Writing Redox Reactions

Objective

To gain a better understanding of the processes of oxidation and reduction by balancing oxidation-reduction, redox, reactions.

Introduction

The **oxidation state** is the imaginary charge an atom would have if shared electrons were divided equally between identical atoms bound to one another, or, for different atoms, if electrons were all assigned to the atom in each bond that has the greater attraction for electrons. **Oxidation** corresponds to an increase in the oxidation number. The compound being oxidized is the **reducing agent**. The reducing agent causes a gain in electrons, a loss of oxygen atoms, or a gain of hydrogen atoms. **Reduction** corresponds to a decrease in oxidation number. The compound being reduced is the **oxidizing agent**. The oxidizing agent causes a loss of electrons, a gain of oxygen atoms, or a loss of hydrogen atoms.

Oxidation States for Common Reagents

Much useful information about the behavior of oxidizing and reducing agents under various conditions can be summarized in the form of charts. Such charts for some common elements are presented in Table 5.1 on page 42 and are repeated again in later experiments where these elements are studied in greater detail. The charts, with their comments on the behavior of the various compounds, will help you predict the probable changes in oxidation state in a particular reaction. Note that the oxidation state is given just before each formula in the chart.
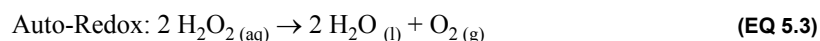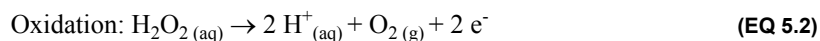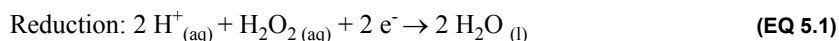
TABLE 5.1

		Oxidation State	Formulas	Comments
		Sulfur Compounds		
↑ o	↓ r	+6	SO_3, H_2SO_4, SO_4^{2-}	Concentrated acid is a strong oxidizing agent.
		+4	SO_2, H_2SO_3, SO_3^{2-}	Active either as oxidizing agent or reducing agent.
		+2	$S_2O_3^{2-}$	Thiosulfate ion decomposes to S and H_2SO_3 in acid solution. Oxidized to $S_4O_6^{2-}$ (tetrathionate ion) by free I_2.
		0	S	
		−1	S_2^{2-} or S_x^{2-}	Polysulfide ion decomposes to S and H_2S in acid solution.
		−2	H_2S, S^{2-}	Strong reducing agent, usually oxidized to S.
		Oxygen Compounds, Peroxides		
↑ o	↓ r		**Acidic Basic**	
		0	O_2	
		−1	H_2O_2 HO_2^-	Active as an oxidizing agent or as a reducing agent.
		−2	H_2O OH^-	
		Chlorine Compounds		
↑ o	↓ r	+7	(Cl_2O_7), $HClO_4$, ClO_4^-	Cl_2O_7 is unstable. $HClO_4$ is a very strong oxidizing agent reduced to Cl^-.
		+5	$HClO_3$, ClO_3^-	Strong oxidizing agent. Reduced to Cl^-.
		+4	ClO_2	Explosive.
		+3	$HClO_2$, ClO_2^-	Good oxidizing agent. Reduced to Cl^-.
		+1	Cl_2O, $HClO$, ClO^-	Good oxidizing agent. Reduced to Cl^-.
		0	Cl_2	Good oxidizing agent. Reduced to Cl^-.
		−1	Cl^-	
		Nitrogen Compounds		
↑ o	↓ r	+5	N_2O_5, HNO_3, NO_3^-	Strong oxidizing agent, usually reduced to NO_2 and NO (in dilute. acid). With strong reducing agent may go to NH_3.
		+4	NO_2, (N_2O_4)	A heavy brown gas.
		+3	$(N_2O_3$, $HNO_2)$, NO_2^-	N_2O_3 and HNO_2 are unstable. Nitrites are usually stable. Oxidizing or reducing agents.
		+2	NO	Oxidized by air to NO_2.
		+1	N_2O	Supports combustion vigorously.
		0	N_2	
		−3	NH_3, NH_4OH, NH_4^+	

