

Electrochemistry

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Objectives

At the end of this, we will be able to-

- Know all the terms related to electrochemistry
- Explain electrode potential, electromotive force, and chemical series
- Know about electroplating, product deposition, and several cells

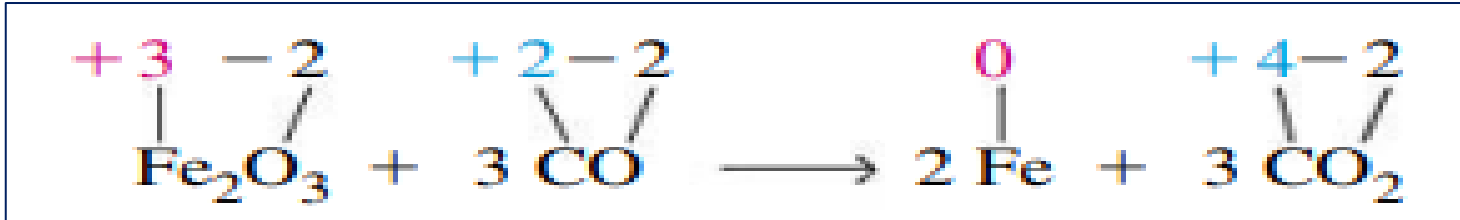
Contents

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- Oxidation number
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- Electromotive force
- Electrode reactions
- Reduction potential
- Chemical series
- Electroplating
- Product deposition within the electrodes
- Galvanic cell, Daniel cell, Dry cell, & Hydrogen fuel cell

Oxidants & Reductants

Oxidation and reduction must always occur together, and such a reaction is called an oxidation reduction, or redox reaction.

Oxidation State



In a redox reaction, the substance that makes it possible for some other substance to be oxidized is called the **oxidizing agent, or oxidant**. In doing so, the oxidizing agent is itself reduced.

The substance that causes some other substance to be reduced is called the **reducing agent, or reductant**. In the reaction, the reducing agent is itself oxidized.

An oxidizing agent (oxidant)-

- causes another substance to be oxidized
- contains an element whose oxidation state decreases in a redox reaction
- gains electrons (electrons are found on the left side of its half-equation)
- is reduced

A reducing agent (reductant)-

- causes another substance to be reduced
- contains an element whose oxidation state increases in a redox reaction
- loses electrons (electrons are found on the right side of its half-equation)
- is oxidized

In general, a substance with an element in one of its highest possible oxidation states is an oxidizing agent. If the element is in one of its lowest possible oxidation states, the substance is a reducing agent.

Electrolytes

An aqueous solution of ions is that it will conduct electricity, provided the concentration of ions is not too low. Aqueous solution of ions conducts electricity because the ions move essentially independently of each other, each one carrying a certain quantity of charge. (In a metallic conductor, such as copper or tungsten, electrons carry the charge.)

Whether or not an aqueous solution is a conductor of electricity depends on the nature of the solute(s). Pure water contains so few ions that it does not conduct electric current. However, some solutes produce ions in solution thereby making the solution an electrical conductor.

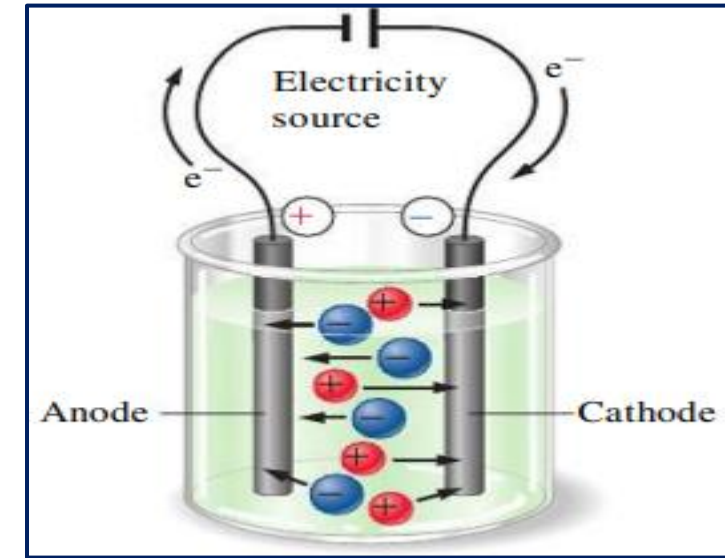
Solutes that provide ions when dissolved in water are called electrolytes.

