10

Oxidation-Reduction and Chemical Properties

Key Concepts

10-1 Oxidation numbers. Periodicity of oxidation numbers.
10-2 Oxidation–reduction reactions. Oxidation state. Oxidizing agents and reducing agents. Disproportionation.
10-3 Balancing oxidation–reduction equations. Oxidation-number method. Half-reaction method.
10-4 Redox titrations. Equivalents. Molarity and normality.
10-5 Oxidation and reduction potentials.
10-6 Chemical properties. Alkali metals. Alkaline earth metals, amphoteric behavior.
10-7 Transition metals. Lanthanide contraction. Transition metal complex ions.
10-8 Lanthanides and actinides.
10-9 Representative elements.

The electron has conquered physics, and
many worship the new idol rather blindly.

H. Poincaré (1907)

In the preceding chapters we saw that the ionization energies, electron affinities, and electronegativities of atoms can be explained on the basis of atomic orbital electronic structures. Now we can proceed to relate electronic structure to the chemical properties of the elements and their compounds. We shall begin by discussing (and balancing equations for) reactions that involve loss and gain of electrons by reactants **(oxidation–reduction reactions)**. Then we shall systematically examine the properties of the elements and their compounds, with emphasis on the oxidation–reduction chemistry of the metallic elements.

10-1 OXIDATION NUMBERS

To make it easier to discuss oxidation–reduction chemistry, we assign an **oxidation number** to each atom in a molecule or complex ion, according to the following rules:

1. The oxidation number for an atom of any free (uncombined) element is zero; thus, the atoms in H_2, O_2, Fe, Cl_2, and Na have zero oxidation numbers.

2. The oxidation number for any simple one-atom ion is equal to its charge; thus the oxidation number of Na^+ is $+1$; of Ca^{2+}, $+2$; and of Cl^-, -1.

3. The oxidation number of hydrogen in any *nonionic* compound is $+1$. This rule applies to the great majority of hydrogen compounds, such as H_2O, NH_3, HCl, and CH_4. For the *ionic* metal hydrides, such as NaH, the oxidation number of hydrogen is -1.

4. The oxidation number of oxygen is -2 in all compounds in which oxygen does not form an O—O covalent bond. Thus, its oxidation number is -2 in H_2O, H_2SO_4, NO, CO_2, and CH_3OH, but in hydrogen peroxide, H_2O_2, it is -1. (Another exception to the rule that oxygen has an oxidation number of -2 is OF_2, in which O is $+2$ and F is -1.)

5. In combinations of nonmetals *not* involving hydrogen or oxygen, the nonmetal that is *more* electronegative is considered negative. Its oxidation number is given the same value as the charge on its most commonly encountered negative ion. In CCl_4, for instance, the oxidation number for chlorine is -1; for carbon it is $+4$. In CH_4, the oxidation number for hydrogen is $+1$; for carbon, it is -4. In SF_6, the oxidation number for fluorine is -1, and for sulfur, it is $+6$; but in CS_2, it is -2 for S and $+4$ for C. In molecules such as N_4S_4 in which the bonds are covalent (the combining atoms have the same or almost the same electronegativity), the concept of oxidation number loses usefulness.

6. The algebraic sum of the oxidation numbers of all atoms in the formula for a neutral compound must be zero. Hence, in NH_4Cl, the total oxidation number for the four hydrogen atoms is $4(+1) = +4$, and the oxidation number for Cl is -1, so the oxidation number for N must be -3.

7. The algebraic sum of oxidation numbers of all atoms in an ion must equal the charge on the ion. Thus, in NH_4^+, the oxidation number of N must be -3, so $-3 + 4 = +1$. In SO_4^{2-}, since the four oxygen atoms have a total oxidation number of -8, the oxidation number for sulfur must be $+6$ if the overall charge on the ion is -2.

8. In chemical reactions, the *total oxidation number is conserved.* It is this rule that makes oxidation numbers useful in modern chemistry. If the oxidation number of an atom increases during a chemical reaction, the atom is **oxidized**; if the number decreases, the atom is **reduced**. In a balanced chemical reaction, *oxidations and reductions must exactly compensate one another.*

Example 1

What is the oxidation number of each atom in NF_3?

Solution

Fluorine lies to the right of nitrogen in the periodic table. Therefore, it is considered negative. Fluorine is assigned an oxidation number of -1, corresponding to the F^- ion. Since there are three fluorines, each with an oxidation number of −1, nitrogen must have an oxidation number of +3 for the sum of all oxidation numbers to be zero.

Example 2

What is the oxidation number of Mo in the molybdate ion, MoO_4^{2-}?

Solution

Since the oxidation number of each oxygen is −2, Mo must have an oxidation number of +6 if the sum 1Mo(+6) + 4O(−2) is to be equal to −2.

Calculating Oxidation Numbers

From the preceding rules, we can calculate the oxidation numbers of the atoms in most molecules and complex ions. Certain oxidation numbers are characteristic of a given element, and these can be related to the position of the element in the periodic table. Figure 10-1 shows how oxidation numbers vary with atomic number. The *maximum* oxidation number generally increases across a period from +1 to +7.

- *Representative metals.* Metals in Groups I–III in the periodic table form ions with positive charges equal to the numbers of their respective groups; that is, their oxidation numbers are the same as their group numbers.

- *Nonmetals.* Nonmetals often assume either of two characteristic oxidation numbers. Their minimum oxidation number is usually $-(8 - gn)$, where gn is the number of the group in the periodic table; thus, each atom can combine with $8 - gn$ hydrogen atoms. For example, one sulfur atom (Group VI) combines with two hydrogen atoms, since sulfur has an oxidation number of −2. The maximum oxidation number of nonmetals is commonly $+gn$, especially in oxygen compounds. Examples are SO_3 and H_2SO_4, in which the oxidation number of sulfur is +6. Most nonmetals also exhibit intermediate oxidation numbers (see Table 10-1).

- *Transition metals.* Among transition metals oxidation numbers follow the trends illustrated in Table 10-2. Early members of the series of transition metals exhibit maximum oxidation numbers of increasing magnitude, up to +7 for manganese in MnO_4^-, which correspond to the group numbers. Thereafter, the maximum oxidation number usually falls again by *one* number for each step to the right across the second half of the transition metals.

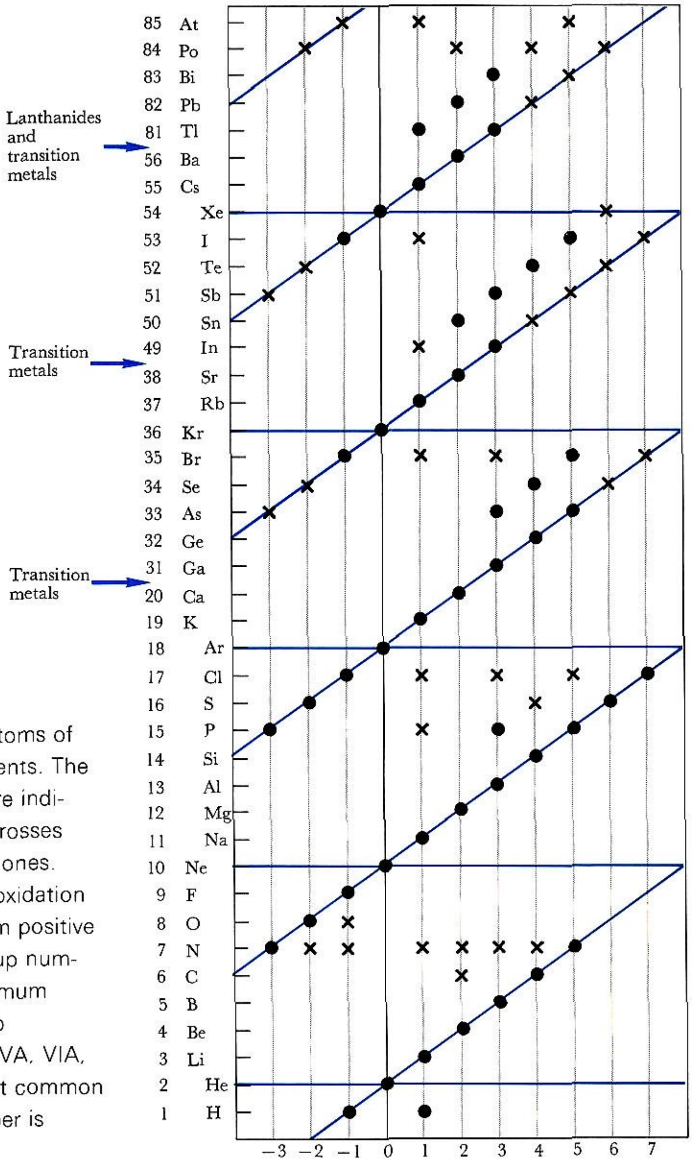

Figure 10-1 Oxidation numbers of atoms of the representative elements. The most common values are indicated by filled circles; crosses show the less common ones. Note the periodicity of oxidation numbers, with maximum positive values equal to the group numbers, *gn*, and with minimum negative values equal to $-(8 - gn)$ for Groups VA, VIA, and VIIA. The next most common positive oxidation number is usually $gn - 2$.

■ *Inner transition metals.* Lanthanide and actinide elements compose another type of transition series, in which adjacent elements have very similar properties. The oxidation number $+3$ is common to all lanthanides and actinides in their compounds. Other oxidation numbers are possible and in some cases more commonly encountered (e.g., Eu^{2+}, Ce^{4+}, and U^{6+}).

Table 10-1

Oxidation Numbers of Nonmetals

Element	Oxidation number	Representative compounds
F	−1	Fluorides: HF, Na^+F^-
O	−2	H_2O, OH^-, O^{2-}, SO_2
	−1	Peroxides: H_2O_2, O_2^{2-}
N	−3	NH_3, NH_4^+, N^{3-}
	+5	HNO_3, NO_3^-, N_2O_5
	All intermediate values	N_2H_4, NH_2OH, N_2O, NO, NO_2^-, NO_2
C	+4	CO_2, CCl_4, CF_4
	−4	CH_4
	Complicated by chain formation	C_2H_6, C_4H_{10}, C_2H_6O
Cl	−1	HCl, Cl^-
	+7	$HClO_4$, ClO_4^-
	Intermediate values	ClO^-, ClO_2^-, ClO_2, ClO_3^-
S	−2	H_2S, S^{2-}
	+4	H_2SO_3, SO_2, HSO_3^-, SO_3^{2-}
	+6	H_2SO_4, SO_3, SO_4^{2-}, SF_6
	Intermediate values	$S_2O_3^{2-}$, $S_2O_4^{2-}$, $S_5O_6^{2-}$
P	−3	PH_3, PH_4^+, P^{3-}
	+5	H_3PO_4, P_4O_{10}, PO_4^{3-}, PCl_5
	Intermediate values	H_3PO_3, H_3PO_2
Si	+4	SiO_2, SiO_4^{4-}
Br	−1	HBr, Br^-
	+5	$HBrO_3$, BrO_3^-, BrF_5
	Intermediate values	BrF, BrF_3
I	−1	HI, I^-
	+5, +3, +1	IO_3^-, ICl_4^-, ICl
	+7	HIO_4, H_5IO_6, IF_7
Se, Te	−2	H_2Se, H_2Te
	+4	SeO_2, TeO_2
	+6	H_2SeO_4, $Te(OH)_6$
As, Sb	−3	AsH_3, SbH_3
	+3	$AsCl_3$, $SbCl_3$
	+5	AsO_4^{3-}, $Sb(OH)_6^-$

10-2 OXIDATION–REDUCTION REACTIONS

An atom with a particular oxidation number is sometimes referred to as being "in the oxidation state" of that number; thus, in H_2O, H is in the +1 oxidation state and O is in the −2 oxidation state. Reactions in which the oxidation states of component atoms change are called **oxidation–**

Table 10-2

Oxidation Numbers of First-Row Transition Metals[a]

Oxidation number	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB
7					$\underline{\mathrm{MnO_4^-}}$					
6				$\underline{\mathrm{CrO_4^{2-}}}$	$\mathrm{MnO_4^{2-}}$	$\mathrm{FeO_4^{2-}}$				
5			$\underline{\mathrm{VO_4^{3-}}}$	$\mathrm{CrOCl_5^{2-}}$	$\mathrm{MnO_4^{3-}}$	*				
4		$\underline{\mathrm{TiO_2}}$	$\underline{\mathrm{VO^{2+}}}$	*	$\underline{\mathrm{MnO_2}}$	*	$\mathrm{CoO_2}$	$\mathrm{NiO_2}$		
3	$\underline{\mathrm{Sc^{3+}}}$	$\mathrm{Ti^{3+}}$	$\mathrm{V^{3+}}$	$\underline{\mathrm{Cr^{3+}}}$	$\mathrm{Mn^{3+}}$	$\underline{\mathrm{Fe^{3+}}}$	$\underline{\mathrm{Co^{3+}}}$	$\mathrm{Ni_2O_3}$	$\mathrm{Cu^{3+}}$	
2	*	TiO	$\mathrm{V^{2+}}$	$\mathrm{Cr^{2+}}$	$\underline{\mathrm{Mn^{2+}}}$	$\underline{\mathrm{Fe^{2+}}}$	$\underline{\mathrm{Co^{2+}}}$	$\underline{\mathrm{Ni^{2+}}}$	$\underline{\mathrm{Cu^{2+}}}$	$\underline{\mathrm{Zn^{2+}}}$
1		*	*	*	$\mathrm{Mn(CN)_6^{5-}}$	*	*	$\mathrm{Ni_2(CN)_6^{4-}}$	$\underline{\mathrm{Cu^+}}$	
0		*	$\mathrm{V(CO)_6}$	$\mathrm{Cr(CO)_6}$	$\mathrm{Mn_2(CO)_{10}}$	$\mathrm{Fe(CO)_5}$	$\mathrm{Co_2(CO)_8}$	$\mathrm{Ni(CO)_4}$		

