

Lecture – 5 Electrochemistry

Electrochemistry Basics

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction.

Introduction

A redox reaction is a reaction that involves a change in oxidation state of one or more elements. When a substance loses an electron, its oxidation state increases; thus, it is oxidized. When a substance gains an electron, its oxidation state decreases, thus being reduced. For example, for the redox reaction



can be rewritten as follows:

- Oxidation: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ (2a)
- Reduction: $\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$ (2b)
- Overall Reaction : $\text{H}_2 + \text{F}_2 \rightarrow 2\text{H}^+ + 2\text{F}^-$ (2c)

Oxidation is the loss of electrons, whereas reduction refers to the acquisition of electrons, as illustrated in the respective reactions above. The species being oxidized is also known as the reducing agent or reductant, and the species being reduced is called the oxidizing agent or oxidant. In this case, H_2 is being oxidized (and is the reducing agent), while F_2 is being reduced (and is the oxidizing agent). The following acronym is useful in remembering this concept:

OIL RIG:

Oxidation Is Losing electrons; Reduction Is Gaining electrons

Example 1: Fe-V Couple

Given the redox reaction $\text{Fe}^{3+} + \text{V}^{2+} \rightarrow \text{Fe}^{2+} + \text{V}^{3+}$, which species is oxidized? Which is reduced? Identify the reducing agent and the oxidizing agent.

SOLUTION

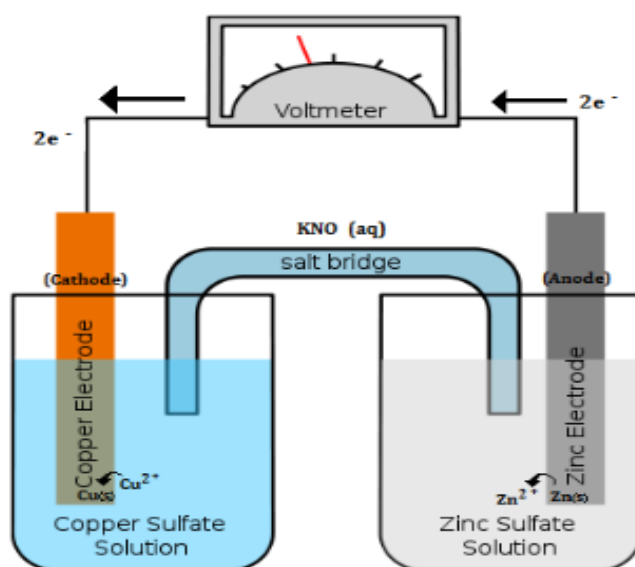
Fe^{3+} is reduced into Fe^{2+} , and V^{2+} is oxidized into V^{3+} . This is because the oxidized species loses electrons, and the reduced species gains electrons. Iron gains an electron ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$), and vanadium loses an electron ($\text{V}^{2+} \rightarrow \text{V}^{3+}$). Thus, Fe^{3+} is the oxidizing agent and V^{2+} is the reducing agent.

Voltaic Cells-Galvanic Cells

Voltaic (galvanic) cells are electrochemical cells that contain a spontaneous reaction, and always have a positive voltage. The electrical energy released during the reaction can be used to do work. A voltaic cell consists of two compartments called half-cells. The half-cell where oxidation occurs is called the anode. The other half-cell, where reduction occurs, is called the cathode. The electrons in voltaic cells flow from the negative electrode to the positive electrode—from anode to cathode (see figure below). (Note: the electrodes are the sites of the oxidation and reduction reactions). The following acronym is useful in keeping this information straight: **Red Cat and An Ox**

Reduction Cathode and Anode Oxidation

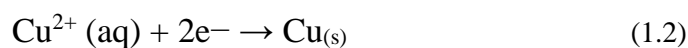
For an oxidation-reduction reaction to occur, the two substances in each respective half-cell are connected by a closed circuit such that electrons can flow from the reducing agent to the oxidizing agent. A salt bridge is also required to maintain electrical neutrality and allow the reaction to continue.



