Chapter 18

Introduction to Electrochemistry

18A Characterizing oxidation/reduction reactions

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

Example, $Ce^{+4} + Fe^{+2} \Leftrightarrow Ce^{+3} + Fe^{+3}$

Iron(II) is oxidized by cerium(IV) ions. A reducing agent is an electron donor. An oxidizing agent is an electron acceptor.

The equation can also be expressed as two half reactions: $Ce^{+4} + e^{-} \Leftrightarrow Ce^{+3}$ (reduction of Ce 4+) $Fe^{+2} @ \Leftrightarrow Fe^{+3} + e^{-}$ (oxidation of Fe+2) The rules for balancing half-reactions (see Feature 18-1) are the same as those for other reaction types, that is, the number of atoms of each element as well as the net charge on each side of the equation must be the same. Thus, for the oxidation of

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

 $5Fe^{2+} \Leftrightarrow 5Fe^{3+} + 5e^{-1}$

 $MnO_4^- + 5Fe^{2+} + 8H^+ \Leftrightarrow Mn^{2+} + 5Fe^{3+} @+ 4H_2O$

TABLE 5.5Balancing Equations for Redox Reactions in AcidicAqueous Solutions by the Half-Equation Method:A Summary

- Write the equations for the oxidation and reduction half-reactions.
- In each half-equation
 - (1) Balance atoms of all the elements except H and O
 - (2) Balance oxygen by using H_2O
 - (3) Balance hydrogen by using H⁺
 - (4) Balance charge by using electrons
- If necessary, equalize the number of electrons in the oxidation and reduction half-equations by multiplying one or both half-equations by appropriate integers.
- Add the half-equations, then cancel species common to both sides of the overall equation.
- Check that both numbers of atoms and charges balance.

EXAMPLE 5-6 Balancing the Equation for a Redox Reaction in an Acidic Solution

The reaction described by expression (5.23) below is used to determine the sulfite ion concentration present in wastewater from a papermaking plant. Use the half-equation method to obtain a balanced equation for this reaction in an acidic solution.

$$\mathrm{SO}_3^{2-}(\mathrm{aq}) + \mathrm{MnO}_4^{-}(\mathrm{aq}) \longrightarrow \mathrm{SO}_4^{2-}(\mathrm{aq}) + \mathrm{Mn}^{2+}(\mathrm{aq})$$
 (5.23)

Analyze

The reaction occurs in acidic aqueous solution. We can use the method summarized in Table 5.5 to balance it.

Solve

The O.S. of sulfur increases from +4 in SO_3^{2-} to +6 in SO_4^{2-} . The O.S. of Mn decreases from +7 in MnO_4^- to +2 in Mn^{2+} . Thus, SO_3^{2-} is oxidized and MnO_4^- is reduced.

Step 1. Write skeleton half-equations based on the species undergoing oxidation and reduction. The half-equations are

$$SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$$

 $MnO_4^{-}(aq) \longrightarrow Mn^{2+}(aq)$

Step 2. Balance each half-equation for numbers of atoms, in this order:

- atoms other than H and O
- O atoms, by adding H₂O with the appropriate coefficient
- H atoms, by adding H⁺ with the appropriate coefficient

The other atoms (S and Mn) are already balanced in the half-equations. To balance O atoms, we add one H₂O molecule to the left side of the first half-equation and four to the right side of the second.

$$SO_3^{2-}(aq) + H_2O(1) \longrightarrow SO_4^{2-}(aq)$$
$$MnO_4^{-}(aq) \longrightarrow Mn^{2+}(aq) + 4 H_2O(1)$$

To balance H atoms, we add two H^+ ions to the right side of the first half-equation and eight to the left side of the second.

$$SO_3^{2-}(aq) + H_2O(1) \longrightarrow SO_4^{2-}(aq) + 2 H^+(aq)$$
$$MnO_4^-(aq) + 8 H^+(aq) \longrightarrow Mn^{2+}(aq) + 4 H_2O(1)$$

(continued)

Step 3. *Balance each half-equation for electric charge.* Add the number of electrons necessary to get the same electric charge on both sides of each half-equation. By doing this, you will see that the half-equation in which electrons appear on the right side is the *oxidation half-equation*. The other half-equation, with electrons on the left side, is the *reduction half-equation*.

