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Electrochemistry

Lecture (13)

Stage 3

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ELECTROCHEMISTRY

Chapter 13

What Are the Key Ideas? The tendency of electrons to be transferred in a chemical reaction depends on the species involved and their concentrations. When the process is spontaneous and reduction and oxidation occur at different locations, the reaction can do work and drive electrons through an external circuit.

Why Do We Need to Know This Material? The topics described in this chapter may one day unlock a virtually inexhaustible supply of clean energy supplied daily by the Sun. The key is electrochemistry, the study of the interaction of electricity and chemical reactions. The transfer of electrons from one species to another is one of the fundamental processes underlying life, photosynthesis, fuel cells, and the refining of metals. An understanding of how electrons are transferred helps us to design ways to use chemical reactions to generate electricity and to use electricity to bring about chemical reactions. Electrochemical measurements also allow us to determine the values of thermodynamic quantities.

What Do We Need to Know Already? This chapter extends the thermodynamic discussion presented in Chapter 8. In particular, it builds on the concept of Gibbs free energy (Section 8.12), its relation to maximum nonexpansion work (Section 8.14), and the dependence of the reaction Gibbs free energy on the reaction quotient (Section 10.3). For a review of redox reactions, see Section K. To prepare for the quantitative treatment of electrolysis, review stoichiometry in Section L.

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The nature of electricity was unknown until the late eighteenth century, when the Italian scientist Luigi Galvani discovered that by touching the muscles of dead animals, mainly frogs, with rods bearing electric charges, he could make their muscles twitch. He believed that electricity came from the muscles themselves. However, at the end of that century another Italian, Alessandro Volta, suggested that the electricity came from the fact that the muscles were between two different metals when touched by the rods. He proved that the electricity came from metals by constructing a tower of alternating discs of different metals in layers separated by paper strips soaked in a solution of sodium chloride (Fig. 13.1). This apparatus, a "voltaic pile," was the first electrical storage device, a simple battery, but because it opened a door to a new understanding of the structure of matter, it amazed the scientists and even the rulers of the day.

Those early observations have evolved into the branch of chemistry called electrochemistry. This subject deals not only with the use of spontaneous chemical reactions to produce electricity but also with the use of electricity to drive nonspontaneous reactions forward. Electrochemistry also provides techniques for monitoring chemical reactions and for measuring properties of solutions such as the pK_a of an acid and the thermodynamic characteristics of reactions. Electrochemistry even allows us to monitor the activity of our brain and heart (perhaps while we are trying to master chemistry), the pH of our blood, and the presence of pollutants in our water supply.

REPRESENTING REDOX REACTIONS

An electric current is the flow of electrons through a circuit. When the current is generated chemically, the electrons emerge from a location where oxidation takes place and travel to a location where reduction occurs. Because oxidation and reduction are involved in the generation of an electric current, redox reactions (Section K) are central to the discussion of electrochemistry. In this chapter we take a closer look at them and see how they and other types of reactions can be used to generate electricity.

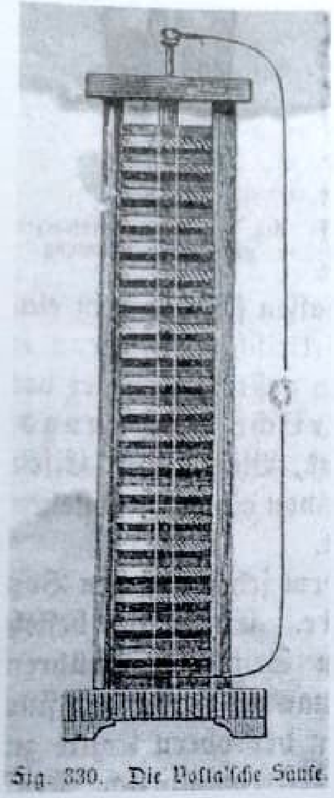

FIGURE 13.1 Volta used this stack of alternating disks of two different metals separated by paper soaked in salt water to produce the first sustained electric current.

For a quantitative discussion of redox reactions we need to be able to write balanced chemical equations. Some redox reactions can be tricky to balance, and special techniques, which we describe in Sections 13.1 and 13.2, have been developed to simplify the procedure.

The chapter begins with a review of redox reactions, which are particularly important for understanding the chemical production of electricity, a topic that occupies the major part of this chapter. Redox reactions are also important in the final part of the chapter, which discusses the use of electricity to bring about chemical reactions.