		Oxidation State	Formulas	Comments
			Chromium Compounds	
			Acidic **Basic**	
		+6	$Cr_2O_7^{2-}$ CrO_4^{2-}	Strong oxidizing agents. Dichromate ion is orange and chromate ion is yellow.
		+3	Cr^{3+} $Cr(OH)_4^{2-}$	Amphoteric. Cr^{3+} is green to violet. $Cr(OH)_4^{2-}$ is green.
		+2	Cr^{2+}	An uncommon ion, because it is a strong reducing agent that reduces water to hydrogen gas.
		0	Cr	The metal.
			Manganese Compounds	
		+7	MnO_4^-	Purple. Strong oxidizing agent, reduced to Mn^{2+} in acid solution or to MnO_2 (sometimes MnO_4^{2-}) in neutral or basic solution.
		+6	MnO_4^{2-}	Green. Easily reduced to MnO_2.
		+4	MnO_2, $MnO(OH)_2$	Brown as precipitated from solution.
		+3	Mn^{3+}, $Mn(OH)_3$	Mn^{3+} is unstable, gives Mn^{2+} and MnO_2.
		+2	Mn^{2+}, $Mn(OH)_2$	Colorless in solution, pale pink as solid Mn(II) salts. $Mn(OH)_2$ is oxidized by air to $Mn(OH)_3$.
		0	Mn	The metal.

Let us comment briefly on the charts for sulfur and oxygen compounds.

It should be obvious from the chart of sulfur compounds that since H_2S represents the lowest possible oxidation state it can act only as a reducing agent in an oxidation-reduction, redox, process. In such a process it can be oxidized to free sulfur or to some higher state, such as a sulfate, its extent of oxidation, depending on the conditions and the strength of the oxidizing agent. Sulfuric acid, H_2SO_4, representing the highest oxidation state, can act only as an oxidizing agent, its reduction products being any lower states of sulfur. However, since sulfurous acid, H_2SO_3, represents an intermediate state of sulfur, it can act either as a reducing agent with substances that can take on electrons, or as an oxidizing agent with substances that can lose electrons.

Hydrogen peroxide and the peroxides are important oxidizing agents, both commercially and in the laboratory. Note, from Table 5.1 on page 42, that when hydrogen peroxide acts as an oxidizing agent it is reduced to water or, in basic solution, to hydroxide ion. It is oxidized to free oxygen only when it acts as a reducing agent, in the presence of certain catalysts, is due to the ability of one molecule to oxidize another molecule of the same substance (auto-oxidation-reduction). The half-reactions corresponding to these statements are

$$\text{Reduction: } 2\,H^+_{(aq)} + H_2O_{2\,(aq)} + 2\,e^- \rightarrow 2\,H_2O_{\,(l)} \qquad \textbf{(EQ 5.1)}$$

$$\text{Oxidation: } H_2O_{2\,(aq)} \rightarrow 2\,H^+_{(aq)} + O_{2\,(g)} + 2\,e^- \qquad \textbf{(EQ 5.2)}$$

$$\text{Auto-Redox: } 2\,H_2O_{2\,(aq)} \rightarrow 2\,H_2O_{\,(l)} + O_{2\,(g)} \qquad \textbf{(EQ 5.3)}$$

Listed below are some important categories of common oxidizing and reducing agents.

Some Common Oxidizing Agents

1. The halogens and oxygen-reduced to their negative ions, such as the following:

| F_2 reduced to F^- | Cl_2 reduced to Cl^- | O_2 reduced to O^{2-} |

2. Ions in which the metal ion has a stable lower oxidation state such as the following:

| Ce^{4+} reduced to Ce^{2+} | Mn^{3+} reduced to Mn^{2+} | Co^{3+} reduced to Co^{2+} |

3. Oxygen containing complex ions, where the central atom is in a high oxidation state:

| MnO^- reduced to Mn^{2+} | ClO_3^- reduced to Cl^- |
| $Cr_2O_7^{2-}$ reduced to Cr^{3+} | NO_3^- reduced to NO |