[a] Underlined species are those most commonly encountered under ordinary conditions in solids and in aqueous solutions. The asterisk indicates that oxidation numbers have been observed only in rare complex ions or unstable compounds.

reduction (redox) reactions. If an atom's oxidation number increases, the atom is oxidized; if its oxidation number decreases, it is reduced. Species containing an atom or atoms whose oxidation numbers increase are called **reducing agents** (or **reductants**); those containing an atom or atoms whose oxidation numbers decrease are called **oxidizing agents** (or **oxidants**). Some common oxidizing and reducing agents are listed in Table 10-3. The acceptance of electrons by a substance must cause a decrease in oxidation number, whereas the loss of electrons must involve an increase. It follows that an oxidation–reduction reaction may be thought of as one in which the reducing agent gives electrons to the oxidizing agent. Thus, in rusting, iron reduces oxygen, and oxygen oxidizes (the origin of the term) iron:

$$\underbrace{4\mathrm{Fe} + 3\mathrm{O}_2}_{12e^- \uparrow} \rightarrow 4\mathrm{Fe}^{3+} + 6\mathrm{O}^{2-} \quad \text{(in the form of } 2\mathrm{Fe_2O_3})$$

By donating electrons, copper reduces silver ions, and the silver ions oxidize the metallic copper in the reaction

$$\underbrace{\mathrm{Cu} + 2\mathrm{Ag}^+}_{2e^- \uparrow} \rightarrow \mathrm{Cu}^{2+} + 2\mathrm{Ag}$$

If an atom can have several oxidation states, in the intermediate oxidation states it can be either an oxidizing or a reducing agent. The ion Mn^{3+} can act as an oxidizing agent and be reduced to Mn^{2+}, or it can act as a reducing agent and be oxidized to Mn^{4+}. In fact, Mn^{3+} in solution is unstable and spontaneously **disproportionates** with self-oxidation–reduction to give the +2 and +4 oxidation states:

$$2\mathrm{Mn}^{3+} + 2\mathrm{H_2O} \rightarrow \mathrm{Mn}^{2+} + \mathrm{MnO_2} + 4\mathrm{H}^+$$

Table 10-3

Common Oxidizing and Reducing Agents

Oxidizing agents

1. Free (elemental) nonmetals become negative ions:

Fluorine	$F_2 + 2e^- \rightarrow 2F^-$
Oxygen	$O_2 + 4e^- \rightarrow 2O^{2-}$
Chlorine	$Cl_2 + 2e^- \rightarrow 2Cl^-$
Bromine	$Br_2 + 2e^- \rightarrow 2Br^-$
Iodine	$I_2 + 2e^- \rightarrow 2I^-$
Sulfur	$S + 2e^- \rightarrow S^{2-}$

2. Positive (usually metal) ions become neutral:

$Ag^+ + e^- \rightarrow Ag$

$2H^+ + 2e^- \rightarrow H_2$

3. Higher oxidation states become lower:

$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$Cu^{2+} + e^- \rightarrow Cu^+$ (often written as $Cu^{2+}|Cu^+$)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (or $Fe^{3+}|Fe^{2+}$)

$Cr_2O_7^{2-}|Cr^{3+}$

$ClO_3^-|Cl^-$

$NO_3^-|(NO_2, NO, N_2O, NH_4^+$, etc.)

$Ce^{4+}|Ce^{3+}$

Reducing agents

1. Metals yield ions plus electrons:

$Zn \rightarrow Zn^{2+} + 2e^-$

$Na \rightarrow Na^+ + e^-$

All metals yielding their common ions may be included here.

2. Nonmetals combine with other nonmetals, such as O and F, which they take from compounds with metals:

$C + [O^{2-}] \rightarrow CO + 2e^-$

Here $[O^{2-}]$ represents oxygen in a -2 oxidation state in combination with a metal such as Fe in the following total equation:

$3C + Fe_2O_3 \rightarrow 3CO + 2Fe$

3. Lower oxidation states become higher:

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (or $Fe^{2+}|Fe^{3+}$)

$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$ (or $SO_3^{2-}|SO_4^{2-}$)

$NO + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e^-$ (or $NO|NO_3^-$)

Furthermore, when each oxidizing agent reacts it becomes a potential reducing agent, and vice versa. This process is similar to that described by the Brønsted–Lowry acid–base theory (Section 5-3), in which every acid, by giving up a proton, becomes a base, and every base, by accepting a proton, becomes an acid.

10-3 BALANCING OXIDATION–REDUCTION EQUATIONS

Let's look at a reaction involving $K_2Cr_2O_7$ and HI. If we assume that the reactants and products are known,* then the problem is how to find the mole ratios and balance the equation for the reaction. We start with the equation

$$K_2Cr_2O_7 + HI + HClO_4 \rightarrow KClO_4 + Cr(ClO_4)_3 + I_2 + H_2O \qquad (10\text{-}1)$$

Two methods have been developed for balancing redox equations systematically. With the **oxidation-number method** we use the fact that the amount of oxidation must equal the amount of reduction in the total chemical reaction. With the **ion–electron method** we consider a redox reaction to be the formal sum of two half-reactions, one that donates electrons and one that accepts them.

Oxidation-Number Method

1. Identify the elements that change oxidation number during the reaction. Write the oxidation numbers of these atoms above the appropriate symbols on both sides of the equation. In equation 10-1, chromium (Cr) goes from +6 in $K_2Cr_2O_7$ to +3 in $Cr^{3+}(ClO_4^-)_3$. Imagine that each Cr atom accepts three electrons to change its oxidation state from +6 to +3. Iodine goes from −1 in HI to zero in I_2 and loses one electron per atom in the process.

2. Now choose enough of the reductant and oxidant so the electrons lost by one are used completely by the other. There must be three times as many I atoms involved as Cr, and since $K_2Cr_2O_7$ has two Cr atoms, the reaction requires six HI molecules:

$$K_2\overset{+6}{Cr_2}O_7 + 6H\overset{-1}{I} + HClO_4 \rightarrow KClO_4 + 2\overset{+3}{Cr}(ClO_4)_3 + 3\overset{0}{I_2} + H_2O$$

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*At this point you should not feel that you should be able to predict products of reactions. As you gain experience, especially in the laboratory, you will be able to make more and more predictions.

3. Balance the other metal ions that do not change oxidation number (K^+ in this case):

$$\mathrm{K_2\overset{+6}{Cr}_2O_7 + 6H\overset{-1}{I} + HClO_4 \rightarrow 2KClO_4 + 2\overset{+3}{Cr}(ClO_4)_3 + 3\overset{0}{I}_2 + H_2O}$$

4. Balance the anions that do not change (ClO_4^- in this case):

$$\mathrm{K_2Cr_2O_7 + 6HI + 8HClO_4 \rightarrow 2KClO_4 + 2Cr(ClO_4)_3 + 3I_2 + H_2O}$$

5. Balance the hydrogens, and make sure that oxygen is also balanced:

$$\mathrm{K_2Cr_2O_7 + 6HI + 8HClO_4 \rightarrow 2KClO_4 + 2Cr(ClO_4)_3 + 3I_2 + 7H_2O}$$

The balancing process is thus completed. The sequence of balancing steps can be summarized as: oxidation numbers–cations–anions–hydrogens–oxygens. In what follows we shall balance the same equation by another method.

Ion–Electron (Half-Reaction) Method

It is often useful to pretend that oxidation and reduction are occurring separately, and then to combine enough of each half-reaction to cancel all the free electrons. Chemical reactions occurring at electrodes in batteries or electrolysis cells (Chapter 1, Section 1-7) are examples of half-reactions that actually occur. For example,

$$\begin{aligned} \mathrm{Cu^{2+} + 2}e^- &\rightarrow \mathrm{Cu} && \text{(cathode)} \\ \mathrm{2H_2O} &\rightarrow \mathrm{O_2 + 4H^+ + 4}e^- && \text{(anode)} \end{aligned}$$

Redox reactions that occur in solution can be considered as the sum of two such half-reactions that proceed without the addition of an external driving force (the battery). In all electron-transfer reactions *the number of electrons donated by the reducing agent must equal the number of electrons accepted by the oxidizing agent.*

The $K_2Cr_2O_7$ reaction can be balanced by half-reactions as follows:

1. First, simplify the reaction by eliminating all **spectator ions** (those ions that do not really participate in the reaction), such as K^+ or ClO_4^-.

$$\mathrm{Cr_2O_7^{2-} + I^- + H^+ \rightarrow Cr^{3+} + I_2 + H_2O}$$

2. Now construct two balanced half-reactions, one involving Cr and one involving I.

a. The unbalanced reactions are

$$\begin{aligned} \mathrm{Cr_2O_7^{2-}} &\rightarrow \mathrm{2Cr^{3+}} \\ \mathrm{2I^-} &\rightarrow \mathrm{I_2} \end{aligned}$$

b. Balance the atoms in each half-reaction by adding H^+ and H_2O if the reactions occur in an acid medium, or H_2O and OH^- if the reactions occur in a basic one:

$$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O \qquad \text{(Cr, O, and H atoms balanced)}$$

$$2I^- \rightarrow I_2 \qquad \text{(no } H^+ \text{ or } OH^- \text{ on either side; no atoms needed)}$$

c. Balance the charge by adding electrons:

$$6e^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
$$2I^- \rightarrow I_2 + 2e^-$$

If the half-reaction is balanced properly, the number of electrons will indicate exactly the change in oxidation number. The two Cr require six electrons, and the two I^- produce two electrons.

3. Multiply the half-reactions by coefficients that make the number of electrons transferred in each half-reaction the same:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$6I^- \rightarrow 3I_2 + 6e^-$$

4. Add the two half-reactions and cancel species that appear on both sides of the overall reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

As a precaution, make sure that the *number of atoms* on both sides is the same, that the *charges* balance, and that there are *no net electrons left.* At this point the equation as it stands is balanced. However, for some applications it is useful to complete the equation by restoring the "uninvolved" species and by grouping ions to form known species:

$$Cr_2O_7^{2-} + 8H^+ + 6HI \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$K_2Cr_2O_7 + 8HClO_4 + 6HI \rightarrow 2Cr(ClO_4)_3 + 2KClO_4 + 3I_2 + 7H_2O$$

This process can be summarized as: half-reactions–whole reaction–uninvolved ions.

As a second example, let's balance the equation representing the reaction between potassium permanganate ($KMnO_4$) and ammonia (NH_3) that produces potassium nitrate (KNO_3), manganese dioxide (MnO_2), potassium hydroxide (KOH), and water.

■ *Oxidation-number method.* The unbalanced reaction is

$$KMnO_4 + NH_3 \rightarrow KNO_3 + MnO_2 + KOH + H_2O$$

In this reaction manganese and nitrogen change oxidation number:

$$\overset{7+}{\mathrm{Mn}} \rightarrow \overset{4+}{\mathrm{Mn}} \qquad \text{(change of } -3)$$

$$\overset{3-}{\mathrm{N}} \rightarrow \overset{5+}{\mathrm{N}} \qquad \text{(change of } +8)$$

To conserve overall oxidation numbers, we need eight manganese atoms for three nitrogen atoms:

$$8\mathrm{K}\overset{+7}{\mathrm{Mn}}\mathrm{O_4} + 3\overset{-3}{\mathrm{N}}\mathrm{H_3} \rightarrow 3\mathrm{K}\overset{+5}{\mathrm{N}}\mathrm{O_3} + 8\overset{+4}{\mathrm{Mn}}\mathrm{O_2} + \mathrm{KOH} + \mathrm{H_2O}$$

Potassium (K^+) is the cation that does not change oxidation number; it now must be balanced:

$$8\mathrm{K}\overset{+7}{\mathrm{Mn}}\mathrm{O_4} + 3\overset{-3}{\mathrm{N}}\mathrm{H_3} \rightarrow 3\mathrm{K}\overset{+5}{\mathrm{N}}\mathrm{O_3} + 8\overset{+4}{\mathrm{Mn}}\mathrm{O_2} + 5\mathrm{KOH} + \mathrm{H_2O}$$

The hydrogen atoms must be balanced:

$$8\mathrm{KMnO_4} + 3\mathrm{NH_3} \rightarrow 3\mathrm{KNO_3} + 8\mathrm{MnO_2} + 5\mathrm{KOH} + 2\mathrm{H_2O}$$

The oxygen atoms must balance; there are 32 on each side, and the process is complete.