: The figure above shows that Zn(s) is continuously oxidized, producing aqueous Zn²⁺:



Conversely, in the cathode, Cu²⁺ is reduced and continuously deposits onto the copper bar:

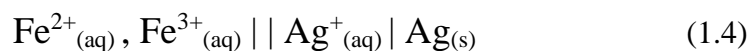


As a result, the solution containing Zn(s) becomes more positively charged as the solution containing Cu(s) becomes more negatively charged. For the voltaic cell to work, the solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing KNO₃ is added to keep the solutions neutral by adding NO₃⁻, an anion, into the anode solution and K⁺, a cation, into the cathode solution. As oxidation and reduction proceed, ions from the salt bridge migrate to prevent charge buildup in the cell compartments.

The cell diagram is a shorthand notation to represent the redox reactions of an electrical cell. For the cell described, the cell diagram is as follows

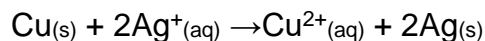


- A double vertical line (||) is used to separate the anode half reaction from the cathode half reaction. This represents the salt bridge.
- The anode (where oxidation occurs) is placed on the left side of the ||.
- The cathode (where reduction occurs) is placed on the right side of the ||.
- A single vertical line (|) is used to separate different states of matter on the same side, and a comma is used to separate like states of matter on the same side. For example:

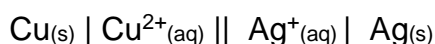


Example 2

Write the cell diagram for this reaction:



SOLUTION

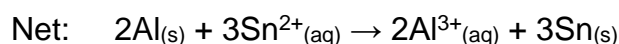
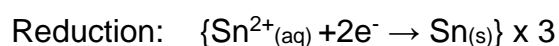
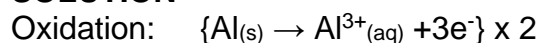


Example 3 Al-Sn Couple

Write cell reactions for this cell diagram:



SOLUTION



Cell Potential

The oxidation of Zn(s) into Zn²⁺ and the reduction of Cu²⁺ to Cu(s) occur spontaneously. In other words, the redox reaction between Zn and Cu²⁺ is spontaneous. This is due to the difference in potential energy between the two substances. The difference in potential energy between the anode and cathode dictates the direction of electronic movement. Electrons move from areas of higher potential energy to areas of lower potential energy. In this case, the anode has a higher potential energy; electrons therefore move from anode to cathode. The potential difference between the two electrodes is measured in units of volts. One volt (V) is the potential difference necessary to generate a charge of 1 coulomb (C) from 1 joule (J) of energy.

For a voltaic cell, this potential difference is called the **cell potential (or EMF for electromotive force, although it is not really a force)**, which is denoted **E_{cell}**. For a spontaneous reaction, E_{cell} is positive and ΔG (Gibbs free energy, used to determine if a reaction occurs spontaneously) is negative. Thus, when ΔG is negative the reaction is spontaneous. Merging electrochemistry with thermodynamics gives this formula:

$$\Delta G = -n F E_{\text{cell}} \quad (1.6)$$

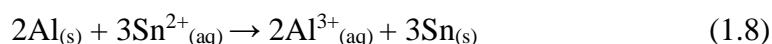
Cell potential is different for each voltaic cell; its value depends upon the concentrations of specific reactants and products as well as temperature of the reaction. For standard cell potential, temperature of the reaction is assumed to be 25° Celsius, the concentration of the reactants and products is 1 M, and reaction occurs at 1 atm pressure.