Oxidation:
$$SO_3^{2^-}(aq) + H_2O(l) \longrightarrow SO_4^{2^-}(aq) + 2 H^+(aq) + 2 e^-$$

(net charge on each side, -2)Reduction: $MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2^+}(aq) + 4 H_2O(l)$
(net charge on each side, +2)

Step 4. *Obtain the overall redox equation by combining the half-equations.* Multiply the oxidation half-equation by 5 and the reduction half-equation by 2. This results in 10 e⁻ on each side of the overall equation. These terms cancel out. *Electrons must not appear in the final equation.*

Overall:

$$5 \text{SO}_3^{2^-}(aq) + 5 \text{H}_2\text{O}(1) \longrightarrow 5 \text{SO}_4^{2^-}(aq) + 10 \text{H}^+(aq) + 10 \text{e}^-$$

$$\frac{2 \text{MnO}_4^-(aq) + 16 \text{H}^+(aq) + 10 \text{e}^-}{5 \text{SO}_3^{2^-}(aq) + 2 \text{MnO}_4^-(aq) + 5 \text{H}_2\text{O}(1) + 16 \text{H}^+(aq) \longrightarrow 5 \text{SO}_4^{2^-}(aq) + 2 \text{MnO}_4^-(aq) + 5 \text{H}_2\text{O}(1) + 10 \text{H}^+(aq) \longrightarrow 5 \text{SO}_4^{2^-}(aq) + 2 \text{Mn}^{2^+}(aq) + 8 \text{H}_2\text{O}(1) + 10 \text{H}^+(aq)$$

Step 5. *Simplify.* The overall equation should not contain the same species on both sides. Subtract $5 H_2O$ from each side of the equation in step 4. This leaves $3 H_2O$ on the right. Also subtract $10 H^+$ from each side, leaving $6 H^+$ on the left.

$$5 \text{SO}_3^{2-}(aq) + 2 \text{MnO}_4^{-}(aq) + 6 \text{H}^+(aq) \longrightarrow 5 \text{SO}_4^{2-}(aq) + 2 \text{Mn}^{2+}(aq) + 3 \text{H}_2\text{O}(l)$$

Step 6. *Verify.* Check the overall equation to ensure that it is balanced both for numbers of atoms and electric charge. For example, show that in the balanced equation from step 5, the net charge on each side of the equation is $-6:(5 \times 2-) + (2 \times 1-) + (6 \times 1+) = (5 \times 2-) + (2 \times 2+) = -6$.

Assess

The final check completed in step 6 gives us confidence that our result is correct. This is an important step; always take the time to complete it. It is also worth pointing out that, in this example, there was only one atom per formula that was oxidized or reduced. (Refer to the skeleton half-equations given in step 1.) Many students have difficulty balancing half-equations in which more than one atom per formula is oxidized or reduced, as is the case when $Cr_2O_7^{2^-}$ is reduced to Cr^{3^+} . Had we used $Cr_2O_7^{2^-}$ instead of MnO_4^- in equation (5.23), the balanced chemical equation for the reaction would have been $3 SO_3^{2^-} + Cr_2O_7^{2^-} + 8 H^+ \rightarrow 3 SO_4^{2^-} + 2 Cr^{3^+} + 4 H_2O$.

PRACTICE EXAMPLE A: Balance the equation for this reaction in acidic solution.

 $\operatorname{Fe}^{2+}(\operatorname{aq}) + \operatorname{MnO}_4^{-}(\operatorname{aq}) \longrightarrow \operatorname{Fe}^{3+}(\operatorname{aq}) + \operatorname{Mn}^{2+}(\operatorname{aq})$

PRACTICE EXAMPLE B: Balance the equation for this reaction in acidic solution.

 $UO^{2+}(aq) + Cr_2O_7^{2-}(aq) \longrightarrow UO_2^{2+}(aq) + Cr^{3+}(aq)$

Comparing Redox Reactions to Acid/Base Reactions

* Oxidation/reduction reactions can be considered analogous to the Brønsted-Lowry concept of acid/base reactions.