▪ *Half-reaction method.* Begin by simplifying the reaction. The K^+ ion does not change, so it is omitted:

$$\mathrm{MnO_4^-} + \mathrm{NH_3} \rightarrow \mathrm{NO_3^-} + \mathrm{MnO_2} + \mathrm{OH^-} + \mathrm{H_2O}$$

In this reaction, MnO_4^- is reduced and NH_3 is oxidized:

$$\mathrm{MnO_4^-} \rightarrow \mathrm{MnO_2}$$
$$\mathrm{NH_3} \rightarrow \mathrm{NO_3^-}$$

Since OH^- is involved in the reaction, H_2O and OH^- are used to balance the atoms in each half-reaction:

$$\mathrm{MnO_4^-} + 2\mathrm{H_2O} \rightarrow \mathrm{MnO_2} + 4\mathrm{OH^-}$$
$$\mathrm{NH_3} + 9\mathrm{OH^-} \rightarrow \mathrm{NO_3^-} + 6\mathrm{H_2O}$$

Electrons are added to balance the charge for each half-reaction:

$$3e^- + \mathrm{MnO_4^-} + 2\mathrm{H_2O} \rightarrow \mathrm{MnO_2} + 4\mathrm{OH^-}$$
$$\mathrm{NH_3} + 9\mathrm{OH^-} \rightarrow \mathrm{NO_3^-} + 6\mathrm{H_2O} + 8e^-$$

The half-reactions are multiplied by 8 and 3, respectively, and then added:

$$\cancel{24e^-} + 8\mathrm{MnO_4^-} + \cancel{16\mathrm{H_2O}} \rightarrow 8\mathrm{MnO_2} + \overset{5}{\cancel{32}}\mathrm{OH^-}$$
$$3\mathrm{NH_3} + \cancel{27\mathrm{OH^-}} \rightarrow 3\mathrm{NO_3^-} + \overset{2}{\cancel{18}}\mathrm{H_2O} + \cancel{24e^-}$$
$$\overline{8\mathrm{MnO_4^-} + 3\mathrm{NH_3} \rightarrow 8\mathrm{MnO_2} + 3\mathrm{NO_3^-} + 5\mathrm{OH^-} + 2\mathrm{H_2O}}$$

Example 3

Balance the following equation involving the oxidation of sulfite (SO_3^{2-}) to sulfate (SO_4^{2-}) by chlorate (ClO_3^-). Use both oxidation-number and ion–electron methods.

$$ClO_3^- + SO_3^{2-} \rightarrow Cl^- + SO_4^{2-}$$

Solution By the oxidation-number method,

gains $6e^-$

$$\overset{+5}{ClO_3^-} + \overset{+4}{SO_3^{2-}} \rightarrow \overset{-1}{Cl^-} + \overset{+6}{SO_4^{2-}}$$

loses $2e^-$

Three moles of SO_3^{2-} are needed to balance the oxidation-number change for each ClO_3^-:

$$ClO_3^- + 3SO_3^{2-} \rightarrow Cl^- + 3SO_4^{2-}$$

Since 12 oxygens appear on each side, the equation is balanced.

In the ion–electron method the reaction is divided into halves:

$$\begin{aligned} &ClO_3^- \rightarrow Cl^- \\ &SO_3^{2-} \rightarrow SO_4^{2-} \end{aligned}$$

Balance the oxygens by adding H^+ ions and H_2O:

$$\begin{aligned} &6H^+ + ClO_3^- \rightarrow Cl^- + 3H_2O \\ &H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ \end{aligned}$$

Add electrons to each half-reaction to balance charge:

$$\begin{aligned} 6e^- + 6H^+ + ClO_3^- &\rightarrow Cl^- + 3H_2O \\ H_2O + SO_3^{2-} &\rightarrow SO_4^{2-} + 2H^+ + 2e^- \end{aligned}$$

Balance the electrons by multiplying the lower half-reaction by 3:

$$\begin{aligned} 6e^- + 6H^+ + ClO_3^- &\rightarrow Cl^- + 3H_2O \\ 3H_2O + 3SO_3^{2-} &\rightarrow 3SO_4^{2-} + 6H^+ + 6e^- \end{aligned}$$

Add the two half-reactions to give a balanced equation:

$$\begin{aligned} \cancel{6e^-} + \cancel{6H^+} + ClO_3^- &\rightarrow Cl^- + \cancel{3H_2O} \\ \cancel{3H_2O} + 3SO_3^{2-} &\rightarrow 3SO_4^{2-} + \cancel{6H^+} + \cancel{6e^-} \\ \hline ClO_3^- + 3SO_3^{2-} &\rightarrow Cl^- + 3SO_4^{2-} \end{aligned}$$

10-4 REDOX TITRATIONS

One *equivalent* (equiv) of an acid or base in a neutralization reaction is the quantity of acid or base that will release or take up 1 mole of protons. In a similar way, 1 equiv of an oxidizing or reducing agent in a redox reaction is defined as the amount of compound that will produce 1 mole of oxidation-number change. In the reaction

$$\mathrm{Na} \rightarrow \mathrm{Na}^+ + e^-$$

the sodium undergoes a change in oxidation number of one unit, so the equivalent weight of sodium *in this reaction* is equal to its atomic weight. In the oxidation of a Group IIA metal,

$$\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^-$$

each atom of magnesium changes by two oxidation-number units, and each mole of magnesium metal furnishes 2 equiv of reducing ability. Therefore, the equivalent weight of Mg in this reaction is half its atomic weight.

The equivalent weight of HCl in an acid–base neutralization reaction is equal to its molecular weight. The equivalent weight of HCl in a redox reaction depends on the change in oxidation number of chlorine during the reaction. If a chloride ion is oxidized to Cl_2,

$$\overset{-1}{\mathrm{Cl}^-} \rightarrow \overset{0}{\tfrac{1}{2}\mathrm{Cl}_2} + e^-$$

then there is one redox equivalent per HCl, and the equivalent weight and molecular weight of HCl are identical. But if the reaction is

$$\overset{-1}{\mathrm{Cl}^-} + 3\mathrm{H}_2\mathrm{O} \rightarrow \overset{+5}{\mathrm{ClO}_3^-} + 6\mathrm{H}^+ + 6e^-$$

then each HCl furnishes 6 equiv of reducing power, and the equivalent weight is one-sixth the molecular weight.

In titrations using solutions of oxidants or reductants as reagents, it is convenient to use equivalents, for when all of an oxidizing agent in a sample has reacted with a solution's reducing agent from the burette, the number of equivalents of oxidant and reductant is the same. As with neutralization reactions, the *normality* of a solution is the *number of equivalents per liter of solution.*

Example 4

A 50.0-ml solution containing 1.00 g of KMnO_4 is used in titrating a reducing agent. During the reaction, MnO_4^- is reduced to Mn^{2+}. What is the molarity of the solution? What is the normality?

Solution First, we find the molarity:

$$1.00\,\cancel{\mathrm{g\ KMnO}_4} \times \frac{1\ \text{mole}}{158\,\cancel{\mathrm{g\ KMnO}_4}} \times \frac{1}{0.0500\ \text{liter}} = 0.127\ \text{mole liter}^{-1}$$
$$= 0.127M$$

The reduction of MnO_4^- to Mn^{2+} is

$$\overset{+7}{MnO_4^-} + 8H^+ + 5e^- \rightarrow \overset{+2}{Mn^{2+}} + 4H_2O$$

Since Mn changes by five oxidation units in this reaction, the equivalent weight of $KMnO_4$ is one-fifth the molecular weight, and the normality is five times the molarity:

$$\begin{aligned} 0.127 \text{ mole liter}^{-1} \times 5.00 \text{ equiv mole}^{-1} &= 0.635 \text{ equiv liter}^{-1} \\ &= 0.635N \end{aligned}$$

Example 5

A 31.25-ml solution of $0.100M$ $Na_2C_2O_4$ (sodium oxalate) in acid is titrated with 17.38 ml of $KMnO_4$ solution of unknown strength. What is the normality of the $Na_2C_2O_4$ and of the $KMnO_4$, and the molarity of the $KMnO_4$?

Solution The reaction is

$$2\overset{+7}{MnO_4^-} + 5\overset{+3}{C_2O_4^{2-}} + 16H^+ \rightarrow 2\overset{+2}{Mn^{2+}} + 10\overset{+4}{CO_2} + 8H_2O$$

Manganese goes from +7 to +2, so each MnO_4^- provides 5 equiv of oxidizing power. Carbon goes from +3 to +4, so each $C_2O_4^{2-}$, with *two* carbon atoms, provides 2 equiv of reducing power. Another way of understanding this is to write the two half-reactions:

$$\begin{aligned} MnO_4^- + 8H^+ + 5e^- &\rightarrow Mn^{2+} + 4H_2O \\ C_2O_4^{2-} &\rightarrow 2CO_2 + 2e^- \end{aligned}$$

For this reaction the $0.100M$ $Na_2C_2O_4$ solution is $0.200N$. The milliequivalents of oxidant and reductant are equal at neutralization. [One milliequivalent (meq) is 10^{-3} equiv.] So

$$\begin{aligned} \text{meq } Na_2C_2O_4 &= \text{meq } KMnO_4 \\ 31.25 \text{ ml} \times \frac{0.200 \text{ meq}}{1 \text{ ml}} &= 17.38 \text{ ml} \times \frac{x \text{ meq}}{1 \text{ ml}} \end{aligned}$$

(Note that 1 meq ml^{-1} = 1 equiv liter^{-1}.)

$$\begin{aligned} \text{Normality of } KMnO_4 &= x = 0.360N \\ \text{Molarity of } KMnO_4 &= \frac{0.360 \cancel{\text{ equiv}} \text{ liter}^{-1}}{5 \cancel{\text{ equiv}} \text{ mole}^{-1}} \\ &= 0.0720 \text{ mole liter}^{-1} \\ &= 0.0720M \end{aligned}$$

The importance of writing the equations or half-reactions when dealing with equivalents is illustrated by the fact that MnO_4^- can be reduced in various circumstances in the following ways:

$$\begin{aligned} MnO_4^- + e^- &\rightarrow MnO_4^{2-} \\ MnO_4^- + 2H_2O + 3e^- &\rightarrow MnO_2 + 4OH^- \\ MnO_4^- + 8H^+ + 4e^- &\rightarrow Mn^{3+} + 4H_2O \\ MnO_4^- + 8H^+ + 5e^- &\rightarrow Mn^{2+} + 4H_2O \end{aligned}$$

The number of equivalent weights per mole of $KMnO_4$ in these examples is 1, 3, 4, and 5. The last reaction is the one most frequently encountered, but the others also occur. The normality of any $KMnO_4$ solution thus depends on how we use it.

10-5 OXIDATION AND REDUCTION POTENTIALS

The **oxidation potential,** $\mathscr{E}$, of a reaction is a measure of the tendency for a reaction of the type

Reduced substance → oxidized substance + electrons

to take place, in comparison with the reaction

$$\tfrac{1}{2}H_2(g) \rightarrow H^+ + e^-$$

which is *assigned* an oxidation potential of zero. If the oxidation potential of a reaction is positive, the reaction has a stronger tendency to occur than does the oxidation of H_2. This is true for sodium metal; its standard oxidation potential at 25°C, $\mathscr{E}^0$, is

$$Na(s) \rightarrow Na^+ + e^- \qquad \mathscr{E}^0 = +2.71 \text{ volts (V)}$$

The drive toward the oxidized state of Na in water is so strong that water itself is decomposed, and hydrogen ions are reduced to H_2 gas.

If the oxidation potential for a reaction is negative, the favored drive is toward the reduced rather than the oxidized state:

$$Ag(s) \rightarrow Ag^+ + e^- \qquad \mathscr{E}^0 = -0.80 \text{ V}$$

Thus the reverse of this reaction will occur. We shall return to a systematic study of oxidation potentials in Chapter 19, where we will see how they are measured in electrolytic cells. At the moment, we want to use them only as measures of the relative tendency of elements to exist in different oxidation states in solution.

The qualification, "in solution," in the preceding sentence is an important one. The first ionization energy of sodium measures the tendency of a *gaseous atom* of Na to lose an electron and to form a *gaseous ion.* In contrast, the oxidation potential measures the tendency of *solid* Na to lose an electron and form a *hydrated* sodium ion in aqueous solution. This is a much more useful quantity in most chemical applications. Sometimes the result of oxidation of a metal in solution is not a hydrated cation but an oxide complex:

$$Mn(s) + 4H_2O \rightarrow MnO_4^- + 8H^+ + 7e^- \qquad \mathscr{E}^0 = -0.771 \text{ V}$$

The oxidation potential of Mn to MnO_4^- is much more meaningful in solution chemistry than is the energy required to strip seven electrons from a Mn atom in the gas phase.

Although we find it convenient to work with oxidation potentials, the accepted international convention is to use **reduction potentials**. If the oxidation potential for the oxidation of metallic sodium to sodium ion is +2.71 V, the reduction potential for the reduction of a sodium ion to metallic sodium is −2.71 V.

Example 6

The oxidation potential of metallic calcium is +2.76 V. Write an equation for the oxidation of calcium in aqueous solution. What is the reduction potential of Ca^{2+}? Is Ca^{2+} a good oxidizing agent?

Solution The equation is

$$Ca(s) \rightarrow Ca^{2+} + 2e^- \qquad \mathscr{E}^0 = +2.76\ \mathrm{V}$$

The reduction potential refers to the reverse reaction

$$Ca^{2+} + 2e^- \rightarrow Ca(s) \qquad \mathscr{E}^0 = -2.76\ \mathrm{V}$$

The very negative reduction potential (−2.76 V) shows that Ca^{2+} is definitely *not* a good oxidizing agent.

10-6 CHEMICAL PROPERTIES: THE *s*-ORBITAL METALS

Knowing the electronic structures of atoms, we can interpret the chemical properties of the metals in a reasonable way. Don't try to memorize all the facts given here; instead, try to pick out of the descriptive material those properties that show regular trends across the periodic table, and those that can be explained by electronic structure. Not every chemical property becomes absolutely clear once we know the electronic structure of an atom of an element, but much of what we observe *does* make sense now, and it is this sense that we shall look for in the mass of chemical data.

Group IA. Alkali Metals: Li, Na, K, Rb, and Cs

All the alkali metals have an s^1 outer electronic configuration. The electron is lost easily; these elements thus have low ionization energies and low electronegativities. Ionization energy and electronegativity decrease from Li to Cs as the distance between the outer shells and the nucleus increases.

