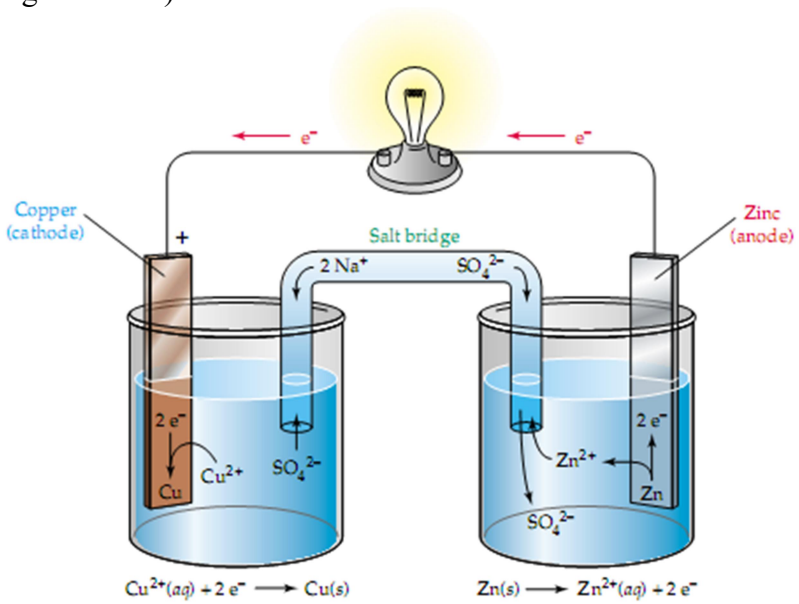
4.5 Voltaic (Galvanic) Cells

Electrochemical cells are of two basic types: galvanic cells (also called voltaic cells) and electrolytic cells. In a galvanic cell, a spontaneous chemical reaction generates an electric current. In an electrolytic cell, an electric current drives a non-spontaneous reaction.

4.5.1 Construction of Zn-Cu Galvanic Cell

Consider a standard cell made up of two half-cells, one a strip of metallic Cu immersed in 1 *M* copper(II) sulfate solution and the other a strip of Zn immersed in 1 *M* zinc sulfate solution (see figure below).



Chemical analysis shows that the dark colored deposit is finely divided copper metal and that the solution now contains zinc ions. Therefore, the reaction is:

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

This is a redox reaction in which Zn is oxidized to Zn^{+2} and Cu^{+2} is reduced to Cu.

We can represent the oxidation and reduction aspects of the reaction by separating the overall process into half-reactions, one representing the oxidation reaction and the other representing the reduction:

Oxidation half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$

Reduction half-reaction: $Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$

The two solutions are connected by a salt bridge, a U-shaped tube that contains a gel permeated with a solution of an inert electrolyte, such as Na_2SO_4.

The electrode at which oxidation takes place is called the anode (the zinc strip in this example), and the electrode at which reduction takes place is called the cathode (the copper strip). The anode and cathode half-reactions must add to give the overall cell reaction:

Anode (oxidation) half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$

Cathode (reduction) half-reaction: $Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$

Overall cell reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

4.5.2 Cell Notation

Cell notation is a shorthand way of expressing a certain reaction in an electrochemical cell. The cell anode and cathode (half-cells) are separated by two bars or slashes representing a salt bridge, with the anode on the left and cathode on the right. For the Daniell cell in the above Figure, which uses the reaction:

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

We can write the following expression:

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

In this notation, a single vertical line (|) represents a phase boundary, such as that between a solid electrode and an aqueous solution, and the double vertical line (||) denotes a salt bridge.

Sample Exercise 10: Given the following shorthand notation

$$Pt(s) \mid Sn^{2+}(aq), Sn^{4+}(aq) \parallel Ag^{+1}(aq) \mid Ag(s)$$

Write a balanced equation for the cell reaction, and give a brief description of the cell.