Solutes that do not provide ions in water are called nonelectrolytes.

All electrolytes provide ions in water but not all electrolytes are equal in their tendencies for providing ions.

A strong electrolyte is a substance that is essentially completely ionized in aqueous solution. Stated another way, a strong electrolyte has a strong (or high) tendency for providing ions.

A weak electrolyte is a substance that is only partially ionized in aqueous solution. A weak electrolyte has a weak (or small) tendency for providing ions.



Two graphite rods called electrodes are placed in a solution. The external source of electricity pulls electrons from one rod and forces them onto the other, creating a positive charge on one electrode and a negative charge on the other (right). In the solution, positive ions (cations) are attracted to the negative electrode, the cathode; negative ions (anions) are attracted to the positive electrode, the anode. Thus, electric charge is carried through the solution by the migration of ions.

Electrode Potentials and Their Measurement

A redox reaction occurs between Cu(s) and $\text{Ag}^+(\text{aq.})$, but not between Cu(s) and $\text{Zn}^{2+}(\text{aq.})$. Specifically, we see that silver ions are reduced to silver atoms on a copper surface, whereas zinc ions are not reduced to zinc atoms on a copper surface. **Ag^+ ions are more readily reduced than is Zn^{2+} .**

In electrochemical studies, a strip of metal, M , is called an electrode.

An electrode immersed in a solution containing ions of the same metal, is called a half-cell.

Two kinds of interactions are possible between metal atoms on the electrode and metal ions in solution.

- A metal ion from solution may collide with the electrode, gain electrons from it, and be converted to a metal atom M . The ion is reduced.
- A metal atom M on the surface may lose n electrons to the electrode and enter the solution as the ion. The metal atom is oxidized.

An equilibrium is quickly established between the metal and the solution,



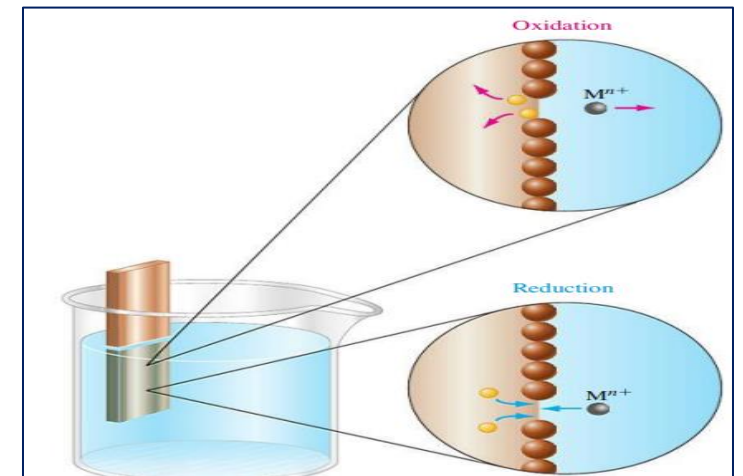
Any changes produced at the electrode or in the solution as a consequence of this equilibrium are too slight to measure.

Measurements must be based on a combination of two different half-cells. tendency for electrons to flow from the electrode of one half-cell to the electrode of the other.

Electrodes are classified according to whether oxidation or reduction takes place there.

If oxidation takes place, the electrode is called the anode.