These metals are the most reactive known, and never occur naturally in the metallic state. They occur in combination with oxygen, chlorine, or other elements, always in the +1 oxidation state. All their compounds are ionic, even the hydrides. Virtually any substance capable of being reduced will be reduced in the presence of an alkali metal. The oxidation potentials of the alkali metals, from Li to Cs, are

$$\begin{array}{llll} \mathrm{Li}(s) & \rightarrow \mathrm{Li}^+ + e^- & \mathscr{E}^0 = +3.05\ \mathrm{V} \\ \mathrm{Na}(s) & \rightarrow \mathrm{Na}^+ + e^- & \mathscr{E}^0 = +2.71\ \mathrm{V} \\ \mathrm{K}(s) & \rightarrow \mathrm{K}^+ + e^- & \mathscr{E}^0 = +2.92\ \mathrm{V} \\ \mathrm{Rb}(s) & \rightarrow \mathrm{Rb}^+ + e^- & \mathscr{E}^0 = +2.92\ \mathrm{V} \\ \mathrm{Cs}(s) & \rightarrow \mathrm{Cs}^+ + e^- & \mathscr{E}^0 = +2.92\ \mathrm{V} \end{array}$$

Each of these metals has a strong tendency to lose electrons and become oxidized in solution. In contrast, it is difficult to reduce their ions; potassium ions have a reduction potential of −2.92 V. Lithium loses electrons in solution more readily than Cs, in spite of the higher ionization energy of Li, because the small size of a Li^+ ion permits water molecules to approach the center of the ion more closely; this makes the hydrated ion quite stable.

Water attacks all the alkali metals, and the reaction with all these metals is violent and exothermic. A typical reaction is

$$\mathrm{Na}(s) + \mathrm{H_2O} \rightarrow \mathrm{Na}^+ + \mathrm{OH}^- + \tfrac{1}{2}\mathrm{H_2}(g) \qquad \Delta H^0_{298} = -167\ \mathrm{kJ}$$

The hydrogen gas evolved is ignited by the heat of the reaction and burns spontaneously in air. The alkali metals ordinarily are stored in kerosene or some other unreactive hydrocarbon.

Because the alkali metals are the strongest reducing agents known, the free metals cannot be prepared conveniently by reduction of their compounds with another substance:

$$\mathrm{Li}^+ + \text{reducing substance} \rightarrow \mathrm{Li} + \text{oxidized substance}$$

Instead, the metals are usually prepared by the electrolysis of their molten compounds.

The easily lost valence electron is responsible for the metallic properties of the alkali metals. With only one mobile electron per atom, metallic bonds are weak. The bonds become weaker with increasing atomic number as the valence electrons become more distant from the nucleus. The metals have low melting and boiling points, and are soft, malleable, and ductile. Lithium can be cut with a knife with difficulty, but Cs is as soft as cheese. Cesium has the lowest ionization energy of any element; its valence electron can be ejected most easily by light in a photoelectric cell. The photoelectric effect is used in photo cells and in television cameras such as the iconoscope, in which the optical image falling on cesium-coated cathodes is converted to electrical impulses.

Almost all the compounds of the alkali metals are soluble in water. The alkali metal ions in solution are colorless. Color is produced when an electron in an atom is excited from one energy level to another, and when the difference in energy of these levels is in the visible portion of the spectrum. The alkali metal ions have no free electrons to be excited by energies in the visible region. The oxides of the alkali metals are basic, and all react with water to form basic hydroxides that are soluble and completely dissociated.

Alkali metals have the interesting property of being soluble in liquid ammonia and forming intensely blue solutions that leave behind the original metal when the ammonia evaporates. The atoms dissociate into positive ions and electrons, and the electrons associate with the NH_3 solvent molecules. Such electrons are known as **solvated electrons**. The intense color has been shown to arise from the solvated electrons and not from the metal ions; the same color can be produced by introducing electrons into ammonia from a platinum electrode.

Group IIA. Alkaline Earth Metals: Be, Mg, Ca, Sr, and Ba

The chemistry of the alkaline earth metals is the chemistry of atoms with two easily lost electrons. All are typical metals and strong reducing agents (although not quite as strong as the alkali metals). The nuclear charge has increased by one from the alkali metals in a given period, but the screening of the nucleus by electrons in inner orbitals is similar for both groups, so the net nuclear charge is greater. Thus, the alkaline earth atoms are smaller and have higher first ionization energies than those of alkali metals in corresponding periods. Their oxidation potentials in aqueous solution are

$$\begin{array}{llll}
\mathrm{Be}(s) & \rightarrow \mathrm{Be}^{2+} + 2e^- & \mathscr{E}^0 = +1.85\ \mathrm{V} \\
\mathrm{Mg}(s) & \rightarrow \mathrm{Mg}^{2+} + 2e^- & \mathscr{E}^0 = +2.37\ \mathrm{V} \\
\mathrm{Ca}(s) & \rightarrow \mathrm{Ca}^{2+} + 2e^- & \mathscr{E}^0 = +2.76\ \mathrm{V} \\
\mathrm{Sr}(s) & \rightarrow \mathrm{Sr}^{2+} + 2e^- & \mathscr{E}^0 = +2.89\ \mathrm{V} \\
\mathrm{Ba}(s) & \rightarrow \mathrm{Ba}^{2+} + 2e^- & \mathscr{E}^0 = +2.90\ \mathrm{V}
\end{array}$$

They are more electronegative than are the alkali metals; nevertheless all their compounds, with the exception of some Be compounds, are ionic. Beryllium is the first example of the general observation that within a group elements with lower principal quantum number will be less metallic because their outer electrons are closer to the nucleus and are held more tightly. This behavior is reflected in the greater electronegativities of the smaller atoms within a group (Table 10-4). Beryllium has a lower oxidation potential, or lower tendency to lose an electron in solution, for the same reason that it has a higher first ionization energy than other elements in the group. It is true that Be, like Li, has a high hydration energy because of its small size. This leads us to expect a strong tendency to oxidize in aqueous solution and a large positive oxidation potential. However, Be has an extraordinarily high ionization energy and energy of vaporization (Table 10-4), and these two effects combine to dominate in the oxidation of Be to Be^{2+}, so the oxidation potential is somewhat lower than might be expected.

The second ionization energies of these metals are usually double their first ionization energies; thus, we might expect $+1$ ions to form and the $+1$ oxidation state to exist in solution. But this is not the case. The hydration of the doubly charged cation gives it enough extra stability to overcome the energy required to remove the second electron. Any solution of Ca^+ ions

Table 10-4

Properties of the Alkaline Earth Metals

Element	Be	Mg	Ca	Sr	Ba
Electronegativity	1.6	1.3	1.0	0.95	0.89
Metallic radius (Å)	0.89	1.36	1.74	1.91	1.98
Melting point (°C)	1278	651	842	769	725
Boiling point (°C)	2970	1107	1487	1384	1140
Heat of fusion (kJ mole^{-1})	11.7	9.2	9.2	9.2	7.5
Heat of vaporization (kJ mole^{-1})	295	129	150	139	151
MCl_2 (melting point, °C)	405	708	772	873	963
MCl_2 (boiling point, °C)	520	1412	1600	1250	1560
Equivalent conductivity of MCl_2 (ohm^{-1} mole^{-1})	0.086	29.0	52.0	—	—

would disproportionate spontaneously to Ca metal and Ca^{2+} ions:

$$2Ca^{+} \rightarrow Ca(s) + Ca^{2+}$$

The solution chemistry of the alkaline earth metals is exclusively that of the +2 oxidation state.

The free metals do not occur in nature because they are too reactive. Beryllium and magnesium are found in complex silicate minerals such as beryl ($Be_3Al_2Si_6O_{18}$) and asbestos ($CaMg_3Si_4O_{12}$) (Chapter 14). Emerald is impure beryl, colored with a trace of chromium. Magnesium, calcium, strontium, and barium occur as the relatively insoluble carbonates, sulfates, and phosphates. Calcium and magnesium are much more common than the other elements in the group. Calcium carbonate, $CaCO_3$, is found as chalk, limestone, and marble, usually from deposits of shells and skeletons of marine organisms. Like the alkali metals, the pure alkaline earth metals are commonly prepared from molten compounds by electrolysis because of the difficulty of finding anything with a higher oxidation potential with which to reduce them chemically.

The pure metals have higher melting and boiling points than do alkali metals because they have two electrons per atom for forming metallic bonds. For the same reason, they are harder, although they still can be cut with a sharp steel knife. Beryllium and magnesium are the only elements in this group commonly used as structural metals; because of their lightness they are used pure or in alloys for aircraft and spacecraft, in which weight is an important factor.

Alkaline earth compounds are generally less soluble in water than the compounds of the alkali metals. The hydrides of Ca, Sr, and Ba (CaH_2, SrH_2, and BaH_2) are ionic and are white powders that release H_2 gas upon reaction with water:

$$CaH_2 + 2H_2O \rightarrow Ca^{2+} + 2OH^{-} + 2H_2$$

The oxides, all with the expected 1:1 atomic ratio (BeO, CaO, and so on), are hard, relatively insoluble in water, and basic with the exception of BeO. In water, the basic oxides form hydroxides, which also are only slightly soluble:

$$CaO(s) + H_2O \rightarrow Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2(s)$$

$Ba(OH)_2$ is strongly basic; $Mg(OH)_2$ is weakly basic.

Beryllium is definitely the odd man out in Group IIA. Its oxide is **amphoteric**, showing both acidic and basic properties. It is virtually insoluble in water, but in strong acid it acts as if it were basic:

$$BeO + 2H^+ + 3H_2O \rightarrow Be(H_2O)_4^{2+}$$

and in strong base it acts as if it were acidic:

$$BeO + 2OH^- + H_2O \rightarrow Be(OH)_4^{2-}$$

In both cases, the cation is so small that only a coordination number of 4 is possible. The coordinating groups are arranged tetrahedrally around Be. The amphoteric behavior of BeO arises because Be is so small and electronegative; Be^{2+} attracts electrons from neighboring water molecules and makes it easier for them to lose a proton to the surroundings:

$$Be^{2+} + 4H_2O \rightarrow Be(OH)_4^{2-} + 4H^+$$

Beryllium shows many other signs of nonmetallic behavior in addition to the amphoterism of its oxide. Its melting and boiling points and heats of vaporization are unusually high, reversing the trends within the rest of Group IIA (Table 10-4). These facts suggest that the covalent bonds in Be, like those in diamond, persist in the liquid. Solid $BeCl_2$ is composed of covalently bonded chains that are held together only by weak intermolecular forces; $BeCl_2$ has the low melting point expected of a molecular, covalent compound instead of an ionic solid such as $CaCl_2$. Finally, liquid $BeCl_2$ does not conduct electricity, a fact that indicates the absence of ions.

10-7 THE FILLING OF THE *d* ORBITALS: TRANSITION METALS

The transition metals are hard metals with high melting and boiling points. The atoms tend to become smaller with increasing atomic number across a period because of the increased nuclear charge. Atoms in the second transition-metal series, Y to Cd, are larger than those in the first, Sc to Zn. But atoms in the third transition-metal series, Lu to Hg, are not as much larger than the atoms in the second series as would be expected. The reason is that the first *inner* transition-metal series, the lanthanides, is interposed after La. There is a steady decrease in size from La to Lu because of increasing nuclear charge, which produces the **lanthanide contraction**. Therefore, hafnium is not as large as it would have been had it followed directly after La. The nuclear charge in Zr is 18 greater than that in Ti, but that in Hf is 32 greater than that in Zr. The result is that the second- and third-series transition metals have not only the same outer electronic configurations in corresponding groups, but almost the same size as well. Thus, the second and third series are more similar in properties than either is to the first. Titanium resembles Zr and Hf less than Zr and Hf resemble one another. Vanadium is distinct from Nb and Ta, but the very names of Ta and Nb reflect how difficult it is to separate them. Tantalum and niobium were discovered in 1801 and 1802, but for nearly half a century many chemists thought that they were the same element. Because of the difficulty in isolating it, Ta was named after Tantalus, the Greek mythological figure who was doomed to an eternity of frustrating labor. Niobium, in turn, was named for Niobe, the daughter of Tantalus.

The Structure of Transition-Metal Ions

In the K^+ and Ca^{2+} ions, the 4*s* orbital is slightly more stable than the 3*d*, and added electrons go into the 4*s* orbital. In contrast, at Sc^{3+}, the 3*d* orbital energy dips below the 4*s*, and it remains there for all higher atomic numbers. The lone electron in Sc^{2+} is in a 3*d* orbital, not in the 4*s*. This behavior is typical of all transition metals. The crossover of *s*- and *d*-orbital energies occurs at the beginning of a transition-metal series. Although the *s* orbitals fill first in Groups IA and IIA, it is the *d* orbitals that are occupied in transition-metal ions. The outer electronic configuration of Ti^{2+} is $3d^2$, not $4s^2$.

The lowest oxidation state in all the 3*d* transition metals, with the exception of Cu and a few rare compounds of other metals, is +2, with both *s* electrons lost. Other higher oxidation states occur with the loss of more electrons from the *d* orbitals, up to a maximum equal to the number of *unpaired* electrons in the *d* orbitals. This is why the maximum oxidation number increases from +3 in Sc to +7 in Mn (five *d* plus two *s*), and thereafter falls by one per group to +2 in Zn (loss of only the two *s* electrons). The most common oxidation states are +2 and +3. In the first half of the series, the maximum oxidation state for each element—Sc(III), Ti(IV), V(V), Cr(VI), and Mn(VII)—is also common (Table 10-2).

These generalizations are true for the first transition series. There are some higher oxidation states observed in the second and third series, as in RuO_4 and OsO_4. It is more important for you to know the behavior of the first transition series than to remember the exceptions in the heavier metals.