Solution

The anode (oxidation) half reaction is:

$$Sn^{+2}(aq) \longrightarrow Sn^{4+}(aq)$$

The cathode (reduction) half reaction is:

$$2x[Ag^{+}(aq) \longrightarrow Ag(s)]$$

Summing the two reactions will give

$$Sn^{+2}(aq) + 2Ag^{+}(aq) \longrightarrow Sn^{4+}(aq) + Ag(s)$$

4.5.3 Standard Reduction Potentials

The standard potential of any galvanic cell is the sum of the standard half-cell potentials for oxidation at the anode and reduction at the cathode:

$$E^{o}_{cell} = E^{o}_{ox} + E^{o}_{red}$$

Consider, for example, a cell in which gas is oxidized to ions at the anode and ions are reduced to copper metal at the cathode (Figure below).

Anode (oxidation): $H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^-$

Cathode (reduction): $Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$

Overall cell reaction: $H_2(g) + Cu^{2+}(aq) \longrightarrow 2\,H^+(aq) + Cu(s)$

The standard potential for this cell, 0.34 V at 25°C, is a measure of the combined driving forces of the oxidation and reduction half-reactions

$$E^{o}_{cell} = E^{o}_{ox} + E^{o}_{red} = E^{o}_{H2—H+} + E^{o}_{Cu+2—Cu} = 0.34V$$

The standard hydrogen electrode (S.H.E.) consists of a platinum electrode in contact with H_2 gas and aqueous H^+ ions at standard-state conditions [1 atm H_2(g), 1 M H^+(aq), 25°C]. The corresponding half-reaction, written in either direction, is assigned an arbitrary potential of exactly 0 V:

$$2\,H^+(aq, 1\,M) + 2\,e^- \longrightarrow H_2(g, 1\,atm) \qquad E^\circ = 0\,V$$

$$H_2(g, 1\,atm) \longrightarrow 2\,H^+(aq, 1\,M) + 2\,e^- \qquad E^\circ = 0\,V$$

With this choice of standard reference electrode, the entire potential of the cell:

$$Pt(s)\,|\,H_2(1\text{ atm})\,|\,H^+(1\text{ M})\,\|\,Cu^{2+}(1\text{ M})\,|\,Cu(s)$$

can be attributed to the half-cell

$$\underset{\uparrow\ 0.34\text{ V}}{E^\circ_{cell}} = \underset{\uparrow\ 0\text{ V}}{E^\circ_{H_2 \rightarrow H^+}} + \underset{\uparrow\ 0.34\text{ V}}{E^\circ_{Cu^{2+} \rightarrow Cu}} = 0.34\text{ V}$$

Because the Cu^{+2}/Cu half-reaction is a reduction, the corresponding half-cell potential, is called a standard reduction potential:

$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \qquad \text{Standard reduction potential: } E^\circ = 0.34\text{ V}$$

In a cell in which this half-reaction occurs in the opposite direction, the corresponding half-cell potential has the same magnitude but opposite sign:

Whenever the direction of a half-reaction is reversed, the sign of E° must also be reversed. Thus, the standard potential for an oxidation half-reaction is the negative of the standard reduction potential.

Therefore, the half-cell reactions involve oxidation of Zn and reduction of H^+. Alternatively, we could identify the direction of the half-reactions by noting that the H^+ concentration decreases as the reaction progresses.

Anode (oxidation):	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$	$E^\circ = ?$
Cathode (reduction):	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	$E^\circ = 0\text{ V}$
Overall cell reaction:	$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$	$E^\circ = 0.76\text{ V}$

Since the anode and cathode half-cell potentials must sum to give the overall cell potential, the E° value for oxidation of Zn to Zn^{+2} must be 0.76 V and the standard *reduction* potential for the Zn^{+2}/Zn half-cell is therefore -0.70 V.