Some Common Reducing Agents

1. The metal oxidized to their positive ions - such as these

| Sn oxidized to Sn^{4+} | Zn oxidized to Zn^{2+} |

2. Ions in which the metal has another higher oxidation state, such as the following:

| Sn^{2+} oxidized to Sn^{4+} | Fe^{2+} oxidized to Fe^{3+} | Hg_2^{2+} oxidized to Hg^{2+} |

3. Carbon and organic compounds may be oxidized to CO or CO_2 and H_2O:

   a. C (coke, much used in industry) oxidized to CO or to CO_2

   b. alcohols $\rightarrow$ carboxylic acids

   CH_3CH_2OH (ethanol) may be oxidized to CH_3COOH (ethanoic acid) $+ 4\ H^+ + 4\ e^-$
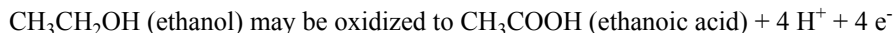
   c. aldehydes $\rightarrow$ carboxylic acids.

   $HCHO$ (formaldehyde) $+ H_2O \rightarrow HCOOH$ (formic acid) $+ 2\ H^+ + 2\ e^-$

Balancing of Oxidation-Reduction (Redox) Equations

In balancing any oxidation-reduction, redox, reaction, you must first know all of the reactants and products. If you do not, you will not be able to balance it correctly. Once the reactants and products are known, balance the reaction by keeping in mind that, in a redox reaction which is essentially an electron-transfer reaction, relative amounts of reactants must be taken in such a way that all the electrons supplied by the oxidation process are used in the reduction process. There are several methods for doing this, each differing in mechanics of operation, but all based on the same principle.

The Half-Reaction Method

Separated half-reactions, or electron reactions, are written for the oxidation and for the reduction processes. In developing these, we can first determine the number of electrons required from the change in oxidation number, then insert H^+ (or OH^- if the solution is basic) to balance the charges, and finally add H_2O to balance the atoms.

The reverse process is sometimes used. First, balance the atoms in half-reactions by inserting H^+ and H_2O as needed, then insert as many electrons as needed to balance the charges. Study the following example:

EXAMPLE 5.2

Let us consider the oxidation of potassium sulfite, K_2SO_3, by potassium dichromate, $K_2Cr_2O_7$, in an acid solution (assume hydrochloric acid for this example). Referring to the charts of oxidation states for sulfur compounds, we find that sulfite ions will be oxidized to sulfate ions ignoring the spectator ions of potassium:

$$SO_3^{2-}{}_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} \qquad \textbf{(EQ 5.4)}$$

We need another oxygen atom on the left; this is supplied by water, and we write the hydrogens as $2\ H^+$ on the right. (Note that we keep oxidation states of oxygen -2 and hydrogen +1 on both sides of the equation, since they are not the substances oxidized and reduced.) Our partial equation then becomes:

$$H_2O_{(l)} + SO_3^{2-}{}_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + 2\ H^+{}_{(aq)} \qquad \textbf{(EQ 5.5)}$$
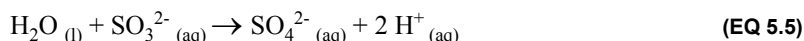
We still need to balance the charges so they are the same on both sides of the equation. To do so we add two electrons to the right:

$$H_2O_{(l)} + SO_3^{2-}{}_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + 2\ H^+{}_{(aq)} + 2\ e^- \qquad \textbf{(EQ 5.6)}$$
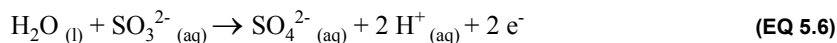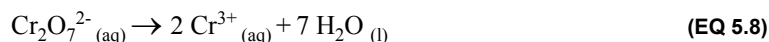
Thereby completing the oxidation half-reaction, and demonstrating the fact that in an oxidation process, electrons are lost.