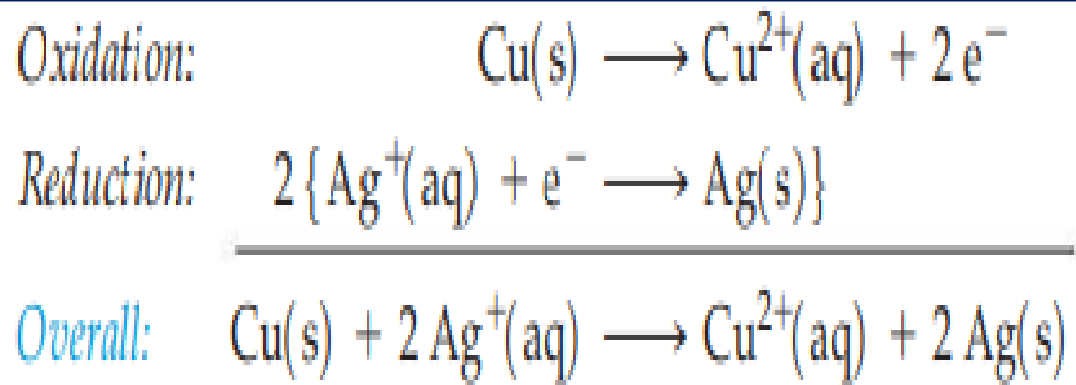
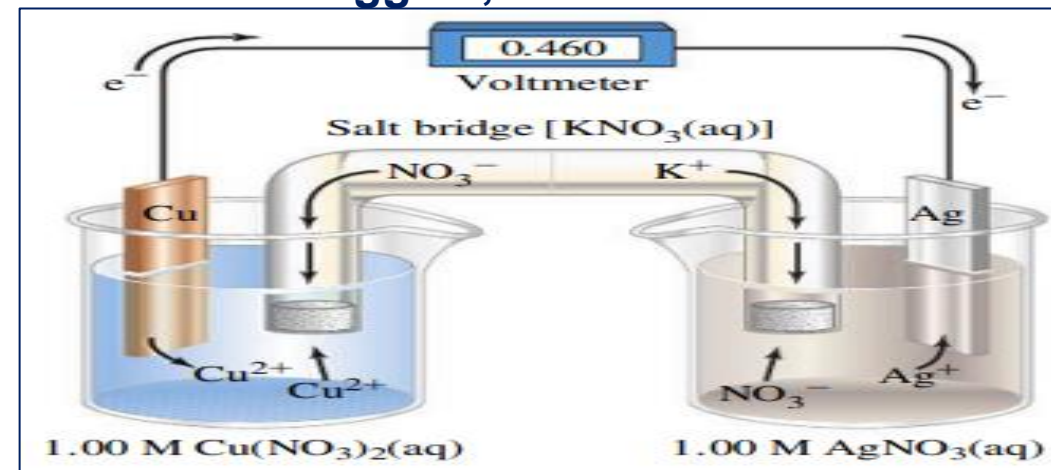
If reduction takes place, the electrode is called the cathode.



The half-cell consists of a metal electrode, M , partially immersed in an aqueous solution of its ions, (The anions required to maintain electrical neutrality in the solution are not shown.)

Electrode Potentials and Their Measurement

Figure shows a combination of two half-cells, one with a Cu electrode in contact with $\text{Cu}^{2+}(\text{aq.})$ and the other with an Ag electrode in contact with $\text{Ag}^+(\text{aq.})$. The two electrodes are joined by wires to an electric meter here, a voltmeter. To complete the electric circuit, the two solutions must also be connected electrically. Charge is carried through solutions by the migration of ions. The solutions must either be in direct contact through a porous barrier or joined by a third solution in a U-tube called a salt bridge. The properly connected combination of two half-cells is called an electrochemical cell. As the arrows suggest, Cu atoms release electrons at the anode and enter the $\text{Cu}(\text{NO}_3)_2(\text{aq.})$ as Cu^{2+} ions. Electrons lost by the Cu atoms pass through the wires and the voltmeter to the cathode, where they are gained by Ag^+ ions from the $\text{AgNO}_3(\text{aq.})$ producing a deposit of metallic silver. Simultaneously, anions NO_3^- from the salt bridge migrate into the copper half-cell and neutralize the positive charge of the excess Cu^{2+} ions; cations (K^+) migrate into the silver half-cell and neutralize the negative charge of excess NO_3^- ions. The overall reaction that occurs as the electrochemical cell spontaneously produces electric current is,