Acid + base \rightarrow base + acid 1 2

* When an acid donates a proton, it becomes a conjugate base that is capable of accepting a proton.

* Similarly, when a reducing agent donates an electron, it becomes an oxidizing agent that can then accept an electron.

EXAMPLE 18-1

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

 $2H^{+} + Cd(s) \rightleftharpoons H_{2} + Cd^{2+}$ $2Ag^{+} + H_{2}(g) \rightleftharpoons 2Ag(s) + 2H^{+}$ $Cd^{2+} + Zn(s) \rightleftharpoons Cd(s) + Zn^{2+}$

What can we deduce regarding the strengths of H⁺, Ag⁺, Cd²⁺, and Zn²⁺ 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 $Ag^+ > H^+ > Cd^{2+} > Zn^{2+}$.

Oxidation/Reduction Reactions in Electrochemical Cells

Many oxidation/reduction reactions can be carried out in either of two ways:

 the oxidant and the reductant are brought into direct contact in a suitable container.
 the reaction is carried out in an electrochemical cell in which the reactants do not come in

direct contact.

Silver ions migrate to the metal and are reduced: $Ag^+ + e^- \Leftrightarrow Ag(s)$ At the same time, an equivalent quantity of copper is oxidized $Cu(s) \Leftrightarrow Cu^{+2} + 2e^-$

The net ionic equation: $2Ag^+ + Cu(s) \Leftrightarrow 2Ag(s) + Cu^{+2}$

Figure 18-1 Photograph of a "silver tree" created by immersing a coil of copper wire in a solution of silver nitrate. 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 or the electrodes are not connected externally, the cell is said to be at open circuit and delivers the full cell potential.



Figure 18-2a shows the arrangement of an electrochemical cell (galvanic).

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.





Figure 18-2-c An electrolytic cell

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:

 $Ag^{+} + e^{-} \Leftrightarrow Ag(s)$ $Fe^{+3} + e^{-} \Leftrightarrow Fe^{+2}$ $NO_{3}^{-} + 10H^{+} + 8e^{-} \Leftrightarrow NH_{4}^{+} + 3H_{2}O$

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

 $Cu(s) \Leftrightarrow Cu^{+2} + 2e^{-2}$ $2Cl^{-} \Leftrightarrow Cl_{2}(g) + 2e^{-2}$ $Fe^{+2} \Leftrightarrow Fe^{+3} + e^{-2}$

Types of Electrochemical Cells

Electrochemical cells are either galvanic or electrolytic.

Galvanic cells store electrical energy; electrolytic cells consume electricity. The reactions at the two electrodes in such cells tend to proceed spontaneously and produce a flow of electrons from the anode to the cathode via an external conductor.

Galvanic cells operate spontaneously, and the net reaction during discharge is called the spontaneous cell reaction

An electrolytic cell requires an external source of electrical energy for operation.

For both galvanic and electrolytic cells,

- (1) reduction always takes place at the cathode, and
- (2) oxidation always takes place at the anode.

However, when the cell is operated as an electrolytic cell, the cathode in a galvanic cell becomes the anode.

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.

Representing Cells Schematically

Shorthand notation to describe electrochemical cells:

```
Cu | Cu<sup>+2</sup> (0.0200 M) | Ag<sup>+</sup> (0.0200 M) | Ag
```

➤ A single vertical line indicates a phase boundary, or interface, at which a potential develops.

> The double vertical lines represent two-phase boundaries, one at each end of the salt bridge.

> There is a liquid-junction potential at each of these interfaces.

Currents in Electrochemical Cells

Charge is transported through such an electrochemical cell by three mechanisms:

- 1. Electrons carry the charge within the electrodes as well as the external conductor.
- 2. Anions and cations are the charge carriers within the cell. At the lefthand electrode, copper is oxidized to copper ions, giving up electrons to the electrode.
- 3. The ionic conduction of the solution is coupled to the electronic conduction in the electrodes by the reduction reaction at the cathode and the oxidation reaction at the anode.