Referring to the charts of oxidation states for chromium compounds, we find that the dichromate ion will be reduced to the chromic ion, Cr^{3+}, as will be evidenced by the green color of the solution. The several steps are as follows. First balance the number of chromium atoms by putting a 2 in front of Cr^{3+}:

$$Cr_2O_7^{2-}{}_{(aq)} \rightarrow 2\ Cr^{3+}{}_{(aq)} \qquad \textbf{(EQ 5.7)}$$

Next, balance the oxygen atoms by adding $7\ H_2O$:

$$Cr_2O_7^{2-}{}_{(aq)} \rightarrow 2\ Cr^{3+}{}_{(aq)} + 7\ H_2O_{(l)} \qquad \textbf{(EQ 5.8)}$$

Then balance the hydrogen atoms and oxygen by inserting $14\ H^+$ to react with the 7 oxygen atoms to form the $7\ H_2O$:

$$Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+{}_{(aq)} \rightarrow 2\ Cr^{3+}{}_{(aq)} + 7\ H_2O_{(l)} \qquad \textbf{(EQ 5.9)}$$
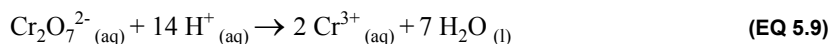
Finally, we balance the charges. As above written, we have 12 positive on the left and 6 positive on the right, or a net charge of +6 on the left. We therefore need 6 electrons on the left to complete the reduction half-reaction:
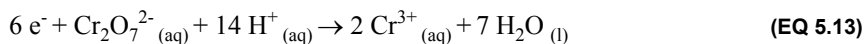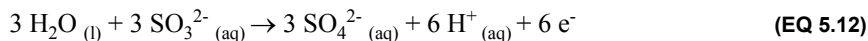
$$6\ e^- + Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+{}_{(aq)} \rightarrow 2\ Cr^{3+}{}_{(aq)} + 7\ H_2O_{(l)} \qquad \textbf{(EQ 5.10)}$$
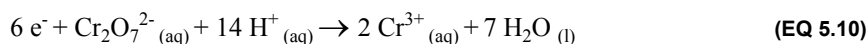
This emphasizes the fact that in a reduction process electrons are gained. Note the requirement of 6 electrons corresponds to the charge in oxidation state of chromium from +6 to +3, so two chromium atoms decrease by a total of 6 charges.

Finally, we may combine the two processes in such a way that we balance electrons gained against electrons lost.
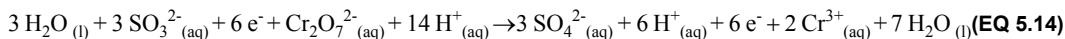
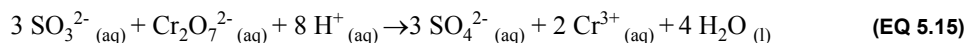To do this we multiply the oxidation half-reaction by 3 and add algebraically to the reduction half-reaction:

$$(H_2O_{(l)} + SO_3^{2-}{}_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + 2\ H^+{}_{(aq)} + 2\ e^-)\ 3 \qquad \textbf{(EQ 5.11)}$$
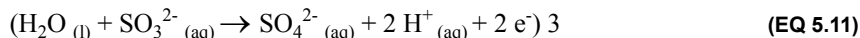
Now that the number of electrons transferred for the oxidation and reduction half-reactions are equal, 6 e⁻, the two half-reactions are:

$$3\ H_2O_{(l)} + 3\ SO_3^{2-}{}_{(aq)} \rightarrow 3\ SO_4^{2-}{}_{(aq)} + 6\ H^+{}_{(aq)} + 6\ e^- \qquad \textbf{(EQ 5.12)}$$

$$6\ e^- + Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+{}_{(aq)} \rightarrow 2\ Cr^{3+}{}_{(aq)} + 7\ H_2O_{(l)} \qquad \textbf{(EQ 5.13)}$$