The standard cell potential is denoted E^o_{cell}, and can be written as oxidation potential + reduction potential. For voltaic cells:

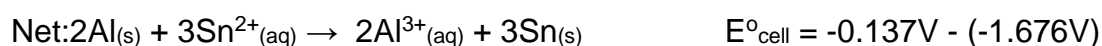
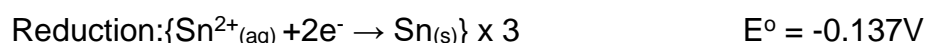
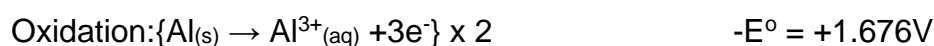
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{Anode}} \quad (1.7)$$

Example 4

Calculate E^o_{cell} for the following redox reaction under standard conditions:



Solution



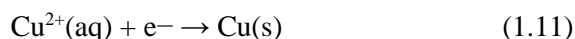
$$E^{\circ}_{\text{cell}} = +1.539 \text{ V.}$$

Because the values of the standard potential are given in the form of standard reduction potential for each half-reaction, to calculate the standard cell potential E_{cell}, the

substance is being oxidized must be identified; then the standard reduction potential of the oxidation reaction is subtracted from the standard reduction potential of the reducing reaction. For example:



Zn is being oxidized, and Cu is being reduced. The potentials for the two half reaction are given in the reduction form:



The cell potentials indicate which reaction takes place at the anode and which at the cathode. The cathode has a more positive potential energy, and thus:

- Cu is the cathode
- Zn is the anode.

To calculate E°_{cell} , subtract the E° of the oxidized half reaction from the E° cell of the reduction half reaction, which is:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad (1.12)$$

- Oxidation half reaction: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{e}^-$ $E^\circ = -0.763\text{V}$
 - Reduction half reaction: $\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu(s)}$ $E^\circ = +0.342\text{V}$
- Net reaction:



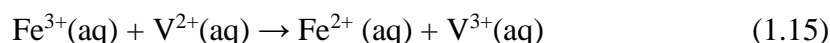
Therefore:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = 0.340\text{V} - (-0.763\text{V}) = +1.103\text{V} \quad (1.14)$$

Example 5: Iron/Vanadium Chemistry

Calculate the cell potential in the following redox reaction under standard conditions:



SOLUTION

Consult the table of standard reduction potentials ([Table P1](#)) for each half reaction:



The cell potential is

$$E^{\circ} \text{ cell} = E^{\circ} \text{ cathode} - E^{\circ} \text{ anode} = 0.771\text{V} - (-0.255\text{V}) = 1.026\text{V} \quad (1.18)$$

Balancing Redox Reactions

Method 1: Oxidation Number Method

- Step 1: Assign oxidation numbers to each atom.
- Step 2: Determine the net change in charge to determine the ratio of atoms
- Step 3: Use the ratio to eliminate the net charge change
- Step 4: Use the ratio as coefficients for the elements
- Step 5: Add H⁺ (under acidic conditions), OH⁻ (under basic conditions), and H₂O to balance charges.

Method 2: Half-Reaction Method

- Step 1: Determine oxidation numbers for each atom
- Step 2: Use oxidation numbers to determine what is oxidized and what is reduced.
- Step 3: Write a half-reaction for reduction
- Step 4: Write a half-reaction for oxidation
- Step 5: Balance all elements except H and O
 - if have acid redox reaction: Balance the O using H₂O, balance the H using protons
 - if have base redox reaction: Balance O using OH⁻
- Step 6: Add up the charge on each side
- Step 7: Balance the charges by adding electrons
- Step 8: Multiply the half-reactions by factors that cancel out electrons
- Step 9: Add the two half-reactions back together to eliminate out intermediates

Voltaic Cell	Voltage (V)
Common alkaline flashlight battery	1.5
Lead-acid car battery (6 cells = 12 V)	2.0
Calculator battery (mercury)	1.3
Lithium-ion laptop battery	3.7
Electric eel (~5000 cells in 6-ft eel = 750 V)	0.15
Nerve of giant squid (across cell membrane)	0.070

18A Characterizing oxidation/reduction reactions

In an oxidation/reduction reaction or redox reaction, electrons are transferred from one reactant to another.

Comparing Redox Reactions to Acid/Base Reactions

Example: $\text{Ce}^{+4} + \text{Fe}^{+2} \rightarrow \text{Ce}^{+3} + \text{Fe}^{+3}$ can be considered analogous to the

oxidation of iron(II) by cerium(IV) ions. A reducing agent is an electron donor. An oxidizing agent is an electron acceptor.