18C Electrode potentials

The potential difference between the of the tendency for the reaction:

to proceed from a nonequilibrium stat

2Ag(s) + Cu⁻¹

 $\Delta G = - nFE_{cell}$

If the reactants and products are in their *standard states*, the resulting cell potential is called the standard cell potential. This is related to the standard free energy change and Ke

 $\Delta G^{\circ} = -nFE^{\circ}_{cell} = -RT \ln K_{eq}$

-The standard state of a substance is the physical state (solid, liquid, or gas) that a substance would be in under standard conditions. Thus, the standard state for carbon is solid, for water is liquid and for hydrogen is gas. Why? Because at **1.00** atm. and 25 $^{\circ}$ C, these substances are in the physical state specified.

- This reference state allows us to obtain relative \blacktriangleright The cell potential E_{cell} is related to the values of such thermodynamic quantities as free energy, activity, enthalpy, and entropy.

> - All substances are assigned unit activity in their standard states.

- For gases, the standard state has the properties of an ideal gas but at one atmosphere pressure. It is thus said to be a *hypothetical state*.

- For pure liquids and solvents, the standard states

are real states and are the pure substances at a specified temperature and pressure. For solutes in dilute solution, the standard state is a hypothetical state that has the properties of an infinitely dilute solute but at unit concentration (molar or molal concentration, or mole fraction). - where R is the gas constant and T is The standard state of a solid is a real state and is the pure solid in its most stable crystalline form.

18C-1 Sign Convention for Cell Potentials

IUPAC ----The convention for cells is called the *plus right rule*. This rule implies that we always measure the cell potential by connecting the positive lead of the voltmeter to the right-hand electrode in the schematic or cell drawing (Ag electrode in Figure 18-4 and the common, or ground, lead of the voltmeter to the lefthand electrode (Cu electrode in Figure 18-4).

> If we always follow this convention, the value of E_{cell} is a measure of the tendency of the cell reaction to occur spontaneously in the direction written below, from left to right.

Cu | Cu²⁺(0.0200 M) || Ag⁺(0.0200 M) | Ag

➤ That is, the direction of the overall process has Cu metal being oxidized to Cu²⁺ in the lefthand compartment and Ag⁺ being reduced to Ag metal in the right-hand compartment. In other words, the reaction being considered is

 $Cu(s) + 2Ag^+ \Leftrightarrow 2Ag(s) + Cu^{+2}$

Implications of the IUPAC Convention

> If E_{cell} is positive, the right-hand electrode is positive, ΔG is negative Hence, the reaction in the direction being considered would occur spontaneously if the cell were short-circuited or connected to some device to perform work (e.g., light a lamp, power a radio, or start a car).

 $E_{cell} = E_{right} - E_{left}$

> On the other hand, If E_{cell} is negative, the right-hand electrode is negative, ΔG is positive, and the reaction in the direction considered is not the spontaneous cell reaction.

The IUPAC convention is consistent with the signs that the electrodes actually develop in a galvanic cell. That is, in the Cu/Ag cell

Cu | Cu²⁺(0.0200 M) || Ag⁺(0.0200 M) | Ag

the Cu electrode becomes electron rich (negative)^{Cu electrode} (left) because of the tendency of Cu to be oxidized to Cu²⁺, and the Ag electrode is electron deficient (positive) because of the tendency for Ag ⁺ to be reduced to Ag. (a) As the galvanic cell discharges spontaneously, the silver electrode is the cathode, while the copper electrode is the anode.



 $\Delta G = - nFE_{cell}$

 $\Delta G < 0$ spontaneous

For the same cell written in the opposite direction

Ag | AgNO₃ (0.0200 M) || CuSO₄ (0.0200 M) | Cu

the measured cell potential would be $E_{cell} = -0.412$ V, and the reaction considered is

 $2Ag(s) + Cu^{2+} \Leftrightarrow 2Ag^{+} + Cu(s)$

> This reaction is not the spontaneous cell reaction because E_{cell} is negative, and ΔG is thus positive. It does not matter to the cell which electrode is written in the schematic on the right and which is written on the left. The spontaneous cell reaction is always

 $Cu(s) + 2Ag^+ \Leftrightarrow 2Ag(s) + Cu^{+2}$

By convention, we just measure the cell in a standard manner and consider the cell reaction in a standard direction

Finally, we must emphasize that, no matter how we may write the cell schematic or arrange the cell in the laboratory, if we connect a wire or a low-resistance circuit to the cell, the spontaneous cell reaction will occur.