13.1 Half-Reactions

The key to writing and balancing equations for redox reactions is to think of the reduction and oxidation processes separately. We saw in Section K that oxidation is the loss of electrons and reduction the gain of electrons.

A **half-reaction** is the oxidation or reduction part of a reaction considered alone. An oxidation half-reaction shows the removal of electrons from a species that is being oxidized in a redox reaction. For example, Volta used silver and zinc plates in one of his voltaic piles to carry out the reaction

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

To show the oxidation of zinc explicitly we write

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

An oxidation half-reaction is a *conceptual* way of reporting an oxidation: the electrons are never actually free. In an equation for an oxidation half-reaction, the electrons released always appear on the right of the arrow. Their state is not given, because they are in transit and do not have a definite physical state. The reduced and oxidized species in a half-reaction jointly form a **redox couple**. In this example, the redox couple consists of Zn^{2+} and Zn, and is denoted Zn^{2+}/Zn. A redox couple has the form Ox/Red, where Ox is the oxidized form of the species and Red is the reduced form.

A note on good practice: Distinguish a conceptual half-reaction from an actual ionization, where the electron is removed and which we would write, for example, as $Na(g) \longrightarrow Na^{+}(g) + e^{-}(g)$, with the state of the electron specified.

Now consider reduction. To show the addition of electrons to a species, we write the corresponding half-reaction for electron gain. For example, to show the reduction of Ag^{+} ions to Ag metal we write

$$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$$

This half-reaction, too, is conceptual: the electrons are not actually free. In the equation for a reduction half-reaction, the electrons gained always appear on the left of the arrow. In this example, the redox couple is Ag^{+}/Ag.

> ***Half-reactions express the two contributions (oxidation and reduction) to an overall redox reaction.***

13.2 Balancing Redox Equations

Balancing the chemical equation for a redox reaction by inspection can be a real challenge, especially for one taking place in aqueous solution, when water may participate and we must include H_2O and either H^{+} or OH^{-}. In such cases, it is easier to simplify the equation by separating it into its reduction and oxidation half-reactions, balance the half-reactions separately, and then add them together to obtain the balanced equation for the overall reaction. When adding the equations for half-reactions, we match the number of electrons released by oxidation with the number used in reduction, because electrons are neither created nor destroyed in chemical reactions. The procedure is outlined in Toolbox 13.1 and illustrated in Examples 13.1 and 13.2.

In redox reactions, it is conventional to write H^{+} rather than H_3O^{+}.

TOOLBOX 13.1 HOW TO BALANCE COMPLICATED REDOX EQUATIONS

CONCEPTUAL BASIS

When balancing redox equations, we express the gain of electrons (reduction) and the loss of electrons (oxidation) as separate half-reactions, and then balance both atoms and charge in each of the two half-reactions. When we combine the half-reactions, the number of electrons released in the oxidation must equal the number used in the reduction.

PROCEDURE

In general, first balance the half-reactions separately, then combine them.

Step 1 Identify the species being oxidized and the species being reduced from the changes in their oxidation numbers.

Step 2 Write the two skeletal (unbalanced) equations for the oxidation and reduction half-reactions.

Step 3 Balance all elements in the half-reactions except O and H.

Step 4 In acidic solution, balance O by using H_2O and then balance H by using H^+. In basic solution, balance O by using H_2O; then balance H by adding H_2O to the side of each half-reaction that needs H and adding OH^- to the other side.

When we add $\ldots OH^- \ldots \rightarrow \ldots H_2O \ldots$ to a half-reaction, we are effectively adding one H atom to the right. When we add $\ldots H_2O \ldots \rightarrow \ldots OH^- \ldots$, we are effectively adding one H atom to the left. Note that one H_2O molecule is added for each H atom needed. If necessary, cancel like species on opposite sides of the arrow.

Step 5 Balance the electric charges by adding electrons to the left for reductions and to the right for oxidations until the charges on the two sides of the arrow are the same.

Step 6 If necessary, multiply each half-reaction by the factor required to give equal numbers of electrons in the two half-reactions, and then add the two equations and include physical states. In some cases it is possible to simplify the half-reactions before they are combined.

Finally, simplify the appearance of the complete equation by canceling species that appear on both sides of the arrow and check to make sure that charges as well as numbers of atoms balance.

Examples 13.1 and 13.2 illustrate this procedure.