We could also have calculated the standard reduction potential for the Zn^{+2}/Zn half-cell from the observed standard potential of the Daniell cell (1.10 V) and the standard reduction potential for the Cu^{+2}/Cu half-cell (0.34 V):

Anode (oxidation):	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$	$E^\circ = ?$
Cathode (reduction):	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	$E^\circ = 0.34\text{ V}$
Overall cell reaction:	$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$	$E^\circ = 1.10\text{ V}$

Since 1.10 V = 0.76 V + 0.34 V we would again conclude that the E° value for oxidation of Zn to Zn^{+2} is 0.76 V and the standard reduction potential for the Zn^{+2}/Zn half-cell is -0.76 V.

4.5.4 Electromotive Force (emf)

The standard free-energy change for a reaction is related to the standard cell potential by the equation:

$$\Delta G^\circ = -nFE^\circ$$

The standard free-energy change is also related to the equilibrium constant for the reaction:

$$\Delta G^\circ = -RT \ln K$$

Combining these two equations, we obtain:

$$-nFE^\circ = -RT \ln K$$

$$E^\circ = \frac{RT}{nF} \ln K = \frac{2.303RT}{nF} \log K$$

Since 2.303 RT/F has a value of 0.0592 V at 25°C, we can rewrite this equation in the simplified form

$$E^\circ = \frac{0.0592\ \text{V}}{n} \log K \qquad \text{in volts, at 25°C}$$

Sample Exercise 13: Use the standard reduction potentials in table to calculate the equilibrium constant at 25°C for the reaction.

$$6\ Br^-(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq) \longrightarrow 3\ Br_2(l) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$$

SOLUTION

Find the relevant half-reactions in Table 18.1, and write them in the proper direction for oxidation of Br^- and reduction of $Cr_2O_7^{2-}$. Before adding the half-reactions to get the overall reaction, multiply the Br^-/Br_2 half-reaction by a factor of 3 so that the electrons will cancel:

$$3 \times [2\ Br^-(aq) \longrightarrow Br_2(l) + 2\ e^-] \qquad E^\circ = -1.09\ \text{V}$$

$$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l) \qquad E^\circ = 1.33\ \text{V}$$

$$6\ Br^-(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq) \longrightarrow 3\ Br_2(l) + 2\ Cr^{3+}(aq) + 7\ H_2O(l) \qquad E^\circ = 0.24\ \text{V}$$

Note that E° for the Br^-/Br_2 *oxidation* is the negative of the tabulated standard *reduction* potential (1.09 V), and remember that we don't multiply this E° value by a factor of 3 because electrical potential is an intensive property. The E° value for the overall reaction is the sum of the E° values for the half-reactions: $-1.09\ \text{V} + 1.33\ \text{V} = 0.24\ \text{V}$. To calculate the equilibrium constant, use the relation between $\log K$ and nE°, with $n = 6$:

$$\log K = \frac{nE^\circ}{0.0592\ \text{V}} = \frac{(6)(0.24\ \text{V})}{0.0592\ \text{V}} = 24 \qquad K = 1 \times 10^{24} \qquad \text{at 25°C}$$

E° is positive, so K should be greater than 1, in agreement with the solution.

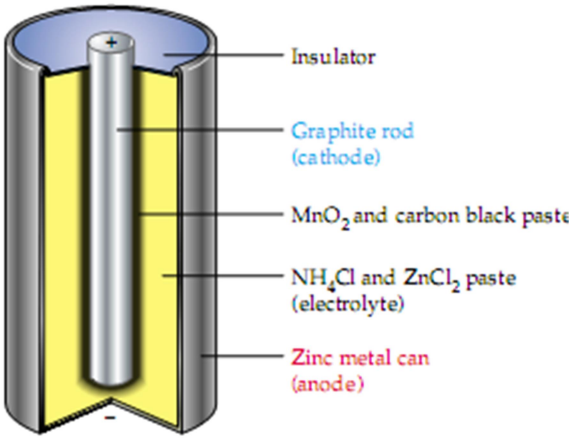
4.5.6 Batteries

A battery is a galvanic cell or, more commonly, a group of galvanic cells connected in series, where the potentials of the individual cells add to give the total battery potential.
Batteries are a source of direct current and have become an essential source of portable power in our society.