> The only way to achieve the reverse reaction is to connect an external voltage source and force the electrolytic reaction

 $2Ag(s) + Cu^{2+} \Leftrightarrow 2Ag^{+} + Cu(s)$ to occur.

Half-Cell Potentials

•The potential of a cell is the difference between two electrode.

• According to the IUPAC sign convention, as long as the liquid-junction potential is negligible,

 $E_{\rm cell} = E_{\rm right} - E_{\rm left}$

We cannot determine absolute potentials of electrodes,
we can easily determine relative electrode potentials.

Discharging a Galvanic Cell

Cell potential in the galvanic cell as a function of time. The cell current, which is directly related to the cell potential, also decreases with the same time behavior.





In 18-4(b), the voltmeter is replaced with a lowresistance current meter, and the cell discharges



In 18-4(c), after equilibrium is reached, the cell potential is again measured with a voltmeter and found to be

The Standard Hydrogen Reference Electrode

For relative electrode potential data to be widely applicable and useful, we must have a generally agreed-upon reference half-cell against which all others are compared.

The standard hydrogen electrode (SHE) is a reference half-cell that is easy to construct, reversible, and highly reproducible in behavior. It is a typical gas electrode

➤ The metal conductor is a piece of platinum that has been coated, or platinized, with finely divided platinum (platinum black) to increase its specific surface area. This electrode is immersed in an aqueous acid solution of known, constant hydrogen ion activity. The solution is kept saturated with hydrogen by bubbling the gas at constant pressure over the surface of the electrode.

➤ The platinum does not take part in the electrochemical reaction and serves only as the site where electrons are transferred.

The half-reaction responsible for the potential at this electrode is $2H^+(aq) + 2e^- \Leftrightarrow H_2(g)$

The hydrogen electrode can be represented schematically as

Pt, $H_2(p = 1.00 \text{ atm}) |(H^+ = x \text{ M})||$

➤ The potential of a hydrogen electrode depends on temp. and the activities of hydrogen ion and molecular hydrogen in the solution.

At pH=1.00 and $a_{H+} = 1.00$, the potential of the hydrogen



Electrode Potential and Standard Electrode Potential

•An electrode potential is defined as the potential of a cell in which the electrode in question is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode.

• If we want to obtain the potential of a silver electrode in contact with a solution of Ag+

•The left-hand electrode is the standard hydrogen electrode with a potential that has been assigned a value of 0.000 V,

$$E_{cell} = E_{right} - E_{left} = E_{Ag} - E_{SHE}$$
$$= E_{Ag} - 0.000 = E_{ag}$$

where E_{Ag} is the potential of the silver electrode.

* Often, the potential of an electrode, such as the silver electrode in Figure 18-7, is referred to as E_{Ag} versus SHE to emphasize that it is the potential of a complete cell measured against the standard hydrogen electrode as a



The standard electrode potential, E₀, of a half-reaction is defined as its electrode potential when the activities of the reactants and products are all unity.

The E₀ value for the half reaction: $Ag^+ + e^- \Leftrightarrow Ag(s)$ can be obtained by measuring E_{cell} with the silver ion activity in the right-hand compartment is 1.00

The cell can be represented as

Pt, H2(p = 1.00 atm) |H⁺ (a_{H+} = 1.00)|| Ag⁺ (a_{Ag+} = 1.00)|Ag

Or alternatively as

$$SHE|| Ag^{+}(a_{Ag^{+}} = 1.00)|Ag$$

The silver electrode is positive with respect to the standard hydrogen electrode.