Oxidation Potentials

The oxidation potentials for the production of ions from neutral atoms are plotted in Figure 10-2 for the first transition series. The driving force for the production of ions decreases as the atomic number increases because the electrons are held more tightly. The +2-ion curve represents the removal of the two *s* electrons and the retention of the original *d* configuration. It is

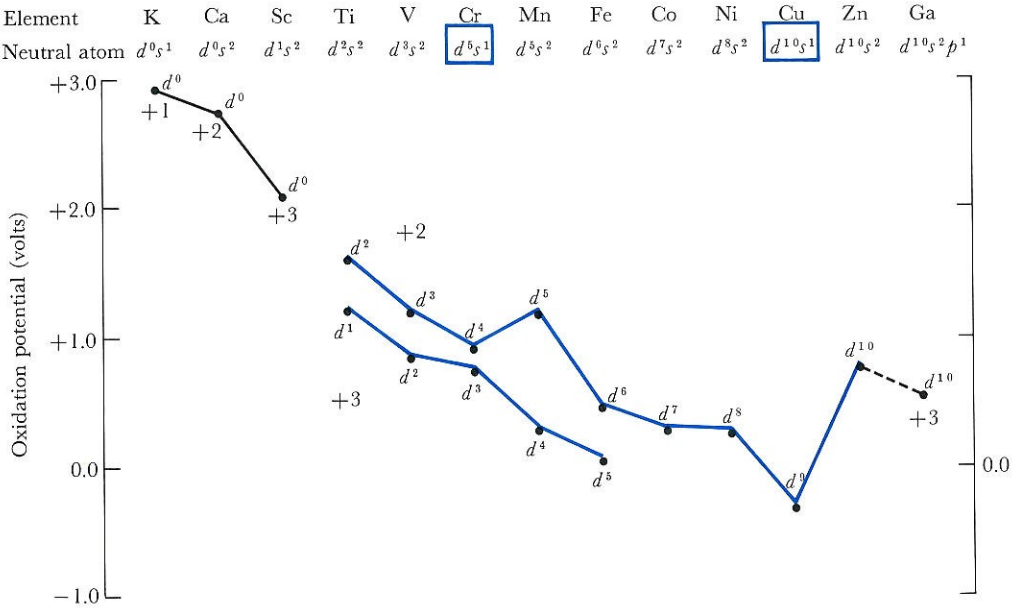


Figure 10-2 Oxidation potentials for the fourth-period metals, including the first transition-metal series. Potentials are for the production of simple cations in solution from the solid metals. The potentials for K, Ca, and Sc are given for the production of +1, +2, and +3 ions with the Ar noble-gas electronic structure. Transition-metal potentials are shown for +2 and +3 ions. By each point is given the outer electronic configuration of the ion.

particularly difficult to remove two electrons in Cu because only one is in the *s* orbital and the second would have to come from the filled d^{10} orbitals. In contrast, it is quite easy to remove the two *s* electrons in Zn and leave the stable, filled d^{10} orbitals untouched. This same effect is observed to a lesser extent in Cr and Mn, in which a half-filled, d^5 configuration is present instead of a filled d^{10}. The *d* electrons must be disturbed when a +3 ion is produced, so we do not have the local fluctuations observed in the +2 curve. The elements preceding the transition series become cations by losing all their electrons outside the inner noble-gas shells; the representative elements following a transition series achieve their maximum oxidation number by losing all their electrons outside the filled d^{10} shells.

Chemical Properties of Individual Groups: Sc and Ti Groups

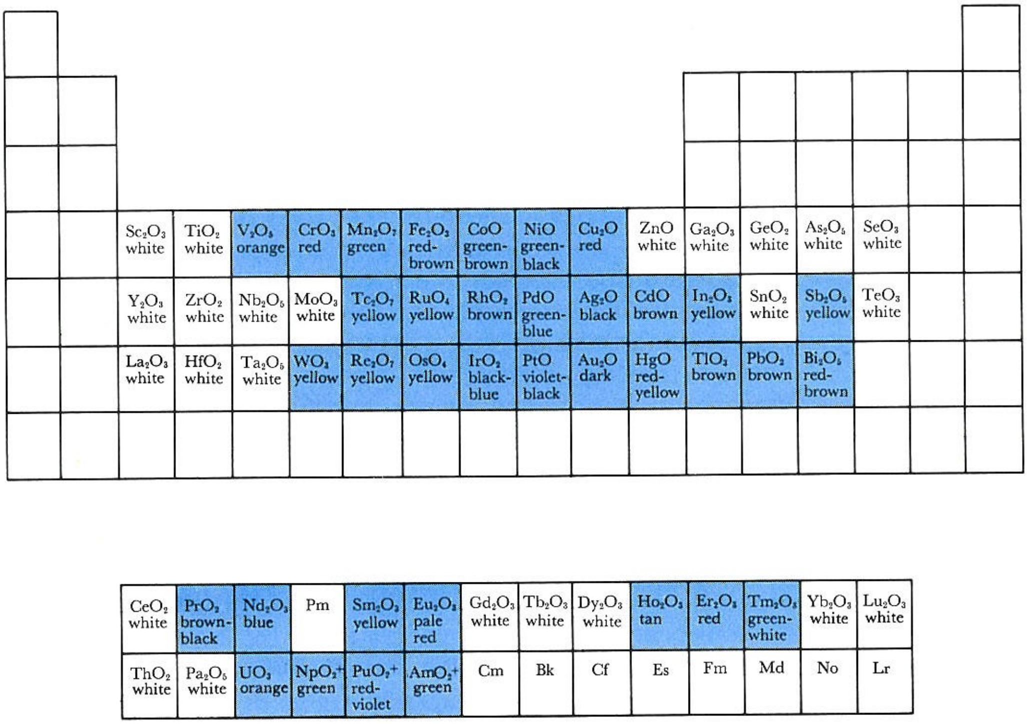
The Sc–Y–Lu triad has the outer electronic configuration d^1s^2, and shows only +3 oxidation states. The properties of these elements are similar to those of Al in Group IIIA. All react with water, as does Al. But Sc_2O_3 is a basic oxide rather than amphoteric, like Al_2O_3, because Sc^{3+} is larger than Al^{3+}. The difference in behavior resembles that between CaO and BeO.

In the Ti–Zr–Hf triad, which has the d^2s^2 electronic configuration, Ti and Zr shows +2, +3, and +4 oxidation states, whereas Hf has only +4. This is an example of a general trend in the transition metals: The lower oxidation numbers are less important for the second and third transition series because the electrons are farther from the nucleus. If they lose some electrons, they are likely to lose all of them. The lower oxidation states of Ti are ionic, and the +4 state is more covalent and nonmetallic. Titanium (II) oxide, TiO, is basic and ionic; it has the NaCl crystal structure. In contrast, the dioxide, TiO_2, is a white, insoluble pigment that has both basic and acidic properties. The chlorides provide a particularly good illustration of this progression of properties. The dichloride, $TiCl_2$, is a strong reducing agent and oxidizes spontaneously in air. It is an ionic solid that decomposes at 475°C in a vacuum. Since it reduces water to H_2, there is no aqueous chemistry of Ti^{2+}. Titanium trichloride, $TiCl_3$, is another strong reducing agent and is an ionic solid that decomposes at 440°C. In contrast, the tetrachloride, $TiCl_4$, is a stable liquid that freezes at −25°C and boils at +136°C. It boils before $TiCl_3$ melts (decomposes) because it is a molecular compound with covalent bonds.

The Vanadium Group and the Colors of Ions and Complex Compounds

The chemistry of the V–Nb–Ta elements is similar to that of the previous triad: V and Ta have the d^3s^2 electronic configuration and Nb has the d^4s^1 configuration. Vanadium has oxidation states of +2, +3, +4, and +5, whereas only the +5 state is important in Nb and Ta (although some +3 and +4 compounds are known). Like Ti, Zr, and Hf, these metals react easily with N, C, and O at high temperatures, and it is difficult to prepare them by the high-temperature reduction processes used with Fe and other metals. At low temperatures an oxide coating protects them; consequently, the metals are more inert than their oxidation potentials would suggest. At the top of the group, V_2O_5 is amphoteric like TiO_2. It dissolves in both acids and bases to form complex and poorly characterized polymers. The +4 oxidation state of V is also on the borderline between ionic and covalent character; VCl_4 is a molecular liquid with a boiling point of 154°C. In contrast, the V(III) compounds are ionic.

The vanadium ions provide good examples of the colors that are typical of transition-metal compounds. Vanadium(V) as VO_4^{3-} is colorless. In aqueous solution, the vanadyl ion, VO^{2+}, is deep blue, the V^{3+} ion is green, and the V^{2+} ion is violet. Only these colors are seen from the entire visible spectrum because the three solutions absorb orange light (ca. 610 nm), red light (ca. 680 nm), and yellow light (ca. 560 nm), respectively. The colors we see are the complementary colors to those absorbed (Table 20-2). Most electronic energy levels are so far apart that the radiation absorbed in an



		Sc_2O_3 white	TiO_2 white	V_2O_5 orange	CrO_3 red	Mn_2O_7 green	Fe_2O_3 red-brown	CoO green-brown	NiO green-black	Cu_2O red	ZnO white	Ga_2O_3 white	GeO_2 white	As_2O_5 white	SeO_3 white		
		Y_2O_3 white	ZrO_2 white	Nb_2O_5 white	MoO_3 white	Tc_2O_7 yellow	RuO_4 yellow	RhO_2 brown	PdO green-blue	Ag_2O black	CdO brown	In_2O_3 yellow	SnO_2 white	Sb_2O_5 yellow	TeO_3 white		
		La_2O_3 white	HfO_2 white	Ta_2O_5 white	WO_3 yellow	Re_2O_7 yellow	OsO_4 yellow	IrO_2 black-blue	PtO violet-black	Au_2O dark	HgO red-yellow	TlO_3 brown	PbO_2 brown	Bi_2O_5 red-brown			

CeO_2 white	PrO_2 brown-black	Nd_2O_3 blue	Pm	Sm_2O_3 yellow	Eu_2O_3 pale red	Gd_2O_3 white	Tb_2O_3 white	Dy_2O_3 white	Ho_2O_3 tan	Er_2O_3 red	Tm_2O_3 green-white	Yb_2O_3 white	Lu_2O_3 white
ThO_2 white	Pa_2O_5 white	UO_3 orange	NpO_2^+ green	PuO_2^+ red-violet	AmO_2^+ green	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 10-3 Oxides of many transition and inner transition metals are colored.

electronic excitation is in the ultraviolet. But in transition-metal complex ions and compounds, the *d*-orbital energy differences are so small that the frequencies of radiation required for transitions are in the visible region; hence, colors are produced (the theory of *d*-orbital energy differences, or splittings, in transition-metal complexes is given in Chapter 20). The smallest energy absorption, in the red region, would leave unabsorbed the wavelengths that produce a complementary blue-green color in the solution or compound. Larger and larger energy absorptions produce blue-green, blue, violet, purple, red-orange, and finally yellow; these are the colors complementary to red, orange, yellow, green, blue, and violet. Clearly, color is an approximate guide to the electronic energy differences in metal complex ions and compounds. The colors of several metal oxides are given in Figure 10-3.

The Chromium Group and the Chromate Ion

The elements Cr, Mo, and W have high melting and boiling points and are hard metals. They are relatively inert to corrosion because films of oxides formed on the surface adhere and protect the metal beneath. The thin layer of Cr_2O_3 on chromium metal makes chrome plating an efficient protection for the more easily attacked metals such as iron. Along with V, these three metals are used mainly as alloying agents in steels. Vanadium gives steels ductility, tensile strength, and shock resistance. Chromium makes stainless steels corrosion resistant, molybdenum acts as a toughening agent, and tungsten (W) is used in steel cutting tools that remain hard even when red hot.

Chromium(III) is the most prevalent oxidation state of chromium. Chromium(II) is a good reducing agent, and Cr(VI) is a good oxidizing agent. As we would expect, the acidity of the oxides varies with the oxidation state: CrO_3 is acidic, Cr_2O_3 is amphoteric, and CrO and $Cr(OH)_2$ are basic. A common anion is the yellow chromate ion, CrO_4^{2-}, which dimerizes in acid to form the orange dichromate ion:

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

The dichromate ion is a powerful oxidizing agent, and the reaction by which dichromate ion is reduced to Cr^{3+} has a large positive reduction potential:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad \mathscr{E}^0 = +1.33\ V$$

We could express the same chemical fact by saying that the reaction by which Cr^{3+} is oxidized to dichromate ion has a low negative oxidation potential, and that the reaction tends to go in the other direction:

$$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \qquad \mathscr{E}^0 = -1.33\ V$$

The Manganese Group and the Permanganate Ion

Of the Mn–Tc–Re triad, Mn is by far the most important. Rhenium was discovered in 1925, and Tc was the first element produced artificially. Technetium was discovered by Perrier and Segré, in 1937, in a sample of Mo that had been irradiated by deuterons (^2_1H particles) in the Berkeley cyclotron by Ernest Lawrence (for whom, incidentally, element 103 was named). The new element was named technetium from the Greek *technetos*, "artificial."

The chief use of Mn metal is to make hard and tough manganese steels. Oxidation states from +2 to +7 are known; the two extremes are the most important. Unlike Ti^{2+}, V^{2+}, and Cr^{2+}, Mn^{2+} shows little tendency to go to higher oxidation states. It is strongly resistant to oxidation and is not a good reducing agent. Manganese(II) in water forms the pink $Mn(H_2O)_6^{2+}$ octahedral complex, and the $MnSO_4$ and $MnCl_2$ salts are also pink. The oxidation states Mn(III) through Mn(VI) are rare, except for the chief natural ore, MnO_2. Mn(VI) does exist as the manganate ion, MnO_4^{2-}. The Mn(VII) state is chiefly important for the deep purple *permanganate* ion, MnO_4^-. It is one of the most powerful common oxidizing agents, with a reduction potential of +1.49 V:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad \mathscr{E}^0 = +1.49\ V$$

Note again that a compound with a high positive reduction potential or a low negative oxidation potential will be a good oxidizing agent because the compound itself will have a strong tendency to go to the reduced form.