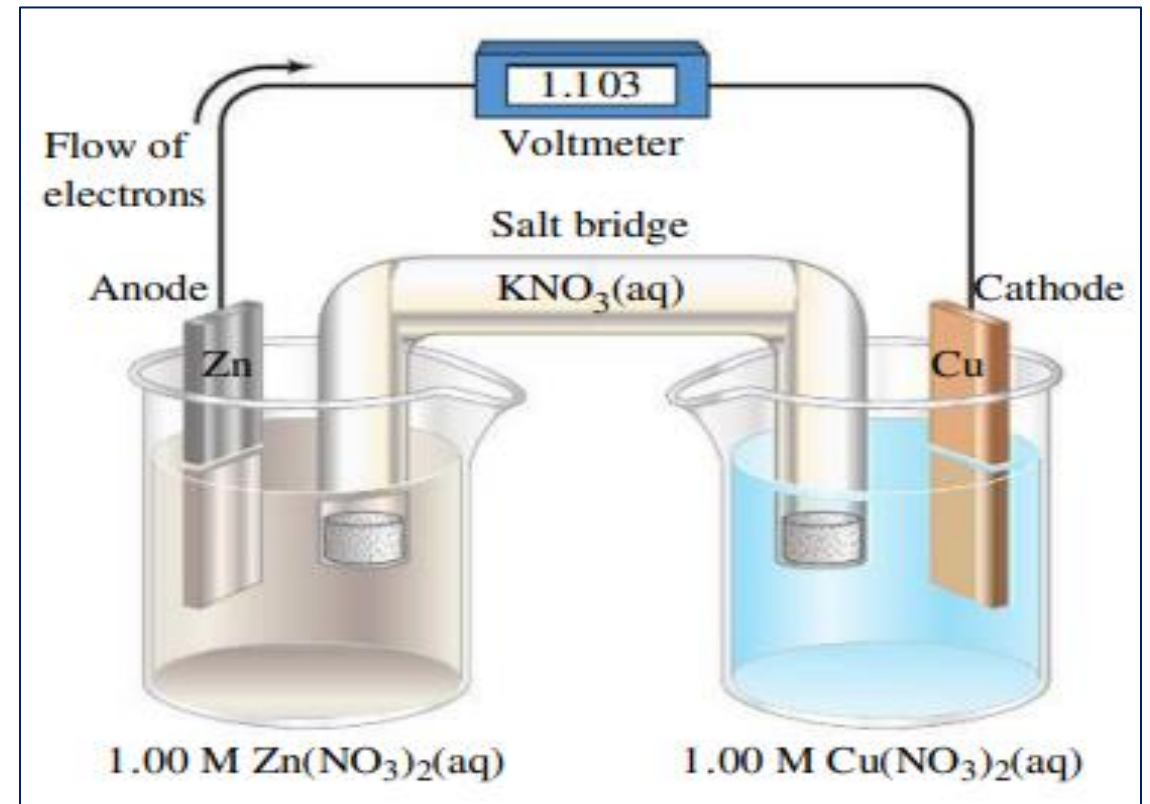
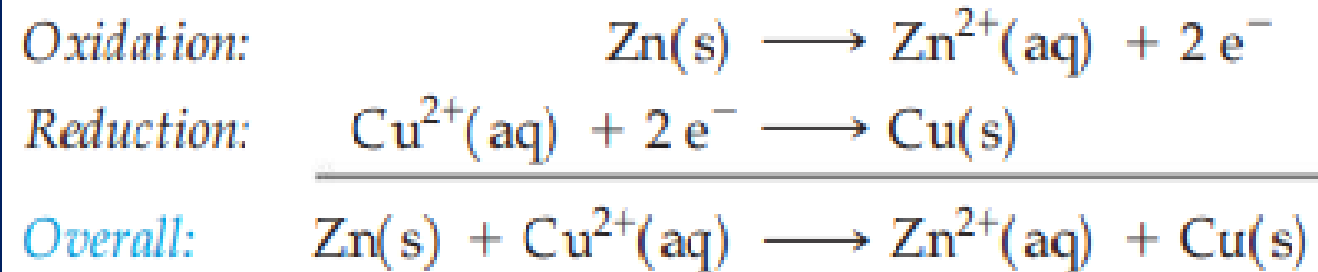


The reading on the voltmeter (0.460 V) is the cell voltage, or the potential difference between the two half-cells. The unit of cell voltage, volt (V), is the energy per unit charge. Thus, a potential difference of one volt signifies an energy of one joule for every coulomb of charge passing through an electric circuit: $1\text{V} = 1\text{ J/C}$ voltage, or potential difference, as the driving force for electrons; the greater the voltage, the greater the driving force. Cell voltage is also called electromotive force (emf), or cell potential, and represented by the symbol E_{cell} .