We can classify batteries primary and secondary. Primary batteries use redox reactions that cannot be returned to their original state by recharging. Secondary batteries are often called storage batteries, or rechargeable batteries. The reactions in these batteries can be reversed, which means that the batteries can be recharged.

Dry-Cell Batteries

The common household batteries used as power sources for flashlights, portable radios, and tape recorders use the *dry cell*, or *Leclanché cell*. A dry-cell battery has a zinc metal can, which serves as the anode, and an inert graphite rod surrounded by a paste of solid manganese dioxide and carbon black, which functions as the cathode (Figure below).



Surrounding the MnO_2-containing paste is the electrolyte, a moist paste of ammonium chloride and zinc chloride in starch. The dry cell is not completely dry but gets its name because the electrolyte is a viscous, aqueous paste rather than a liquid solution. The electrode reactions can be represented in simplified form by the following equations:

Anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$

Cathode: $2\,MnO_2(s) + 2\,NH_4^+(aq) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l)$

The alkaline dry cell

It is a modified version of the Leclanché cell in which the acidic NH_4Cl electrolyte of the Leclanché cell is replaced by a basic electrolyte, either NaOH or KOH. As in the Leclanché cell, the electrode reactions involve oxidation of zinc and reduction of manganese dioxide, but the oxidation product is zinc oxide, as is appropriate to the basic conditions:

Anode: $Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$

Cathode: $2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$

Closely related to the alkaline dry cell is the *mercury battery*, often used in watches, heart pacemakers, and other devices where a battery of small size is required. The anode of the mercury battery is zinc, as in the alkaline dry cell, but the cathode is steel in contact with mercury(II) oxide (HgO) in an alkaline medium of KOH and $Zn(OH)_2$. Zinc is oxidized at the anode, and HgO is reduced at the cathode:

Anode: $Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$

Cathode: $HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)$

Nickel–Cadmium Batteries

Nickel–cadmium, or *"ni–cad," batteries* are popular for use in calculators and portable power tools because, unlike most other dry-cell batteries, they are rechargeable. The anode of a ni–cad battery is cadmium metal, and the cathode is the nickel(III) compound NiO(OH) supported on nickel metal. The electrode reactions are

Anode: $Cd(s) + 2\,OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\,e^-$

Cathode: $NiO(OH)(s) + H_2O(l) + e^- \longrightarrow Ni(OH)_2(s) + OH^-(aq)$

Lead Storage Battery

The *lead storage battery* is perhaps the most familiar of all galvanic cells because it has been used as a reliable source of power for starting automobiles. A typical 12 V battery consists of six cells connected in series, each cell providing a potential of about 2 V. When the cell is discharging (providing current), the electrode half-reactions and the overall cell reaction are:

$$\text{Anode:} \quad Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^- \qquad E° = 0.296\ V$$

$$\text{Cathode:} \quad PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l) \qquad E° = 1.628\ V$$

$$\text{Overall:} \quad Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l) \qquad E° = 1.924\ V$$

Fuel cell

A fuel cell is a galvanic cell in which one of the reactants is a traditional fuel such as methane or hydrogen. A fuel cell differs from an ordinary battery in that the reactants are not contained within the cell but instead are continuously supplied from an external reservoir. Perhaps the best-known example is the hydrogen–oxygen fuel cell, which is used as a source of electric power in space vehicles. This cell contains porous carbon electrodes impregnated with metallic catalysts and an electrolyte consisting of hot, aqueous KOH. The fuel (gaseous H_2) and the oxidizing agent (gaseous O_2) don't react directly but instead flow into separate cell compartments where H_2 is oxidized at the anode and O_2 is reduced at the cathode (Figure below). The overall cell reaction is simply the conversion of hydrogen and oxygen to water:

$$\text{Anode:} \quad 2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$$

$$\text{Cathode:} \quad O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

$$\text{Overall:} \quad 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

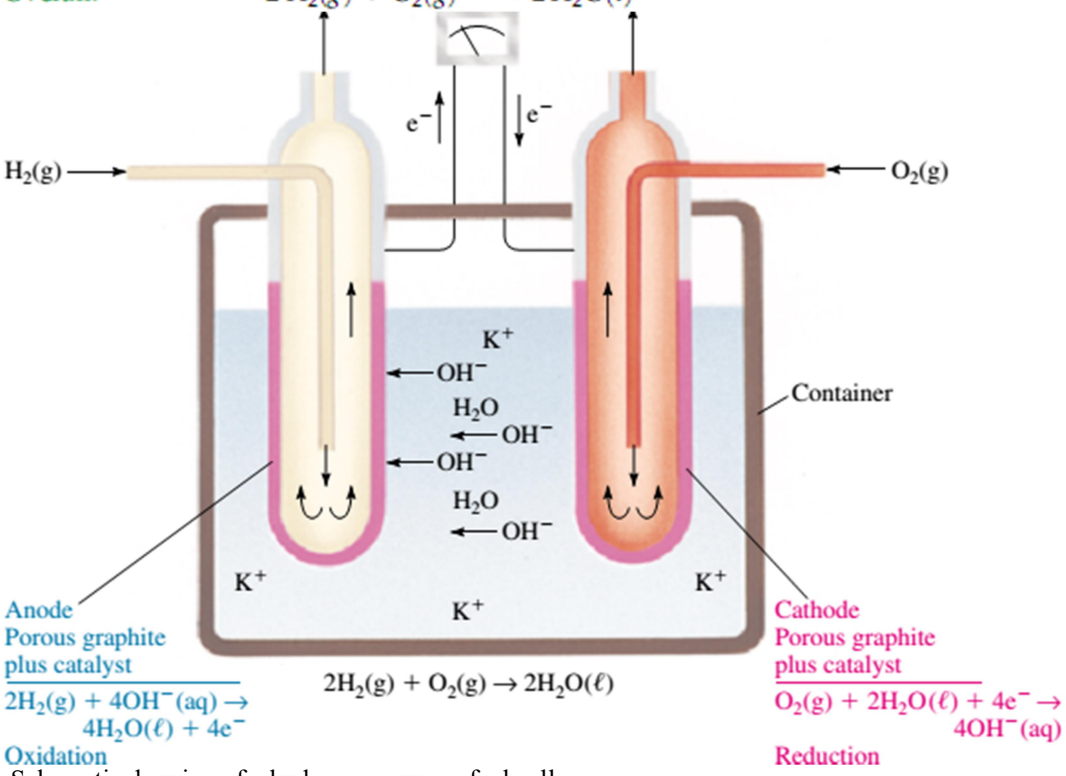


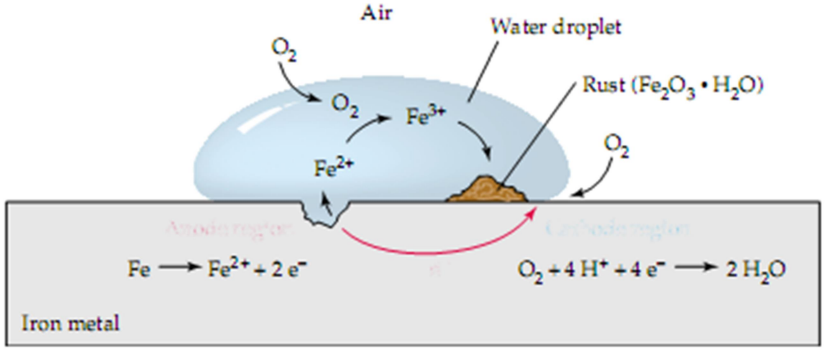
Figure 4: Schematic drawing of a hydrogen–oxygen fuel cell

4.5.7 Corrosion of Metals

Corrosion is the oxidative deterioration of a metal. Corrosion is responsible for the loss of billions of dollars annually in metal products.