Solutions of the permanganate ion are used as disinfectants. (One of our black comedies on World War II has this bitter remark about the medical services available to enlisted men: "The first time you come in, they give you two aspirins; the second time they paint your gums purple. If you show up again, they arrest you for impersonating an officer." The purple, of course, is $KMnO_4$.) Manganese provides an excellent example of the dependence of chemical properties on oxidation state. Manganese(II) exists in solution as a cation and has a basic oxide, MnO, and hydroxide, $Mn(OH)_2$. At the other extreme, the +6 and +7 states exist as anions, MnO_4^{2-} and MnO_4^-, corresponding to the acidic oxides MnO_3 and Mn_2O_7.

The Iron Triad and the Platinum Metals

In Group VIII, the horizontal similarity between Fe, Co, and Ni is greater than that between these and the corresponding elements in the second and third transition series. These nine elements are usually separated into the iron triad, Fe–Co–Ni, and the light and heavy platinum triads, Ru–Rh–Pd and Os–Ir–Pt. Iron, cobalt, and nickel have the electronic configurations d^6s^2, d^7s^2, and d^8s^2, respectively. All show chiefly the +2 and +3 oxidation states. (The +3 state is very rare for Ni.) Iron is one of the most important structural metals. Many of the other transition metals are important chiefly as alloying agents with iron. Iron is found in three main oxide ores: FeO, Fe_2O_3, and the magnetic mixed oxide magnetite, Fe_3O_4 or $FeO \cdot Fe_2O_3$. Iron is produced by high-temperature reduction with the CO from coke in a blast furnace. The result is cast iron with 3–4% carbon. The open hearth and Bessemer processes are means of burning out most of this carbon with streams of oxygen to obtain steels with 0.1–1.5% carbon.

Iron is no more intrinsically reactive than the other transition metals that we have been discussing. Unfortunately, however, the iron oxides do not adhere to the surface of metallic iron. Rust (iron oxide) flakes off as it is formed and exposes fresh metal to attack. Chrome steel or stainless steel is more corrosion resistant, but the customary protection is an added surface layer such as chromium, tin, nickel, or paint. Ferrous or iron(II) compounds are usually green, and the hydrated ferric ion, $Fe(H_2O)_6^{3+}$, is a pale violet. Both +2 and +3 states form octahedral complexes with cyanide: $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$. The traditional names for these anions are *ferrocyanide* and *ferricyanide*. In the modern systematic nomenclature, they are *hexacyanoferrate (II)* and *hexacyanoferrate(III)*. The nomenclature of complex ions is given in Chapter 20.

Cobalt in solution exists mainly as the +2 cation, since Co^{3+} is an excellent oxidizing agent and has a strong tendency to be reduced to Co^{2+}:

$$Co^{3+} + e^- \rightarrow Co^{2+} \qquad \mathscr{E}^0 = +1.84\ V$$

But in many octahedral complexes of Co(III) the ligands (the ions or molecules attached to Co) stabilize it against reduction. Nickel forms octahedral and square planar complexes in the Ni(II) state. Many Ni(II) salts, as well as the hydrated cation, are green. The square planar complexes are usually red or yellow.

Metals in the light and heavy platinum triads are relatively rare, and much work remains to be done on their reactions. All are relatively unreactive, and are found naturally as the pure metals. The oxidation states +2, +3, and +4 are most important, and the metals form octahedral or square planar complex ions in solution. Complex ions of Pt(IV) and Ir(III) are octahedral. Complexes of Pt(II) are square planar. The tetrachloroplatinate (II) ion, $PtCl_4^{2-}$, shows a strong tendency to bind to sulfur in proteins, and has been useful in preparing heavy-atom derivatives of proteins for x-ray crystallographic analysis.

The Coinage Metals

Copper, silver, and gold have the slightly irregular outer electronic configuration $d^{10}s^1$. They have lower melting and boiling points than the preceding transition metals and are moderately soft. These properties are part of a downward trend that began with Group VIB (Cr–Mo–W), which follows from the decreasing number of unpaired *d* electrons. The metals are excellent conductors of electricity and heat since their electronic arrangement makes the *s* electrons extremely mobile. They are malleable and ductile; they are inert and can be found naturally in the metallic state. Although rare enough to be prized, they are much less scarce than the platinum metals. Their relative abundance and their occurrence as uncombined metals made them the first metals to be collected and worked by man. The first metal to be reduced from its ore was probably copper. Metallurgy began when it was discovered that an alloy of copper with tin (a naturally occurring impurity) produced the much harder bronze. Copper artifacts have been unearthed in some of the earliest farming communities in the Middle East, dating from 7000–6000 B.C. Bronze was known in the Sumerian cities of Ur and Eridu from 3500 B.C., during the era that also saw the invention of writing.

These three metals have been the source of more strife and trouble than any other elements. Until a century ago, they were used mainly for their symbolic and decorative qualities. More recently, the physical properties of Ag and Au—electrical and thermal conductivity and corrosion resistance—have become so valuable that the metals no longer can be spared for their traditional coinage roles. Gold is now used for plating external surfaces of delicate components in satellites and space probes.

Copper, silver, and gold have little resemblance to the alkali metals, with which they are associated in the short form of the periodic table derived from Mendeleev's table (Figure 7-1). Copper shows mainly the +2 oxidation state in solution, and +1 to a lesser extent. For Ag, the reverse is true: The +1 state is common, and the +2 and +3 can be obtained only under extreme oxidizing conditions. Gold occurs in the +3 state and less frequently in the +1. The metals have low negative oxidation potentials, thereby indicating their inertness and reluctance to oxidize:

$$\begin{array}{ll} Cu \rightarrow Cu^{2+} + 2e^- & \mathscr{E}^0 = -0.34\ V \\ Ag \rightarrow Ag^+ + e^- & \mathscr{E}^0 = -0.80\ V \\ Au \rightarrow Au^{3+} + 3e^- & \mathscr{E}^0 = -1.42\ V \end{array}$$

Copper(I) is unstable in solution and disproportionates spontaneously to Cu and Cu^{2+}. However, it can be stabilized by complexes such as $CuCl_2^-$. Copper(I) exists as the solid and extremely insoluble Cu_2O and Cu_2S, which are the principal ores of copper. The chemistry of Cu(II) is similar to that of other transition metals in the +2 oxidation state. The hydrated Cu(II) ion has a characteristic blue color, and tetraamminecopper(II), $Cu(NH_3)_4^{2+}$, is an intense blue. The complex is square planar. Silver(I) forms complexes such as $AgCl_2^-$, $Ag(NH_3)_2^+$, and $Ag(S_2O_3)_2^{3-}$, and Au(III) forms the very stable $AuCl_4^-$ complex.

The Chemistry of Photography

All silver halides except AgF are sensitive to light and are the basis of the photographic process (Figure 10-4). In making photographic film, fine crystals of AgBr are spread in gelatin on a film backing. Light from the camera image interacts with the crystalline AgBr in a poorly understood process that appears to involve defects in the crystal structure, and makes the grains, or crystals, more sensitive to reduction. The sensitized AgBr is reduced in the developer by a mild organic reducing agent such as hydroquinone:

$$AgBr + e^- \text{ (reducing agent)} \rightarrow Ag + Br^-$$

Then the unsensitized AgBr grains are dissolved and washed away in a sodium thiosulfate solution, one of the few solutions in which silver halides are soluble:

$$AgBr + 2S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + Br^-$$

(The old name for sodium thiosulfate was sodium hyposulfite; hence, the synonym "hypo" for fixer.)

The Low-Melting Transition Metals

The most distinguishing characteristic of Zn, Cd, and Hg is their weak coherence as metals. They are soft and have low melting and boiling points. Mercury is the only metal that is liquid at room temperature. Zinc and Cd resemble the alkaline earth metals in their chemical behavior. Mercury is more inert and resembles Cu, Ag, and Au. All three elements have a +2

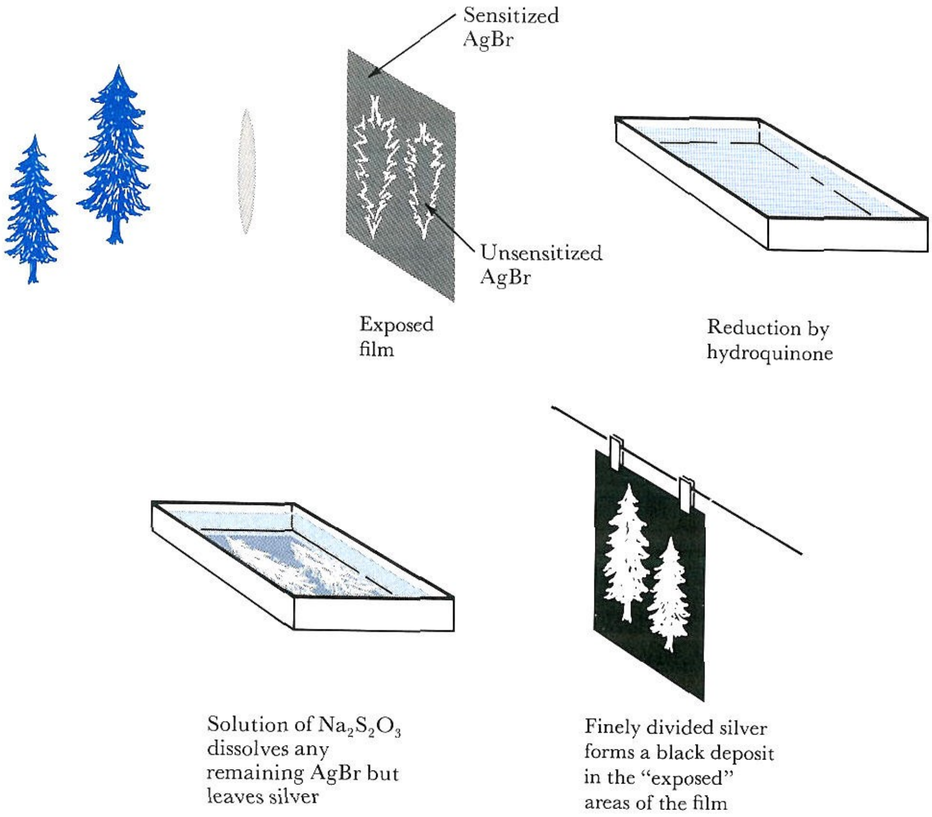


Figure 10-4 In the photographic process, exposure to light renders the silver halide of the film more susceptible to reduction to silver by a reducing agent in the developer. When the unreduced silver halide is dissolved away, a negative image formed by the finely divided silver remains.

oxidation state. Mercury also has a +1 state in compounds such as Hg_2Cl_2. But mercury(I) always appears as the dimeric ion, Hg_2^{2+}, and x-ray and magnetic measurements show that the two Hg atoms are held together by a covalent bond. Therefore, mercury has a +1 oxidation number in Hg_2Cl_2 only in the same formal sense that oxygen is −1 in hydrogen peroxide, H—O—O—H. The chemistry of the +2 state in this group is as expected. The oxides ZnO, CdO, and HgO are only slightly soluble in water but quite soluble in strong acids, as basic oxides should be. Yet ZnO is also soluble in strong bases; hence it is amphoteric. Again, this behavior arises because of the small size of the Zn^{2+} cation and the ease with which it can pull electrons from water molecules and cause them to release protons.

With these elements, the *d* orbitals are filled and the transition series are closed. The next electrons to be added must go into the higher-energy *p* orbitals, and the more rapidly varying representative elements begin.

Trends in the Transition Metals

What systematic trends in behavior of the transition metals can we see from the foregoing material? Some of the trends in properties are as follows.

1. The transition metals can lose, at most, the two *s* electrons and all unpaired *d* electrons in the outer shell. Therefore, the maximum oxidation number is 3 for Sc, and increases by 1 per group to a maximum of 7 for Mn. Thereafter it falls by 1 per vertical column, through Fe, Co, Ni, and Cu, to 2 for Zn. The only exception to this rule is the absence of oxidation number 5 for Co. We shall explain this Co anomaly in Chapter 20 when we discuss transition-metal complexes.

2. Oxidation states lower than this maximum are found; +2 and +3 are especially common.

3. The first transition-metal series, Sc to Zn, shows the full range of oxidation states. The second, and especially the third series, Lu to Hg, show only the higher oxidation states.

4. For a given element with a range of oxidation numbers, the behavior of the lowest oxidation state will be the most metallic, and that of the highest oxidation state will be the least metallic. For example, compounds of V(III) are ionic, whereas V(V) has many compounds with covalent bonds. Among oxides of Cr, CrO is basic, Cr_2O_3 is amphoteric, and CrO_3 is acidic. Titanium dichloride, $TiCl_2$, and $TiCl_3$ are ionic solids, whereas $TiCl_4$ is a molecular liquid.

5. In higher oxidation states, the isolated cation is not stable, even when coordinated to water molecules. Such high oxidation states can be stabilized by coordination to oxide ions. Thus, Sc^{3+} exists as a hydrated ion $Sc(H_2O)_6^{3+}$; Ti(IV) requires the stabilizing influence of coordinating groups such as hydroxide in $Ti(OH)_2(H_2O)_4^{2+}$; and V(V), Cr(VI), and Mn(VII) are coordinated to oxide ions in VO_2^+, CrO_4^{2-}, and MnO_4^-. Oxidation states that are not stable in solution sometimes can be stabilized by the formation of complexes such as $CuCl_2^-$.