Therefore, the standard electrode potential is given a positive sign,

$$Ag^+ + e^- \Leftrightarrow Ag(s)$$
 $E^\circ_{Ag^+/Ag} = +0.799 V$

Figure 18-7 Measurement of the electrode potential for an Ag electrode. If the silver ion activity in the right-hand compartment is 1.00, the cell potential is the standard electrode potential of the Ag1/Ag half-reaction. Figure 18-8 Measurement of the standard electrode potential for $Cd^{2+} + 2e^{-} \Leftrightarrow Cd(s)$.



In contrast to the silver electrode, the cadmium electrode is negative with respect to the standard hydrogen electrode. Therefore, the standard electrode potential of the Cd/Cd2+ couple is *by convention given a negative sign, and* $E^{0}_{Cd2+/Cd}$ = -0.403 V.

The standard electrode potentials for the four half-cells just described can be arranged in the following order:

Half-Reaction	Standard Electrode Potential, V
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
$Cd^{2+} + 2e^{-} \rightleftharpoons Cd(s)$	-0.403
$Zn^{2+} + 2e^{-} \rightleftharpoons Zn(s)$	-0.763

Additional Implications of the IUPAC Sign Convention

An electrode potential is by definition a reduction potential.

An oxidation potential is the potential for the half-reaction written in the opposite way.

The sign of an oxidation potential is, therefore, opposite that for a reduction potential, but the magnitude is the same.

The IUPAC sign convention is based on the actual sign of the half-cell of interest when it is part of a cell containing the standard hydrogen electrode as the other half-cell.

Effect of Concentration on Electrode Potentials: The Nernst Equation

Consider the reversible half-reaction

 $aA + bB + ... + ne^{-} \Leftrightarrow cC + dD + ...$

where the capital letters represent formulas for the participating species,

e⁻ represents the electrons, and the lower case italic letters indicate the number of moles of each species appearing in the half-reaction as it has been written.

The electrode potential for this process is given by the equation

$$E = E^{0} - \frac{RT}{nF} \ln \frac{[C]^{c} [D]^{d} \dots}{[A]^{a} [B]^{b} \dots}$$

 $E = E^{0} - \frac{0.0592}{n} \log \frac{[C]^{c} [D]^{d} \dots}{[A]^{a} [B]^{b} \dots}$

EXAMPLE 18-2

Typical half-cell reactions and their corresponding Nernst expressions follow.

(1)
$$\operatorname{Zn}^{2^+} + 2e^- \rightleftharpoons \operatorname{Zn}(s)$$
 $E = E^0 - \frac{0.0592}{2} \log \frac{1}{[\operatorname{Zn}^{2^+}]}$

No term for elemental zinc is included in the logarithmic term because it is a pure second phase (solid). Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the zinc ion concentration.

(2)
$$\operatorname{Fe}^{3+} + e^{-} \rightleftharpoons \operatorname{Fe}^{2+}(s)$$
 $E = E^{0} - \frac{0.0592}{1} \log \frac{[\operatorname{Fe}^{2+}]}{[\operatorname{Fe}^{3+}]}$

The potential for this couple can be measured with an inert metallic electrode immersed in a solution containing both iron species. The potential depends on the logarithm of the ratio between the molar concentrations of these ions.

(3)
$$2H^+ + 2e^- \rightleftharpoons H_2(g)$$
 $E = E^0 - \frac{0.0592}{2} \log \frac{p_{H_2}}{[H^+]^2}$

In this example, p_{H_2} is the partial pressure of hydrogen (in atmospheres) at the surface of the electrode. Usually, its value will be the same as atmospheric pressure.

(4)
$$\operatorname{MnO_4^-} + 5e^- + 8H^+ \rightleftharpoons \operatorname{Mn^{2+}} + 4H_2O$$

 $E = E^0 - \frac{0.0592}{5} \log \frac{[\operatorname{Mn^{2+}}]}{[\operatorname{MnO_4^-}][H^+]^8}$

In this situation, the potential depends not only on the concentrations of the manganese species but also on the pH of the solution.