Electrode Potentials and Their Measurement

Copper does not displace Zn^{2+} from solution-

In an electrochemical cell consisting of a $\text{Zn (s)}/\text{Zn}^{2+} \text{ (aq.)}$ half-cell and a $\text{Cu}^{2+} \text{ (aq.)}/\text{Cu (s)}$ half-cell, electrons flow from the Zn to the Cu. The spontaneous reaction in the electrochemical cell is,



The displacement of Zn^{2+} occurs by Cu(s) .

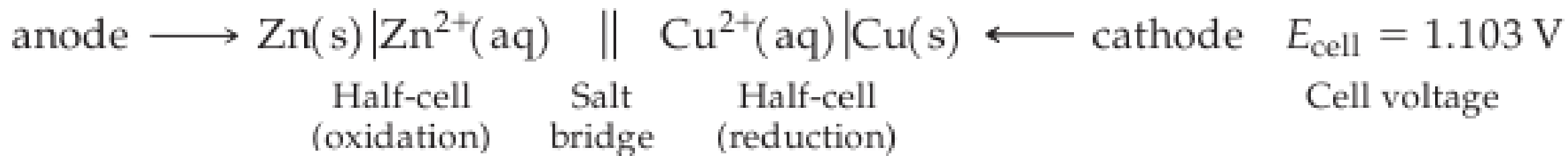
The reverse of reaction does not occur spontaneously.

Cell Diagrams and Terminology

A cell diagram shows the components of an electrochemical cell in a symbolic way-

- The anode, the electrode at which oxidation occurs, is placed at the left side of the diagram.
- The cathode, the electrode at which reduction occurs, is placed at the right side of the diagram.
- A boundary between different phases (for example, an electrode and a solution) is represented by a single vertical line (|).
- The boundary between half-cell compartments, commonly a salt bridge, is represented by a double vertical line (||).
- Species in aqueous solution are placed on either side of the double vertical line.

Different species within the same solution are separated from each other by a comma.



These electrochemical cells produce electricity as a result of spontaneous chemical reactions, they are called voltaic, or galvanic, cells.

Representing a Redox Reaction by Means of a Cell Diagram

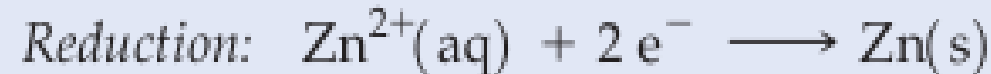
Aluminum metal displaces zinc(II) ion from aqueous solution.

(a) Write oxidation and reduction half-equations and an overall equation for this redox reaction.

(b) Write a cell diagram for a voltaic cell in which this reaction occurs.

The term **displaces** means that aluminum goes into solution as metal. Al is oxidized to $\text{Al}^{3+}(\text{aq})$, and forcing $\text{Zn}^{2+}(\text{aq})$, out of solution as zinc metal. Al is oxidized to Al^{3+} , and Zn^{2+} is reduced to Zn.

(a) The two half equations are



On inspecting these half-equations, we see that the number of electrons involved in oxidation and reduction are different. In writing the overall equation, the coefficients must be adjusted so that equal numbers of electrons are involved in oxidation and in reduction.



(b) Al(s) is oxidized to $\text{Al}^{3+}(\text{aq})$ in the anode half-cell (written on the left of the cell diagram), and $\text{Zn}^{2+}(\text{aq})$ is reduced to Zn(s) in the cathode half-cell (written on the right of the cell diagram).



Deducing the Balanced Redox Reaction from a Cell Diagram

The cell diagram for an electrochemical cell is written as



Write the equations for the half-reactions that occur at the electrodes. Balance the overall cell reaction.