6. Oxidation potentials for the oxidation of transition metals to the +2 or +3 cation in aqueous solution generally decrease as the atomic number increases, thereby reflecting the greater difficulty in removing electrons from the atoms. Ionization energies increase in a corresponding manner.

7. Certain physical properties of the transition metals (melting points, boiling points, and hardness) reflect the number of unpaired *d* electrons in the atoms. These properties increase to a maximum in the Mn group and then decrease with increasing atomic number.

10-8 THE FILLING OF *f* ORBITALS: LANTHANIDES AND ACTINIDES

After the atomic number reaches 57, the energy of the 4*f* orbitals is sufficiently low to allow those orbitals to be utilized. Consequently, after barium in Period 6 the seven $4f$ orbitals can fill successively with electrons, thereby producing the 14 lanthanide metals. Likewise in Period 7 after $Z = 89$, when the $5f$ and the $6d$ orbitals have virtually the same energy, there are 14 actinide metals, which are formed when the seven $5f$ orbitals are filled successively with electrons. The electronic configurations of these inner transition elements are shown in Figure 9-3. As with *d* orbitals in the transition metals, there are irregularities in the *f*-orbital utilization, more so for the actinides than for the lanthanides. But again, it is sufficient now to know the trend and leave the irregularities until later. (Incidentally, it is because the first element of each series—La and Ac—have d^1 configurations instead of f^1 that these series are sometimes shown to begin with Ce and Th, as in the periodic table on the inside front cover.)

All the lanthanides and actinides are typical metals with high luster and conductivity. These metals are chemically reactive, with oxidation potentials in the range 2–3 V. Because of their high oxidation potentials (and also low first ionization energies) the metals tarnish readily in air and react vigorously with water to displace hydrogen.

The most important characteristic of the lanthanides is their close similarity to one another. This similarity is due primarily to the successive electrons going into the low-lying *f* orbitals, which results in small changes in atomic and ionic radii ($\sim$0.01 Å) from one element to the next. The predominant oxidation state for the lanthanides, and to a lesser extent for the actinides, is $+3$; nearly all compounds of these elements are ionic salts with discrete $+3$ ions. Because of their great similarity, lanthanide compounds are found together in nature and are difficult to separate from one another.

The actinides are distinguished from the lanthanides in that they all are radioactive. (Promethium, $Z = 61$, is the only radioactive lanthanide.) The transuranium actinides ($Z = 93$ to $Z = 103$) are man-made elements.

10-9 THE *p*-ORBITAL OR REPRESENTATIVE ELEMENTS

After the interruptions for the transition and inner transition metals, the filling of the outermost *p* orbitals begins again (as with B and Al in Periods 2 and 3) and goes to completion. The alkali metals and alkaline earth metals are remarkable for their smooth gradation of properties within a group. The transition metals also vary gradually from one element to the next. But beginning with Group IIIA, we see sharp variations within a group, although these variations are systematic and fall into a pattern that can be followed across the remainder of the periodic table. The sharp variations occur at the transition between metallic and nonmetallic properties. Some of the trends are shown in Tables 10-5 and 10-6.

Table 10-5 gives the melting points of the halides of Li, Be, B, and C. The Li halides are ionic. Their melting points decrease with the heavier anions because these large anions cannot approach the Li^+ ion as closely

Table 10-5

Melting Points of Halides of Second-Period Elements (°C)

X =	F	Cl	Br	I	
LiX	842	614	547	450	Ionic
BeX_2	800[a]	405	490	510	Covalent
BX_3	−127	−107	−46	50	
CX_4	−184	−23	90	Decomposes	

[a] Extended chains held together by ionic forces.

and are not bound as strongly by electrostatic forces. The carbon tetrahalides exhibit the opposite behavior. They are covalent molecular compounds, and the heavier molecules have a higher melting point because more thermal energy is required to move them. By this criterion, the boron trihalides are also covalent. Beryllium constitutes the borderline case mentioned previously. With elements of similar electronegativity, it forms covalent compounds. With the strongly electronegative F, Be forms long chains similar to those in $BeCl_2$. But because F is so electronegative, Be acquires a positive charge and F a negative charge. The covalently bonded chains are held together by ionic forces.

The border between metallic and nonmetallic behavior is shown in Table 10-6. Note the diagonal character of the border area: The amphoteric properties of Be in Group IIA appear one period lower in the neighboring group, in Al instead of B. Boron is a nonmetal and makes covalent bonds in compounds in which it has a +3 oxidation state. Aluminum also can make covalent bonds but is definitely metallic. The acidic oxide B_2O_3 forms boric acid in water:

$$\tfrac{1}{2}B_2O_3 + \tfrac{5}{2}H_2O \rightarrow B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+$$

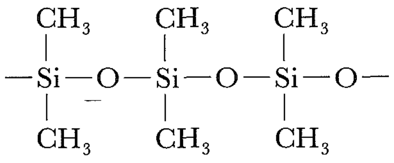
Aluminum oxide, Al_2O_3, is amphoteric, and the oxides of Ga, In, and Tl are basic. Except for boron, the elements in Group IIIA are metals. Gallium has only the +3 oxidation state and a chemistry quite similar to Al; In exhibits both +3 and +1; Tl shows both states, but +1 is more common.

Group resemblances are even less apparent in Group IVA. Carbon is a nonmetal that almost always makes four covalent bonds with other elements. It can polymerize with itself in a chain to form what are classified as organic compounds, and can construct multiple covalent bonds with the same atom. Silicon is a nonmetal with several metallic properties, including a silvery sheen. It can form a limited number of hydrides, called **silanes**, analogous to the hydrocarbons, with the general formula Si_xH_{2x+2}.

Properties of Elements on the Metal–Nonmetal Border of the Periodic Table

$BeCl_2$ Covalent molecular chains held together in solid and liquid by weak intermolecular forces. Narrow liquid range; mp 400 °C, bp 520 °C. Forms a dimer, Be_2Cl_4	BCl_3 Molecular gas; mp −107 °C, bp 13 °C. Hydrolyzes completely in solution	CCl_4 Molecular gas above 76.8 °C. Inert in water
BeF_2 Covalent molecular chains held together in solid by ionic forces, mp 800 °C. BeF_4^{2-} complex in solution	BF_3 Molecular gas; mp −127 °C. BF_4^- complex in solution	CF_4 Molecular gas; mp −184 °C. Inert in water
$Be(OH)_2$ Amphoteric hydroxide	$B(OH)_3$ Boric acid. Forms polymeric ions	CO_2 Gaseous, acidic oxide
$MgCl_2$ Ionic solid; mp 708 °C, bp 1412 °C	$AlCl_3$ Covalent network solid; sublimes 178 °C. Forms dimer, Al_2Cl_6	$SiCl_4$ Volatile molecular liquid; mp −70 °C, bp 57.6 °C. Hydrolyzes completely in water
MgF_2 Ionic solid; mp 1266 °C, bp 2239 °C	AlF_3 Ionic solid; mp 1040 °C. AlF_6^{3-} complex in solution	SiF_4 Molecular gas; mp −90 °C. SiF_6^{2-} complex in solution
$Mg(OH)_2$ Basic hydroxide	$Al(OH)_3$ Amphoteric hydroxide	SiO_2 Solid acidic oxide. Forms polymeric anions

But the chains break beyond $x = 6$, and even these low-molecular-weight silanes are explosively reactive with halogens and oxygen. Silicon can form another class of polymers, the **silicones**, in which the Si atoms are bridged with oxygen atoms:



$$-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$$

These silicones are inert, water repellent, electrically insulating, and stable to heat. Silicon, despite the science fiction writers, is not a suitable alternative to carbon for life forms, at least under terrestrial conditions.

Germanium is a semimetal, and tin and lead are metals. Carbon and silicon show the +4 oxidation state in combination with oxygen-family elements and the halogens. For example, carbon has a +4 oxidation state in CCl_4, CO_2, and CS_2. Germanium and tin have both +4 and +2 states, and the chemistry of lead is almost wholly that of the +2 state.

The same behavior occurs in Group VA, but the break between metals and nonmetals is lower in the group. Nitrogen and phosphorus are nonmetals whose covalent chemistry and oxidation states are governed by the presence of five valence electrons: s^2p^3. Nitrogen and phosphorus most commonly have oxidation states −3, +3, or +5. Arsenic and antimony are semimetals with amphoteric oxides, and only Bi is metallic. For As and Sb, the +3 state is the most important. For Bi it is the only state, except under extraordinary conditions. Bismuth cannot lose all five valence electrons; the energy required is too high. However, it does lose the three 6*p* electrons to produce Bi^{3+}.

The trend in Group VIA is similar to that in the N group. Both oxygen and sulfur are nonmetals. Oxygen is strongly electronegative and has only the −2 oxidation state, except in OF_2 and the peroxides. Sulfur has the −2 state and several positive states as well, especially +4 and +6. Selenium and tellurium are semimetals, but have a chemistry that resembles that of sulfur. Polonium, a rare, radioactive element, has the electrical conductivity of a metal.

With Group VIIA, all metallic properties have been lost; thus the halogens are nonmetals. They are only one electron short of possessing a noble-gas electronic arrangement, and are reduced easily to anions with the s^2p^6 electronic configuration. Their reduction potentials are

$$\begin{aligned}
F_2 + 2e^- &\rightarrow 2F^- & \mathscr{E}^0 &= +2.86\text{ V}\\
Cl_2 + 2e^- &\rightarrow 2Cl^- & \mathscr{E}^0 &= +1.36\text{ V}\\
Br_2 + 2e^- &\rightarrow 2Br^- & \mathscr{E}^0 &= +1.09\text{ V}\\
I_2 + 2e^- &\rightarrow 2I^- & \mathscr{E}^0 &= +0.54\text{ V}
\end{aligned}$$

For Cl, Br, and I, all odd oxidation numbers between −1 and +7 are known. But F, like O, is too electronegative to exhibit the positive states; it occurs only in the −1 state.

Summary

Atoms in complex ions and compounds are assigned **oxidation numbers** as an aid in keeping track of electrons during chemical reactions. Balancing a redox equation is equivalent to requiring that electrons be neither created nor destroyed. The maximum oxidation number exhibited by an atom of an element generally increases across a period. In the third period, for example, we have the following: $Na^+(+1)$, $Mg^{2+}(+2)$, $Al^{3+}(+3)$, $SiCl_4$ $(+4)$, $PF_5(+5)$, $SF_6(+6)$, and $ClO_4^-(+7)$. The oxidation number of an atom is often called the **oxidation state** of that atom (or element) in a compound. Reactions in which the oxidation states of atoms change are called **oxidation–reduction (redox) reactions.** In such reactions the species whose oxidation number increases is called the **reducing agent (reductant)** and the species whose oxidation number decreases is called the **oxidizing agent (oxidant).** In a redox reaction electrons are transferred from the reducing agent to the oxidizing agent. A species that undergoes self-oxidation–reduction is said to **disproportionate.** In a balanced redox equation the total number of electrons lost by the reducing agent is equal to the total number gained by the oxidizing agent. The **equivalent weight** of a redox agent is equal to its molecular weight divided by the oxidation-number change it undergoes in the reaction under consideration. The normality of a redox agent is the number of equivalents in 1 liter of solution. The normality therefore depends on the reaction that the redox agent undergoes.

The tendency of a substance to lose electrons in aqueous solution is known as its **oxidation potential.** The tendency for a substance to gain electrons in aqueous solution is called its **reduction potential.** The oxidation potentials of the alkali metal elements (Li, Na, K, Rb, Cs; all s^1 atoms) to form hydrated cations of +1 charge [$Li(s) \rightarrow Li^+ + e^-; \mathscr{E}^0 = +3.05$ V] are very large. The oxidation potentials of the alkaline earth metals (Be, Mg, Ca, Sr, Ba; all s^2) to form +2 hydrated cations [$Ca(s) \rightarrow Ca^{2+} + 2e^-;$ $\mathscr{E}^0 = +2.76$ V] are also large. The reduction potentials of the halogens to form halide ions are all large ($F_2 + 2e^- \rightarrow 2F^-; \mathscr{E}^0 \doteq +2.86$ V).

The border between metals and nonmetals sweeps diagonally across the periodic table in an ill-defined band that goes approximately from Be and B to Po and At. The oxides of elements at or near the borderline often exhibit **amphoteric** (both acidic and basic) behavior. For example, BeO and Al_2O_3 are amphoteric. The transition metals undergo a smooth variation in melting point, boiling point, hardness, and common oxidation number, all of which can be related to the number of unpaired *d* electrons. Because of the **lanthanide contraction,** elements in the second and third transition series are more similar in size and in chemical properties than are those in the first and second periods.

