

Fundamentals of

Analytical Chemistry

Eighth Edition

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Introduction to Electrochemistry

Electroanalytical Chemistry: •

group of analytical methods based upon electrical properties of analytes when part of an electrochemical cell.

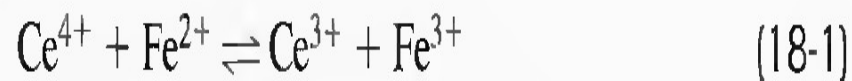
CHARACTERIZING OXIDATION/REDUCTION REACTIONS

18A

Oxidation/reduction reactions are sometimes called **redox** reactions.

A **reducing agent** is an electron donor. An **oxidizing agent** is an electron acceptor.

In an **oxidation/reduction reaction**, electrons are transferred from one reactant to another. An example is the oxidation of iron(II) ions by cerium(IV) ions. The reaction is described by the equation



In this reaction, an electron is transferred from Fe^{2+} to Ce^{4+} to form Ce^{3+} and Fe^{3+} ions. A substance that has a strong affinity for electrons, such as Ce^{4+} , is called an **oxidizing agent**, or an **oxidant**. A **reducing agent**, or **reductant**, is a species, such

as Fe^{2+} , that easily donates electrons to another species. To describe the chemical behavior represented by Equation 18-1, we say that Fe^{2+} is oxidized by Ce^{4+} ; similarly, Ce^{4+} is reduced by Fe^{2+} .

We can split any oxidation/reduction equation into two half-reactions that show which species gains electrons and which loses them. For example, Equation 18-1 is the sum of the two half-reactions



Balancing Redox Equations

Knowing how to balance oxidation/reduction reactions is essential to understanding all the concepts covered in this chapter. Although you probably remember this technique from your general chemistry course, we present a quick review here to remind you of how the process works. For practice, complete and balance the following equation after adding H^+ , OH^- , or H_2O as needed.



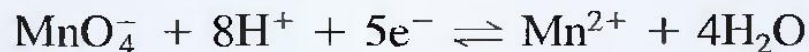
First, we write and balance the two half-reactions involved. For MnO_4^- , we write



To account for the 4 oxygen atoms on the left-hand side of the equation we add $4\text{H}_2\text{O}$ on the right-hand side of the equation, which means that we must provide 8H^+ on the left:



To balance the charge, we need to add 5 electrons to the left side of the equation. Thus,



For the other half-reaction,



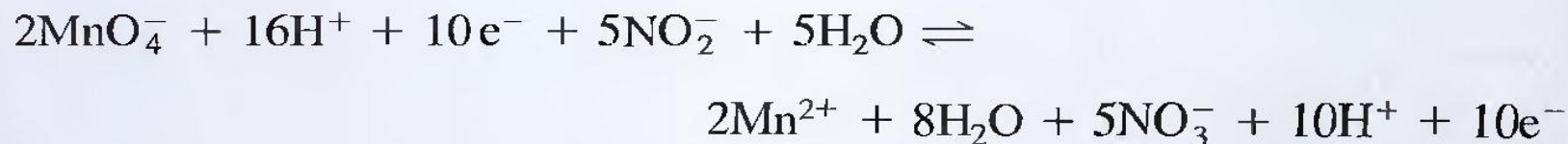
we add one H_2O to the left side of the equation to supply the needed oxygen and 2H^+ on the right to balance hydrogen:



Then we add two electrons to the right-hand side to balance the charge:



Before combining the two equations, we must multiply the first by 2 and the second by 5 so that the number of electrons lost will be equal to the number of electrons gained. We then add the two half-reactions to obtain