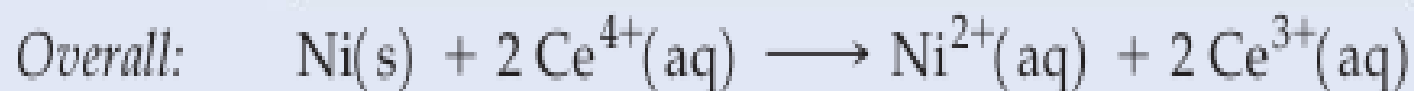
The cerium reduction reaction is



The nickel oxidation reaction is



In these half-equations the number of electrons involved in oxidation and reduction are different. In writing the overall equation, the coefficients must be adjusted so that equal numbers of electrons are involved in oxidation and in reduction.



Standard Hydrogen Electrode

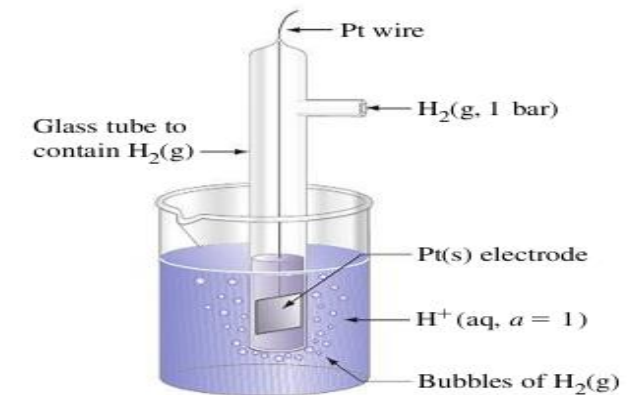
Cell voltages- potential differences between electrodes- are among the most precise scientific measurements possible. Potentials of individual electrodes cannot be precisely established. We could make such measurements, cell voltages by subtracting one electrode potential from another. The same result can be achieved by arbitrarily choosing a particular half-cell that is assigned an electrode potential of zero. Other half cells can then be compared with this reference. The commonly accepted reference is the standard hydrogen electrode.

The standard hydrogen electrode (SHE) involves equilibrium established on the surface of an inert metal (such as platinum) between H_3O^+ (that is, ions from a solution in which they are at unit activity $a_{\text{H}_3\text{O}^+} = 1$) and H_2 molecules from the gaseous state at a pressure of 1 bar. The equilibrium reaction produces a particular potential on the metal surface, but this potential is arbitrarily taken to be zero.



The two vertical lines signify that three phases are present: solid platinum, gaseous hydrogen, and aqueous hydrogen ion.

For simplicity, we will usually write H^+ for H_3O^+ assume that unit activity ($a = 1$) exists at roughly $[\text{H}^+] = 1\text{M}$ and replace a pressure of 1 bar by 1 atm.

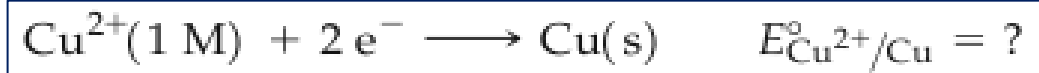


Hydrogen is a gas at room temperature, electrodes cannot be constructed from it. The standard hydrogen electrode consists of a piece of platinum dipped into a solution containing 1 M $\text{H}^+(\text{aq})$ with a stream of hydrogen passing over its surface. The platinum does not react but provides a surface for the reduction of as well as the reverse oxidation half-reaction. $\text{H}_3\text{O}^+(\text{aq})$ to $\text{H}_2(\text{g})$

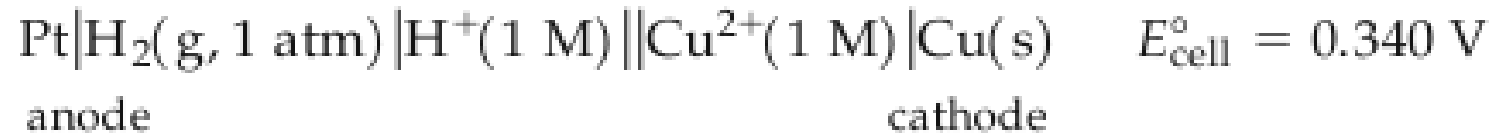
Standard Electrode Potentials

A standard electrode potential, measures the tendency for a reduction process to occur at an electrode. In all cases, the ionic species are present in aqueous solution at unit activity (approximately 1 M), and gases are at 1 bar pressure (approximately 1 atm). Where no metallic substance is indicated, the potential is established on an inert metallic electrode, such as platinum.