Adding the two half-reactions together:

$$3\ H_2O_{(l)} + 3\ SO_3^{2-}{}_{(aq)} + 6\ e^- + Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+{}_{(aq)} \rightarrow 3\ SO_4^{2-}{}_{(aq)} + 6\ H^+{}_{(aq)} + 6\ e^- + 2\ Cr^{3+}{}_{(aq)} + 7\ H_2O_{(l)} \textbf{(EQ 5.14)}$$
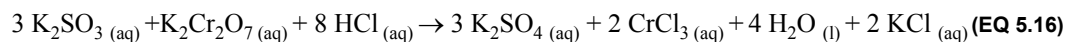
Canceling like terms, $H_2O_{(l)}$, e⁻, and $H^+{}_{(aq)}$, from both sides of the equation the balanced net ionic equation is:

$$3\ SO_3^{2-}{}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 8\ H^+{}_{(aq)} \rightarrow 3\ SO_4^{2-}{}_{(aq)} + 2\ Cr^{3+}{}_{(aq)} + 4\ H_2O_{(l)} \qquad \textbf{(EQ 5.15)}$$

Always check your results to make certain that both atoms and charges are balanced in the equation.

Adding back the potassium and chloride counterions for the reaction gives the balanced molecular equation of:

$$3\ K_2SO_{3\ (aq)} + K_2Cr_2O_{7\ (aq)} + 8\ HCl_{(aq)} \rightarrow 3\ K_2SO_{4\ (aq)} + 2\ CrCl_{3\ (aq)} + 4\ H_2O_{(l)} + 2\ KCl_{(aq)} \textbf{(EQ 5.16)}$$

Post Lab Questions

1. As a review, in the following equations for familiar reactions, underline the reducing agent once and oxidizing agent twice. At the right, indicate the change in oxidation number per atom for each element concerned. If there is no change write no valance change "NVC."

TABLE 5.3

Reactions	Element Oxidized	Oxidation Number increase per atom	Element Reduced	Oxidation number decrease per atom
$2\ Al_{(s)} + 3\ Cl_{2\ (g)} \rightarrow 2\ Al^{3+}_{(aq)} + 6\ Cl^-_{(aq)}$				
$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$				
$Mg_{(s)} + 2\ H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2\ (g)}$				
$Cu^{2+}_{(aq)} + H_2S_{(g)} \rightarrow CuS_{(s)} + 2\ H^+_{(aq)}$				
$Ba_{(s)} + 2\ H_2O_{(l)} \rightarrow Ba^{2+}_{(aq)} + 2\ OH^-_{(aq)} + H_{2\ (g)}$				
$3\ Na_2O_{2\ (s)} + Cr_2O_{3\ (s)} + H_2O_{(l)} \rightarrow 6\ Na^+_{(aq)} + 2\ CrO_4^{2-}{}_{(aq)} + 2\ OH^-_{(aq)}$				
$H_2O_{2\ (aq)} \rightarrow H_2O_{(l)} + \frac{1}{2}\ O_{2\ (g)}$				
$CO_{2\ (g)} + H_2O_{(l)} \rightarrow H_2CO_{3\ (aq)}$				
$CO_{2\ (g)} + C_{(s)} \rightarrow 2\ CO_{(g)}$				
$HCl_{(g)} + NH_{3\ (g)} \rightarrow NH_4Cl_{(s)}$				
$2\ ZnS_{(s)} + 3\ O_{2\ (g)} \rightarrow 2\ ZnO_{(s)} + 2\ SO_{2\ (g)}$				
$4\ H^+_{(aq)} + 2\ Cl^-_{(aq)} + MnO_{2\ (s)} \rightarrow Mn^{2+}_{(aq)} + Cl_{2\ (g)} + 2\ H_2O_{(l)}$				
$10\ H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 8\ I^-_{(aq)} \rightarrow 4\ I_{2\ (s)} + H_2S_{(g)} + 4\ H_2O_{(l)}$				

2. Show the change in oxidation number (give the number of electrons gained or lost *per atom*) in the following:

TABLE 5.4

Reaction	Number of e- lost of gained per atom
$PO_3^{3-}{}_{(aq)} \rightarrow PO_4^{3-\ (aq)}$	P lost 2 e⁻
$NO_2^{-}{}_{(aq)} \rightarrow NO_3^{-}{}_{(aq)}$	
$SO_{2\ (g)} \rightarrow S_2^{2-}{}_{(aq)}$	
$MnO_4^{-}{}_{(aq)} \rightarrow MnO_{2\ (s)}$	
$KClO_{2\ (s)} \rightarrow KCl_{(s)}$	
$NH_{3\ (g)} \rightarrow NH_4^{+}{}_{(aq)}$	
$HCOOH_{(aq)} \rightarrow HCHO_{(aq)}$	

3. Give the formula of a product (derived from the first substance in the statement) that may be formed in the following reactions. (Note: in the example any lower oxidation state compound is possible; but not any higher one. Some are more probable than others.)

