2$	46 Pd $+4$ $+2$	47 Ag $+1$	48 Cd $+2$	49 In $+3$	50 Sn $+4$ $+2$	51 Sb $+5$ $+3$ -3	52 Te $+6$ $+4$ -2	53 I $+7$ $+5$ $+1$ -1	54 Xe $+6$ $+4$ $+2$
55 Cs $+1$	56 Ba $+2$	57 La $+3$	72 Hf $+4$	73 Ta $+5$	74 W $+6$ $+4$	75 Re $+7$ $+6$ $+4$	76 Os $+8$ $+4$	77 Ir $+4$ $+3$	78 Pt $+4$ $+2$	79 Au $+3$ $+1$	80 Hg $+2$ $+1$	81 Tl $+3$ $+1$	82 Pb $+4$ $+2$	83 Bi $+5$ $+3$	84 Po $+2$	85 At -1	86 Rn

Figure 4.11 The oxidation numbers of elements in their compounds. The more common oxidation numbers are in color.



(a)



(b)



(c)

Figure 4.12 Some simple combination redox reactions. (a) Sulfur burning in air to form sulfur dioxide. (b) Sodium burning in chlorine to form sodium chloride. (c) Aluminum reacting with bromine to form aluminum bromide.

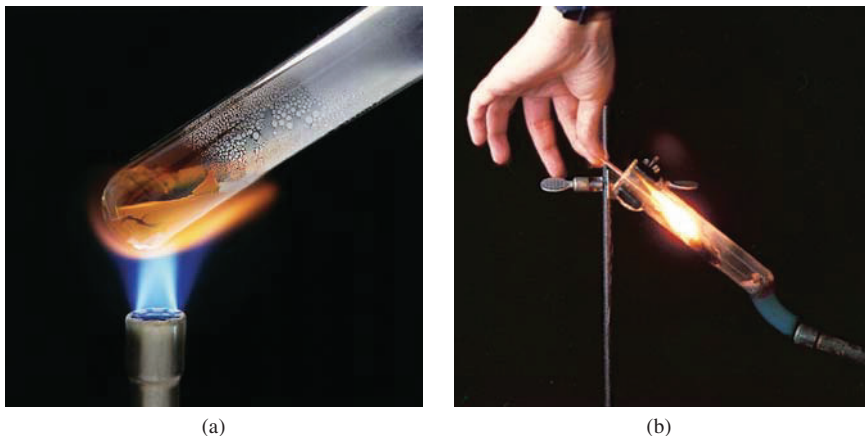
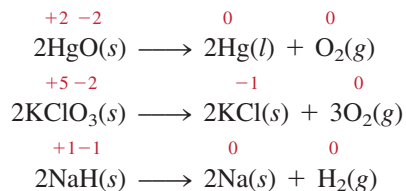


Figure 4.13 (a) On heating, mercury(II) oxide (HgO) decomposes to form mercury and oxygen. (b) Heating potassium chlorate (KClO_3) produces oxygen, which supports the combustion of the wood splint.

Decomposition Reactions

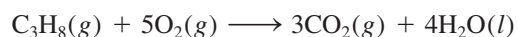
Decomposition reactions are the opposite of combination reactions. Specifically, a **decomposition reaction** is the breakdown of a compound into two or more components (Figure 4.13). For example,



We show oxidation numbers only for elements that are oxidized or reduced.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen, usually with the release of heat and light to produce a flame. The reactions between magnesium and sulfur with oxygen described earlier are combustion reactions. Another example is the burning of propane (C_3H_8), a component of natural gas that is used for domestic heating and cooking:



Assigning an oxidation number to C atoms in organic compounds is more involved. Here, we focus only on the oxidation number of O atoms, which changes from 0 to -2 .



(a)



(b)

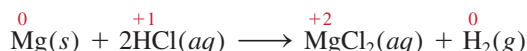
Figure 4.14 Reactions of (a) sodium (Na) and (b) calcium (Ca) with cold water. Note that the reaction is more vigorous with Na than with Ca .

19.1 Redox Reactions

Electrochemistry is the branch of chemistry that deals with the interconversion of electrical energy and chemical energy. Electrochemical processes are redox (oxidation-reduction) reactions in which the energy released by a spontaneous reaction is converted to electricity or in which electrical energy is used to cause a nonspontaneous reaction to occur. Although redox reactions were discussed in Chapter 4, it is helpful to review some of the basic concepts that will come up again in this chapter.

In redox reactions, electrons are transferred from one substance to another. The reaction between magnesium metal and hydrochloric acid is an example of a redox reaction:

Rules for assigning oxidation numbers are presented in Section 4.4.



Recall that the numbers above the elements are the oxidation numbers of the elements. The loss of electrons by an element during oxidation is marked by an increase in the element's oxidation number. In reduction, there is a decrease in oxidation number resulting from a gain of electrons by an element. In the preceding reaction, Mg metal is oxidized and H^+ ions are reduced; the Cl^- ions are spectator ions.

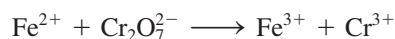
Balancing Redox Equations

Balancing redox reaction on AP will be very simple with just balancing electrons. There will be no acid, base, extra water type problems. Chang's level of difficulty in these examples would be found in some college classes. though.