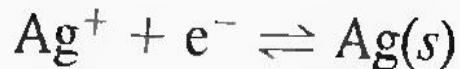


which then rearranges to the balanced equation



18A-2 Oxidation/Reduction Reactions in Electrochemical Cells

Many oxidation/reduction reactions can be carried out in either of two ways that are physically quite different. In one, the reaction is performed by bringing the oxidant and the reductant into direct contact in a suitable container. In the second, the reaction is carried out in an electrochemical cell in which the reactants do not come in direct contact with one another. A marvelous example of direct contact is the famous “silver tree” experiment, in which a piece of copper is immersed in a silver nitrate solution (Figure 18-1). Silver ions migrate to the metal and are reduced:



At the same time, an equivalent quantity of copper is oxidized:

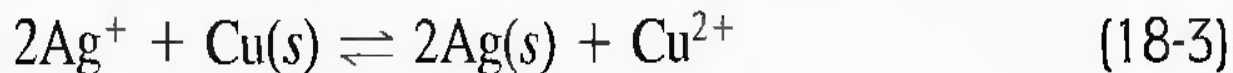




C. D. Winters

Figure 18-1 Photograph of a "silver tree."

By multiplying the silver half-reaction by two and adding the reactions, we obtain a net ionic equation for the overall process.



A unique aspect of oxidation/reduction reactions is that the transfer of electrons—and thus an identical net reaction—can often be brought about in an **electrochemical cell**, in which the oxidizing agent and the reducing agent are physically separated from one another. Figure 18-2a shows such an arrangement. Note that a **salt bridge** isolates the reactants but maintains electrical contact between the two halves of the cell. When a voltmeter of high internal resistance is connected as shown or the electrodes are not connected externally, the cell is said to be at **open circuit** and delivers the full cell potential. When the circuit is open, no net reaction occurs in the cell, although we will show that the cell has the **potential** for doing work. The voltmeter measures the potential difference, or **voltage**, between the two electrodes at any instant. This voltage is a measure of the tendency of the cell reaction to proceed toward equilibrium.

In Figure 18-2b, the cell is connected so that electrons can pass through a low-resistance external circuit. The potential energy of the cell is now converted to electrical energy to light a lamp, run a motor, or do some other type of electrical work. In the cell in Figure 18-2b, metallic copper is oxidized at the left-hand electrode, silver ions are reduced at the right-hand electrode, and electrons flow through the external circuit to the silver electrode. As the reaction goes on, the cell potential, initially 0.412 V when the circuit is open, decreases continuously and approaches zero as the overall reaction approaches equilibrium. When the cell is at equilibrium, both cell half-reactions occur at the same rate, and the cell voltage is zero. A cell with zero voltage does not perform work, as anyone who has found a “dead” battery in a flashlight or in a laptop computer can attest.