TABLE 5.5

Reaction	Possible Products
H_2SO_3 is treated with a reducing agent	$S_{(s)}$, $S_2^{2-}{}_{(aq)}$, or $H_2S_{(g)}$
$HClO_2$ is treated with a reducing agent	
H_2SO_3 is treated with an oxidizing agent	
$SnCl_4$ is treated with zinc dust	
$Cr_2O_7^{2-}$ is treated with $SnCl_2$	
$KMnO_4$ is treated with $FeSO_4$	
MnO_2 is treated with concentrated HCl	

4. Write the half-reaction equation for the oxidation of:

TABLE 5.6

| Reaction	Balanced Net Ionic Equation
NO_2^- (aq) to NO_3^- (aq) (acidic)	
H_2S (g) to SO_4^{2-} (aq) (acidic)	
NH_4^+ (aq) to NO_3^- (aq) (acidic)	
H_2O_2 (aq) to O_2 (g) (basic)	
$Cr(OH)_4^-$ (aq) to CrO_4^- (aq) (basic)	
ClO^- (aq) to ClO_4^- (aq) (acidic)	
$HCOOH$ (aq) to CO_2 (g) (acidic)	

5. Write the half-reaction equation for the reduction of:

TABLE 5.7

Reaction	Balanced Net Ionic Equation
SO_3^{2-} (aq) to H_2S (g) (acidic)	
MnO_4^{2-} (aq) to MnO_2 (s) (basic)	
HO_2^- (aq) to OH^- (aq) (basic)	
$HCOOH$ (aq) to CH_3OH (aq) (acidic)	
ClO_3^- (aq) to Cl^- (aq) (acidic)	
$Cr_2O_7^{2-}$ (aq) to Cr^{3+} (aq) (acidic)	
CH_3NO_2 (aq) to CH_3NH_2 (aq) (acidic)	

6. Given the reactants and products, write balanced net ionic equations for the following reactions. Supply H_2O, H^+, or OH^- as needed.

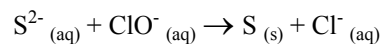   a. Iron filling are added to an aqueous iron(III) chloride solution.

   $$Fe_{(s)} + Fe^{3+}_{(aq)} \rightarrow Fe^{2+}_{(aq)}$$
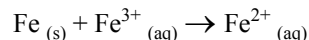
   b. Bismuth metal is dissolved in hot, concentrated nitric acid, HNO_3, giving off a brown gas.

   $$Bi_{(s)} + NO_3^-{}_{(aq)} \rightarrow Bi^{3+}_{(aq)} + NO_{2(g)}$$
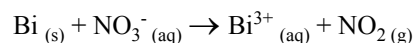
   c. A mixture of sodium sulfide, Na_2S, sodium hypochlorite, $NaClO$, and sodium hydroxide, $NaOH$, solutions is warmed, giving a suspended precipitate.

   $$S^{2-}_{(aq)} + ClO^-_{(aq)} \rightarrow S_{(s)} + Cl^-_{(aq)}$$

   d. Sulfur dioxide gas, SO_2, is bubbled into an acidic potassium dichromate, $K_2Cr_2O_7$, solution.

   $$SO_{2(g)} + Cr_2O_7^{2-}{}_{(aq)} \rightarrow Cr^{3+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$
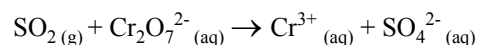
7. Predict the products and write a balanced net ionic equation for the following reactions:

   a. Tin(II) chloride is added to potassium permanganate solution in acidic conditions.

   b. Zinc dust is treated with dilute nitric acid, forming ammonium ions.

   c. Potassium permanganate oxidizes the oxalate ions in calcium oxalate to carbon dioxide in an acidic solution.