To prevent corrosion, we first have to understand how it occurs. One important fact is that the rusting of iron requires both oxygen and water; it doesn't occur in oxygen-free water or in dry air.

A possible mechanism for rusting, consistent with the known facts, is illustrated in figure below. Iron is oxidized more readily in some regions (anode regions) than in others (cathode regions) because the composition of the metal is somewhat inhomogeneous and the surface is irregular.



At an anode region, iron is oxidized to Fe^{2+} ions,

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^- \qquad E° = 0.45\ V$$

while at a cathode region, oxygen is reduced to water:

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \qquad E° = 1.23\ V$$

Corrosion of iron can be prevented, or at least minimized, by shielding the metal surface from oxygen and moisture. A coat of paint is effective for a while, but rust begins to form as soon as the paint is scratched or chipped. Metals such as chromium, tin, or zinc afford a more durable surface coating for iron. The steel used in making automobiles, for example, is coated by dipping into a bath of molten zinc, a process known as galvanizing.

Unit - Five
Some Elements In Nature And Industry

5.1 Some Elements In Nature

An element is the simplest form of matter, which can neither be broken down into simpler substances nor formed from two or more simpler substances by any known physical or chemical process. All other substances are made from combinations of these fundamental substances.

5.1.1 Occurrences Of Elements

Out of the 118 elements known at present, 92 of them occur naturally on the earth, and the remaining have been created in the laboratories and have to be manmade. Although these elements occur naturally, very few are found in the elemental state. Most of the elements occur only the combined state (form of compounds) with other elements.

- *Minerals are solid, naturally occurring deposits in the earth's crust, which contain elements in the combined state, along with associated earthly impurities*

Note: All minerals are not suitable for the extraction of elements

- *Ores are naturally occurring minerals from which the metals can be extracted commercially at low cost and with minimum effort*

The twelve most abundant elements that constitute 99.7% by mass of the earth's crust are in decreasing order of abundance: Oxygen (O), Silicon(Si), Aluminum(Al), Iron(Fe), Calcium(Ca), Magnesium (Mg), Sodium(Na), Potassium(P), Titanium(Ti), Hydrogen (H), Phosphorous(P) and Manganese (Mn).

- *The most common ores of metals are oxides, sulfides, halides, silicates, carbonates and sulfates. Some of these common ores are given below with their mineral names*

Table 5.1 ***Common Classes of Ores***

Anion	Examples and Names of Minerals
none (native ores)	Au, Ag, Pt, Os, Ir, Ru, Rh, Pd, As, Sb, Bi, Cu
oxide	hematite, Fe_2O_3; magnetite, Fe_3O_4; bauxite, Al_2O_3; cassiterite, SnO_2; periclase, MgO; silica, SiO_2
sulfide	chalcopyrite, $CuFeS_2$; chalcocite, Cu_2S; sphalerite, ZnS; galena, PbS; iron pyrites, FeS_2; cinnabar, HgS
chloride	rock salt, NaCl; sylvite, KCl; carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$
carbonate	limestone, $CaCO_3$; magnesite, $MgCO_3$; dolomite, $MgCO_3 \cdot CaCO_3$; rhodochrosite, $MnCO_3$
sulfate	gypsum, $CaSO_4 \cdot 2H_2O$; epsom salts, $MgSO_4 \cdot 7H_2O$; barite, $BaSO_4$
silicate	beryl, $Be_3Al_2Si_6O_{18}$; kaolinite, $Al_2(Si_2O_8)(OH)_4$; spodumene, $LiAl(SiO_3)_2$