Self-Study Questions

1. What is the oxidation number of Co in K_3CoF_6? In K_2CoI_4?
2. How are the suffixes *-ic* and *-ous* associated with oxidation state? Match the following formulas and names:
   a) Sulfuric and sulfurous acids: H_2SO_3 and H_2SO_4
   b) Nitric and nitrous acids: HNO_2 and HNO_3
3. Oxidation numbers are a convenient bookkeeping device for keeping track of electrons; they are useful even though in the actual reaction electrons are not totally removed from one atom and entirely given to another. The principle of conservation behind balancing redox equations is this: In a chemical reaction, electrons are neither created nor destroyed. How does this principle lead inevitably to Rule 8 (Section 10-1): In chemical reactions, the total oxidation number is conserved?
4. How does Rule 5, which deals with the relative oxidation numbers of nonmetals, follow from what you learned in Chapter 9 about ionization energies and electron affinities?
5. How are the most common oxidation states of the representative elements related to their group numbers?
6. What pattern of maximum oxidation numbers can be seen across a period in the transition metals?
7. Is a substance that gives up electrons in a reaction an oxidizing agent or a reducing agent? Is it oxidized or reduced? Does its oxidation number increase or decrease in the process?
8. Give the equivalent weight of sulfuric acid, H_2SO_4, in each of the following processes:
   a) An acid-base titration
   b) A redox reaction in which the sulfate ion goes to sulfite
   c) A redox reaction in which the sulfate ion goes to sulfide
9. What is the normality of a $0.1M$ solution of sulfuric acid in each of the three processes of Question 8?
10. The imaginary element turbidium (Tu) has the following oxidation potential:

    $$\mathrm{Tu} \rightarrow \mathrm{Tu}^{3+} + 3e^- \qquad \mathscr{E}^0 = -3.00\ \mathrm{V}$$

    Is the turbidium a good oxidizing agent? A good reducing agent? Or is it neither? Is the Tu^{3+} ion a good oxidizing agent? A good reducing agent? Or is it neither?
11. What is the difference between oxidation potentials and reduction potentials?
12. Why are Li and Na not found free in nature, whereas Ag and Au are?
13. From which metal can electrons be ejected with light of a longer wavelength, Na or Cs? Why?

14. Which element is more metallic, Be or Ba? What evidence permits you to say this? How can you explain this in terms of electronic configuration?
15. Why is calcium harder than potassium?
16. Why is BeO amphoteric? What does this term mean in relation to chemical behavior?
17. What is the lanthanide contraction? Why does it occur? What detectable chemical effects does it produce?
18. If the first electrons after those in the Kr noble-gas shells go into the 5*s* orbital for Rb and Sr, why is the outer electronic configuration of Zr^{2+} $4d^2$, rather than $5s^2$ as in Sr?
19. How does the maximum oxidation number change with atomic number in the first transition-metal series, Sc to Zn?
20. In a transition metal with several oxidation states, which state is usually most metal-like in its compounds? Can you give an example?
21. As the principal quantum number of the element increases within a transition-metal group (vertical column), do the higher or lower oxidation states become more important? Can you give a reason for this behavior?
22. How is the color of a chemical related to electronic transitions between energy levels?
23. Why are transition-metal compounds more often colored than those of the representative elements?
24. How do the oxides of Cr, Ni, Cu, Al, and many other metals differ from iron oxide in a way that has great economic importance? Try to imagine a world in which iron oxide behaved the same way. What important chemical industry would be badly hurt if this were so?
25. Why do Zn, Cd, and Hg have such low melting points compared with Cr, Mo, and W?
26. Why do amphoteric oxides appear for those elements that lie on a diagonal across the periodic table (Be, Al, Ge, Sb) rather than in one group separating the metals from the nonmetals?
27. How does metallic character change within one group of the table?
28. Are the halogens good reducing agents or good oxidizing agents?
29. What aspect of electronic structure explains the high electrical conductivities of the coinage metals, Cu, Ag, and Au?
30. What are the principal oxidation states of nitrogen and phosphorus?

Problems

Oxidation numbers

1. Xenon forms several nonionic compounds with F and O. Give the oxidation number of the central Xe atom in each of the following compounds: XeO_4, XeF_2, XeO_3, XeF_4, and XeF_6.

2. Xenon can also form a number of ionic compounds, including $CsXeF_7$ and Cs_2XeF_8. What are the ions in each compound? What are the ionic charge and oxidation number of Xe in each ion containing Xe?

3. What is the oxidation number of the central atom in each of the following ions or molecules: $Co(CN)_6^{3-}$, $PtCl_6^{2-}$, CO_3^{2-}, SF_4?

4. What is the oxidation number of nitrogen in each of the following ions or molecules: NH_3, N_2H_4, NO, NO_2, NO_2^-, NO_3^-?

5. What is the oxidation number of platinum in the complex ion $PtCl_4^{2-}$?

6. Assign oxidation numbers to the atoms in the following chemical species: (a) gold, Au; (b) iodine, I_2; (c) barium chloride, $BaCl_2$; (d) ethane, C_2H_6; (e) stannous oxide, SnO; (f) stannic oxide, SnO_2; (g) nitrous oxide, N_2O; (h) phosphorus pentoxide, P_2O_5; (i) magnesium hydroxide, $Mg(OH)_2$; (j) sulfurous acid, H_2SO_3; (k) telluric acid, H_6TeO_6; (l) hypochlorous acid, HClO; (m) perchloric acid, $HClO_4$; (n) dichromate, $Cr_2O_7^{2-}$; (o) cyanide, CN^-.

7. What is the oxidation number of the underlined element in each ion or molecule: $\underline{V}O_2^+$, $\underline{P}_2O_7^{4-}$, $\underline{P}H_3$, $K\underline{N}O_2$, $H_2\underline{O}_2$, $Li\underline{H}$, $Mg_3\underline{N}_2$, $\underline{N}F_3$, $\underline{I}Cl_5$, $\underline{Ag}(NH_3)_2^+$?

Redox equations

8. When the equation

$$MnO_2 + I^- + H^+ \rightarrow Mn^{2+} + I_2 + H_2O$$

is balanced, what is the net charge on each side of the equation? What element is oxidized? What element is reduced?

9. For each of the following reactions, list the substance reduced, the substance oxidized, the reducing agent, and the oxidizing agent.

   a) $6H^+ + MnO_4^- + 5SO_3^{2-} \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$

   b) $8H^+ + Cr_2O_7^{2-} + 6HI \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

   c) $3Cl_2 + 6OH^- \rightarrow ClO_3^- + 5Cl^- + 3H_2O$

10. Phosphine, PH_3, is a colorless, highly toxic gas that smells like rotten fish and is produced in small amounts when animal and vegetable matter decay in moist situations such as damp graveyards. Traces of P_2H_4 are produced simultaneously and cause the PH_3 to ignite in air to give pale, flickering lights commonly called "corpse candles" or "will-o'-the-wisps." In the laboratory, phosphine can be prepared by adding water to calcium phosphide. Write a balanced equation for the reaction. Assign oxidation numbers to each of the elements present.

11. Balance the reaction

$$MnO_4^- + H^+ + H_2S \rightarrow Mn^{2+} + H_2O + S$$

What is the oxidation number of Mn in MnO_4^-? What element is oxidized? What element is the oxidizing agent? Is this latter element oxidized or reduced?

12. Balance the following equations by the oxidation-number method:

   a) $H_2S + Cr_2O_7^{2-} \rightarrow S + Cr^{3+}$ (acidic solution)

   b) $NH_3 + O_2 \rightarrow NO + H_2O$

   c) $NO_2^- + MnO_4^- \rightarrow NO_3^- + MnO_2$ (basic solution)

   d) $NH_3 + ClO^- \rightarrow N_2H_4 + Cl^-$ (basic solution)

   e) $H_2 + OF_2 \rightarrow H_2O + HF$

   f) $MnO_2 + Al \rightarrow Al_2O_3 + Mn$

13. Balance the following equations by the half-reaction method:

   a) $MnO_2 + KOH + O_2 \rightarrow K_2MnO_4 + H_2O$

   b) $CuCl_4^{2-} + Cu \rightarrow CuCl_2^-$ (acidic solution)

c) $NO_3^- + Zn \rightarrow NH_4^+ + Zn^{2+}$ (acidic solution)

d) $ClO_2 \rightarrow ClO_2^- + ClO_3^-$ (basic solution)

e) $Fe^{2+} + Cr_2O_7^{2-} \rightarrow Fe^{3+} + Cr^{3+}$ (acidic solution)

f) $Cu + NO_3^- \rightarrow Cu^{2+} + NO$ (acidic solution)

14. Balance the following equations by any method you choose:

a) $H_3PO_4 + CO_3^{2-} \rightarrow PO_4^{3-} + CO_2 + H_2O$ (neutral solution)

b) $MnO_2 + SO_3^{2-} \rightarrow Mn(OH)_2 + SO_4^{2-}$ (basic solution)

c) $H^+ + Cr_2O_7^{2-} + H_2SO_3 \rightarrow Cr^{3+} + HSO_4^-$ (acidic solution)

d) $MnO_4^- + V^{2+} \rightarrow VO_2^+ + Mn^{2+}$ (acidic solution)

e) $FeSO_4 + NaClO_2 \rightarrow Fe_2(SO_4)_3 + NaCl$ (in sulfuric acid solution)

f) $KNO_2 + KMnO_4 \rightarrow KNO_3 + MnO_2$ (in KOH solution)

g) $MnO_4^- + OH^- + I^- \rightarrow MnO_4^{2-} + IO_3^- + H_2O$

h) $KMnO_4 + NH_3 \rightarrow KNO_3 + MnO_2 + KOH + H_2O$

Molarity, normality, redox equivalents

15. Twelve grams of $KMnO_4$ were dissolved in sufficient water to make a liter of solution. Calculate the molarity of the solution. The solution was divided into parts and used in four different reactions. Reaction 1 was carried out in basic solution, thereby producing MnO_2 as a product. Reaction 2 was carried out in very strong base to give MnO_4^{2-}. Reaction 3 gave Mn^{3+} in acid solution, and reaction 4 yielded Mn^{2+}. Calculate the equivalent weight of $KMnO_4$ and the normality of the potassium permanganate solution for each reaction.

16. A solution of potassium dichromate, $K_2Cr_2O_7$, is made by adding enough water to 3.52 g of the salt to fill a 100-ml volumetric flask. (a) What is the molarity of the solution? (b) The solution will be used in a titration in which the dichromate ion is reduced to Cr^{3+}. What is the normality of the solution?

17. Find the equivalent weight of an oxidizing agent that oxidizes Fe^{2+} to Fe^{3+} if 0.664 g of the compound requires 23.5 ml of $0.540M$ Fe^{2+} solution.

18. (a) When H_3PO_4 reacts with NaOH to produce NaH_2PO_4, how many equivalents of H_3PO_4 are there per mole? (b) When H_3PO_4 is reduced to H_3PO_2, how many equivalents of H_3PO_4 are there per mole?

19. Exactly 6.40 g of gaseous SO_2 are absorbed in 95 ml of water. When absorption is complete, water is added so the final volume of solution is 100 ml. Calculate for each of the following reactions the volume of solution *of this composition* that contains 1 equiv of H_2SO_3: (a) neutralization to SO_3^{2-} with sodium hydroxide; (b) oxidation to SO_4^{2-}; (c) reduction to S^{2-}; (d) reduction to elemental sulfur.

20. An acidic solution is $0.10M$ in TiO^{2+}. What is its normality when reacted with (a) dilute NaOH to produce TiO_2; (b) dilute $FeSO_4$ to produce Ti^{3+}; (c) concentrated H_2SO_4 to produce Ti^{4+}?

21. A slightly acidic solution is $0.01M$ in Cl_2. What is its normality when reacted with (a) dilute $FeSO_4$ to produce Fe^{3+}; (b) dilute H_2O_2 to produce HClO?

22. If chlorine gas is bubbled through a basic solution of potassium iodide, the following reaction occurs:

$$\mathrm{KOH + Cl_2 + KI \rightarrow KCl + KIO_3 + H_2O}$$

Balance the equation. If chlorine gas is bubbled through 25 ml of a $0.10N$ solution of KI in aqueous KOH at STP, what volume of Cl_2 gas is required to react completely with the KI? (KI normality is based on its reducing action.)

23. Given the equation

$$\mathrm{H_2SO_4 + HI \rightarrow H_2S + I_2 + H_2O}$$

calculate the number of moles of sulfuric acid consumed by reaction with 25.00 ml of $0.100N$ HI. (Check first to see if the reaction is balanced.)

24. When H_2S reacts with $KMnO_4$ in acidic solution, the following reaction can be written:

$$\mathrm{MnO_4^- + H_2S + H^+ \rightarrow Mn^{2+} + S + H_2O}$$

Balance the equation. If a $0.05N$ solution of H_2S is used to titrate 50 ml of permanganate solution, 70 ml are required to reach the end point. What is the normality of the original permanganate solution? What is the molarity?

25. A 25.00-ml sample of an unknown copper solution is treated with excess potassium iodide in acidic solution, and the liberated iodine is titrated with $0.0250M$ sodium thiosulfate. If 12.50 ml of the thiosulfate solution are required to reach the end point, what is the molarity of the unknown copper solution? The unbalanced reactions are

$$\mathrm{Cu^{2+} + I^- \rightarrow CuI + I_3^-}$$
$$\mathrm{I_3^- + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}}$$

26. In oxidizing H_2SO_3 to SO_4^{2-}, IO_3^- is reduced to I_2 in acidic solution. Write a balanced chemical equation for this redox reaction. What volume of $0.25N$ KIO_3 is required for the complete oxidation to sulfate of 125 ml of $0.10N$ H_2SO_3?

27. In acidic aqueous solution, permanganate ion will oxidize oxalic acid $(COOH)_2$ to carbon dioxide while being reduced to manganous ion, Mn^{2+}. (a) What are the oxidation numbers of C and Mn in the reactants and products? (None of the substances is a peroxide.) (b) Write a balanced equation for the reaction. (c) What are the molecular weights and equivalent weights of the reactants $KMnO_4$ and $(COOH)_2$? (d) How many moles of permanganate can be reduced by 0.01 mole of oxalic acid? (e) How many equivalents of oxalic acid can be oxidized by 0.04 equiv of potassium permanganate? (f) What is the normality of a solution that contains 15.8 g of potassium permanganate per liter? (g) What is the molarity of a solution that contains 4.5 g of oxalic acid per liter? (h) What weight of oxalic acid can be oxidized to carbon dioxide by 150.0 ml of a solution containing 6.25 g of potassium permanganate per liter?

Suggested Reading

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