(5)
$$\operatorname{AgCl}(s) + e^{-} \rightleftharpoons \operatorname{Ag}(s) + \operatorname{Cl}^{-} \qquad E = E^{0} - \frac{0.0592}{1} \log [\operatorname{Cl}^{-}]$$

This half-reaction describes the behavior of a silver electrode immersed in a chloride solution that is *saturated* with AgCl. To ensure this condition, an excess of the solid AgCl must always be present. Note that this electrode reaction is the sum of the following two reactions:

$$AgCl(s) \rightleftharpoons Ag^{+} + Cl^{-}$$
$$Ag^{+} + e^{-} \rightleftharpoons Ag(s)$$

Note also that the electrode potential is independent of the amount of AgCl present as long as there is at least some present to keep the solution saturated.

The Standard Electrode Potential, E⁰

The standard electrode potential for a half-reaction, E⁰, is defined as the electrode potential when all reactants and products of a half-reaction are at unit activity.

The important characteristics of the standard electrode potential is:

- 1. It is a relative quantity---the potential of an electrochemical cell in which the reference electrode is the standard hydrogen electrode, whose potential has been assigned a value of 0.000 V.
- 2. The standard electrode potential for a half-reaction refers exclusively to a reduction reaction, that is, it is a relative reduction potential.

- 3. The standard electrode potential measures the relative force tending to drive the half-reaction from a state in which the reactants and products are at unit activity to a state in which the reactants and products are at their equilibrium activities relative to the standard hydrogen electrode.
- 4. The standard electrode potential is independent of the number of moles of reactant and product shown in the balanced half-reaction.
- A positive electrode potential indicates that the half-reaction in question is spontaneous with respect to the standard hydrogen electrode half-reaction.
 A negative sign indicates the opposite.
- 6. The standard electrode potential for a half-reaction is temperature dependent.

TABLE 18-1

Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^+ + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu(s)$	+0.337
$UO_2^{2^+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.334
$Hg_2Cl_2(s) + 2e^- \Longrightarrow 2Hg(l) + 2Cl^-$	+0.268
$AgCl(s) + e^{-} \rightleftharpoons Ag(s) + Cl^{-}$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.017
$2\mathrm{H}^+ + 2\mathrm{e}^- \rightleftharpoons \mathrm{H}_2(g)$	0.000
$AgI(s) + e^{-} \rightleftharpoons Ag(s) + I^{-}$	-0.151
$PbSO_4 + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	-0.350
$Cd^{2+} + 2e^{-} \rightleftharpoons Cd(s)$	-0.403
$Zn^{2+} + 2e^{-} \rightleftharpoons Zn(s)$	-0.763

Systems Involving Precipitates or Complex Ions

Figure 18-9 The measurement of the standard electrode potential for the Ag/AgCl electrode.



EXAMPLE 18-3

Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (a) $E^{\circ}_{Ag^+/Ag} = 0.799$ V and (b) $E^{\circ}_{AgCl/Ag} = 0.222$ V.

Solution

(a)
$$Ag^+ + e^- \rightleftharpoons Ag(s)$$
 $E^0_{Ag^+/Ag} = +0.799 V$

The \mbox{Ag}^+ concentration of this solution is given by

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9} M$$

Substituting into the Nernst expression gives

$$E = 0.799 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}$$

(b) We may write this last equation as

$$E = 0.222 - 0.0592 \log [Cl-] = 0.222 - 0.0592 \log 0.0500$$

= 0.299

Limitations to the use of Standard Electrode Potentials

Calculations of cell potentials and equilibrium constants for redox reactions as well as for redox titration curves can sometimes differ significantly from those in laboratory because:

1. Use of Concentrations Instead of Activities:

Most analytical oxidation/reduction reactions are carried out in solutions that have such high ionic strengths that activity coefficients cannot be obtained.

Using concentration instead of activities can lead to errors.

2. Effect of other equilibria such as dissociation, association, complex formation, and solvolysis:

A formal potential is the electrode potential when the ratio of analytical concentrations of reactants and products of a halfreaction are exactly 1.00 and the molar concentrations of any other solutes are specified.

To distinguish the formal potential from the standard electrode potential a prime symbol is added to E_0 .

Figure 18-10 Measurement of the formal potential of the Ag^+/Ag couple in 1 M HClO₄.