When an acid donates a proton, it becomes a conjugate base that is capable

EXAMPLE 18-1

The following reactions are spontaneous and thus proceed to the right, as written:



What can we deduce regarding the strengths of H^+ , Ag^+ , Cd^{2+} , and Zn^{2+} as electron acceptors (or oxidizing agents)?

Solution

The second reaction establishes that Ag^+ is a more effective electron acceptor than H^+ ; the first reaction demonstrates that H^+ is more effective than Cd^{2+} . Finally, the third equation shows that Cd^{2+} is more effective than Zn^{2+} . Thus, the order of oxidizing strength is $\text{Ag}^+ > \text{H}^+ > \text{Cd}^{2+} > \text{Zn}^{2+}$.

18B Electrochemical cells

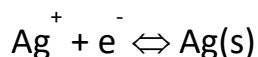
An electrochemical cell consists of two conductors called electrodes, each of which is immersed in an electrolyte solution.

Conduction of electricity from one electrolyte solution to the other occurs by migration of potassium ions in the salt bridge in one direction and chloride ions in the other.

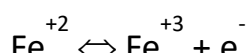
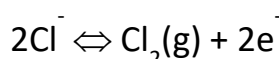
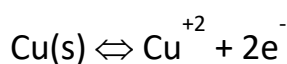
Cathodes and Anodes

A cathode is an electrode where reduction occurs.

Examples of typical cathodic reactions:



An anode is an electrode where oxidation occurs. Typical anodic reactions are:



In a reversible cell, reversing the current reverses the cell reaction.

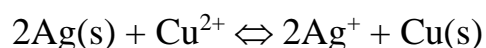
In an irreversible cell, reversing the current causes a different half-reaction to occur at one or both of the electrodes.

Since the negative terminal of the external voltage source is electron rich, electrons flow from this terminal to the copper electrode, Where reduction of Cu^{2+} to Cu(s) occurs. The current is sustained by the oxidation of Ag (s) to Ag^+ at the right hand electrode, producing electrons that flow to the positive terminal of the voltage source.

Note : That in the electrolytic cell, direction of the current is the reverse of that in the galvanic cell in Figure 18.2b. and the reactions at the electrodes are reversed as well.

The silver electrode is forced to become the anode, while the copper electrode is forced to become the cathode.

The net reaction that occurs:

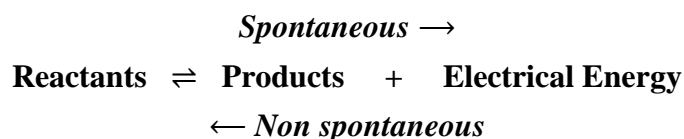


Electrolytic Cells

Voltaic cells are driven by a *spontaneous* chemical reaction that produces an electric current through an outside circuit. These cells are important because they are the basis for the batteries that fuel modern society. But they are not the only kind of electrochemical cell. **The reverse reaction in each case is non-spontaneous** and requires electrical energy to occur.

Introduction

The general form of the reaction can be written as:



It is possible to construct a cell that does work on a chemical system by driving an electric current through the system. These cells are

called **electrolytic cells**, and operate through **electrolysis**. Electrolysis is used to drive an oxidation-reduction reaction in a direction in which it does not occur spontaneously by *driving an electric current through the system* while doing work on the chemical system itself, and therefore is *non-spontaneous*.

Electrolytic cells, like galvanic cells, are composed of two half-cells--one is a reduction half-cell, the other is an oxidation half-cell. The direction of electron flow in electrolytic cells, however, may be reversed from the direction of spontaneous electron flow in galvanic cells, but the definition of both cathode and anode remain the same, where reduction takes place at the cathode and oxidation occurs at the anode. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

Differences between Galvanic and an Electrolytic cells

Electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both require a salt bridge, both have a cathode and anode side, and both have a consistent flow of electrons from the anode to the cathode. However, there are also striking differences between the two cells. The main differences are outlined below:

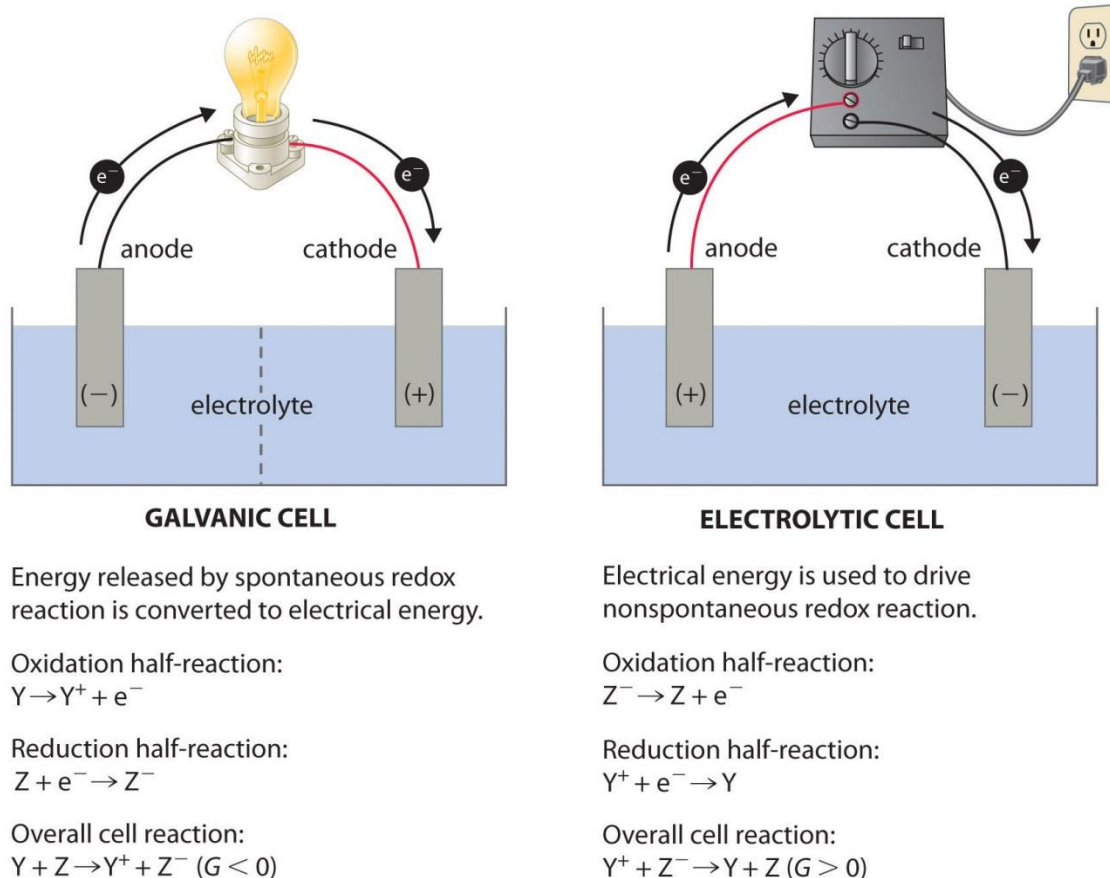


Figure 1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Table 1: Properties of Galvanic and Electrochemical Cells

Electrochemical cell (Galvanic Cell)	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of molten electrolyte.
Here the anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.	Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

Representing Cells Schematically (Cell Notation)

Shorthand notation to describe electrochemical cells:



Recall that standard cell potentials can be calculated from potentials E°_{cell} for both [oxidation](#) and [reduction](#) reactions. A positive cell potential indicates that the reaction proceeds spontaneously in the direction in which the reaction is written. Conversely, a reaction with a negative cell potential proceeds spontaneously in the reverse direction.

Cell notations are a shorthand description of voltaic or galvanic (spontaneous) cells. The reaction conditions ([pressure](#), [temperature](#), concentration, etc.), the anode, the cathode, and the [electrode](#) components are all described in this unique shorthand.

Recall that oxidation takes place at the anode and reduction takes place at the cathode. When the anode and cathode are connected by a wire, [electrons](#) flow from anode to cathode.