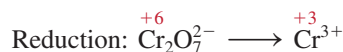
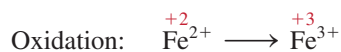
Equations for redox reactions like the preceding one are relatively easy to balance. However, in the laboratory we often encounter more complex redox reactions involving oxoanions such as chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), permanganate (MnO_4^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}). In principle, we can balance any redox equation using the procedure outlined in Section 3.7, but there are some special techniques for handling redox reactions, techniques that also give us insight into electron transfer processes. Here we will discuss one such procedure, called the *ion-electron method*. In this approach, the overall reaction is divided into two half-reactions, one for oxidation and one for reduction. The equations for the two half-reactions are balanced separately and then added together to give the overall balanced equation.

Suppose we are asked to balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) in an acidic medium. As a result, the $\text{Cr}_2\text{O}_7^{2-}$ ions are reduced to Cr^{3+} ions. The following steps will help us balance the equation.

Step 1: Write the unbalanced equation for the reaction in ionic form.



Step 2: Separate the equation into two half-reactions.



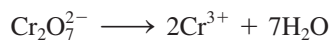
Step 3: Balance each half-reaction for number and type of atoms and charges. For reactions in an acidic medium, add H_2O to balance the O atoms and H^+ to balance the H atoms.

Oxidation half-reaction: The atoms are already balanced. To balance the charge, we add an electron to the right-hand side of the arrow:

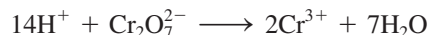


In an oxidation half-reaction, electrons appear as a product; in a reduction half-reaction, electrons appear as a reactant.

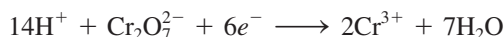
Reduction half-reaction: Because the reaction takes place in an acidic medium, we add seven H_2O molecules to the right-hand side of the arrow to balance the O atoms:



To balance the H atoms, we add 14 H^+ ions on the left-hand side:

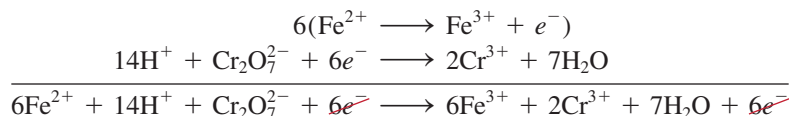


There are now 12 positive charges on the left-hand side and only six positive charges on the right-hand side. Therefore, we add six electrons on the left

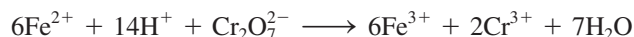


Step 4: Add the two half-equations together and balance the final equation by inspection. The electrons on both sides must cancel. If the oxidation and reduction half-reactions contain different numbers of electrons, we need to multiply one or both half-reactions to equalize the number of electrons.

Here we have only one electron for the oxidation half-reaction and six electrons for the reduction half-reaction, so we need to multiply the oxidation half-reaction by 6 and write



The electrons on both sides cancel, and we are left with the balanced net ionic equation:



Step 5: Verify that the equation contains the same type and numbers of atoms and the same charges on both sides of the equation.

A final check shows that the resulting equation is “atomically” and “electrically” balanced.

For reactions in a basic medium, we proceed through step 4 as if the reaction were carried out in an acidic medium. Then, for every H^+ ion we add an equal number of OH^- ions to *both* sides of the equation. Where H^+ and OH^- ions appear on the same side of the equation, we combine the ions to give H_2O . Example 19.1 illustrates this procedure.

EXAMPLE 19.1

Write a balanced ionic equation to represent the oxidation of iodide ion (I^-) by permanganate ion (MnO_4^-) in basic solution to yield molecular iodine (I_2) and manganese(IV) oxide (MnO_2).

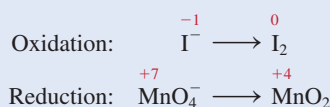
Strategy We follow the preceding procedure for balancing redox equations. Note that the reaction takes place in a basic medium.

Solution *Step 1:* The unbalanced equation is



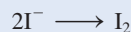
(Continued)

Step 2: The two half-reactions are

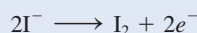


Step 3: We balance each half-reaction for number and type of atoms and charges.

Oxidation half-reaction: We first balance the I atoms:



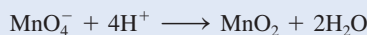
To balance charges, we add two electrons to the right-hand side of the equation:



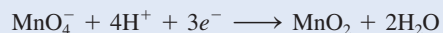
Reduction half-reaction: To balance the O atoms, we add two H_2O molecules on the right:



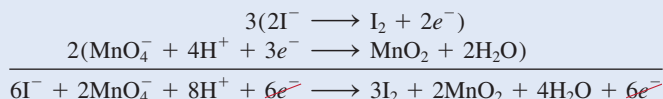
To balance the H atoms, we add four H^+ ions on the left:



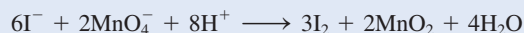
There are three net positive charges on the left, so we add three electrons to the same side to balance the charges:



Step 4: We now add the oxidation and reduction half reactions to give the overall reaction. In order to equalize the number of electrons, we need to multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2 as follows:



The electrons on both sides cancel, and we are left with the balanced net ionic equation:



This is the balanced equation in an acidic medium. However, because the reaction is carried out in a basic medium, for every H^+ ion we need to add equal number of OH^- ions to both sides of the equation:



Finally, combining the H^+ and OH^- ions to form water, we obtain



Step 5: A final check shows that the equation is balanced in terms of both atoms and charges.