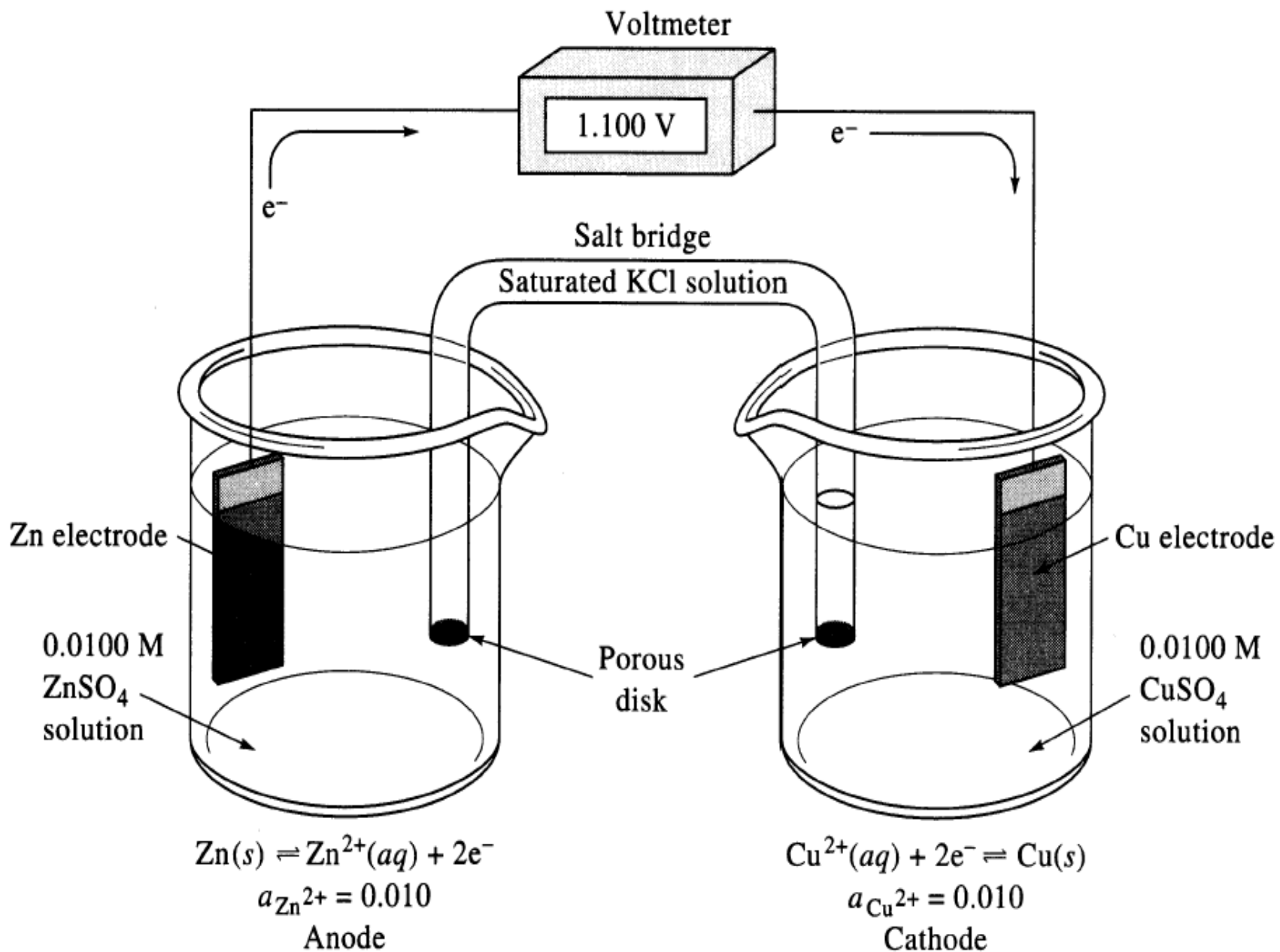
When zero voltage is reached in the cell in Figure 18-2b, the concentrations of Cu(II) and Ag(I) ions will have values that satisfy the equilibrium-constant expression shown in Equation 18-4. At this point, no further net flow of electrons will occur. *It is important to recognize that the overall reaction and its position of equilibrium are totally independent of the way the reaction is carried out, whether it is by direct reaction in a solution or by indirect reaction in an electrochemical cell.*

1.) *Basic Set-up:*

- a) Two electrodes
- b) electrolytes solution
- c) external connection between electrodes (wire)
- d) internal connection via contact with a common solution or by different solutions connected by a salt bridge.

salt bridge – acts to isolate two halves of electrochemical cell while allowing migration of ions and current flow. •

- usually consists of a tube filled with potassium chloride
- separate species to prevent direct chemical reaction



At Cu electrode: $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu(s)} \rightarrow$ reduction – •
gain of e^- net decrease in charge of species

At Zn electrode: $\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+} + 2e^- \rightarrow$ oxidation – loss •
of e^- net increase in charge of species

3.) *Net Reaction in Cell* – sum of reactions occurring in •
the two $\frac{1}{2}$ cells



Potential of overall cell = measure of the •
tendency of this reaction to proceed to
equilibrium

at equilibrium, potential (E_{cell}) = 0 •

∴ Larger the potential, the further the reaction is •
from equilibrium
and the greater the driving force that exists •