E° refers to a reduction, a reduction couple as a subscript to E° is, The substance being reduced is written on the left of the slash sign (/), and the chief reduction product on the right.



To determine the value of for a standard electrode such as that to which half-reaction applies, we compare it with a standard hydrogen electrode (SHE). In this comparison, the SHE is always taken as the electrode on the left of the cell diagram, the anode and the compared electrode is the electrode on the right, the cathode. In the following voltaic cell, the measured potential difference is 0.340 V, with electrons flowing from the H_2 to the Cu electrode.



A standard cell potential, cathode $E_{\text{cell}}^\circ = 0.340 \text{ V}$ is the potential difference, or voltage, of a cell formed from two standard electrodes. The difference is always taken in the following way:

$$E_{\text{cell}}^\circ = E^\circ(\text{right}) - E^\circ(\text{left})$$

(cathode) (anode)

Applying the above cell diagram,

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{Cu}^{2+}/\text{Cu}}^\circ - E_{\text{H}^+/\text{H}_2}^\circ = 0.340 \text{ V} \\ &= E_{\text{Cu}^{2+}/\text{Cu}}^\circ - 0 \text{ V} = 0.340 \text{ V} \\ E_{\text{Cu}^{2+}/\text{Cu}}^\circ &= 0.340 \text{ V} \end{aligned}$$

Cell reaction indicates that, $\text{Cu}^{2+}(1 \text{ M})$ is more easily reduced than is $\text{H}^+(1 \text{ M})$

Standard Electrode Potentials

For cell diagram, in which the zinc electrode appears on the right,



The standard electrode potential for the Zn^{2+}/Zn couple can be written

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ(\text{right}) - E^\circ(\text{left}) \\ &= E^\circ_{\text{Zn}^{2+}/\text{Zn}} - 0 \text{ V} = -0.763 \text{ V} \\ E^\circ_{\text{Zn}^{2+}/\text{Zn}} &= -0.763 \text{ V} \end{aligned}$$

Thus, the standard *reduction* half-reaction is

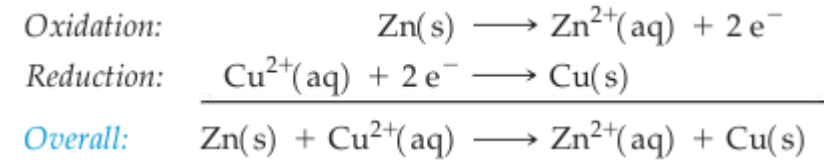


The potential of the standard hydrogen electrode is set at exactly 0 V. Any electrode at which a reduction half-reaction shows a greater tendency to occur than does the reduction of $\text{H}^+ (1 \text{ M})$ to $\text{H}_2(\text{g}, 1 \text{ atm})$, E° has a positive value for its standard electrode potential. Any electrode at which a reduction half-reaction shows a lesser tendency to occur than does the reduction of $\text{H}^+ (1 \text{ M})$ to $\text{H}_2(\text{g}, 1 \text{ atm})$, potential, E° , has a negative value for its standard reduction.

Comparisons of the Standard Copper and Zinc Electrodes

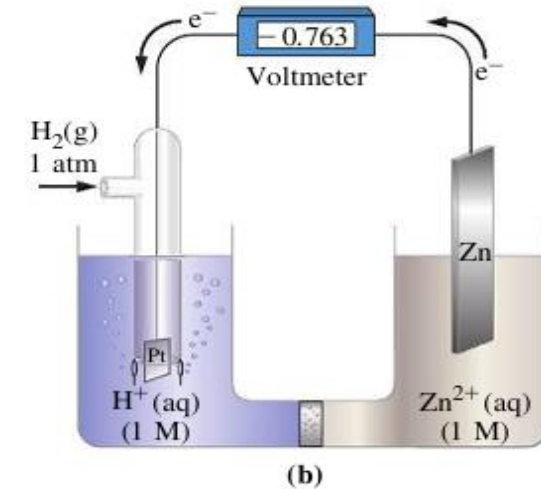
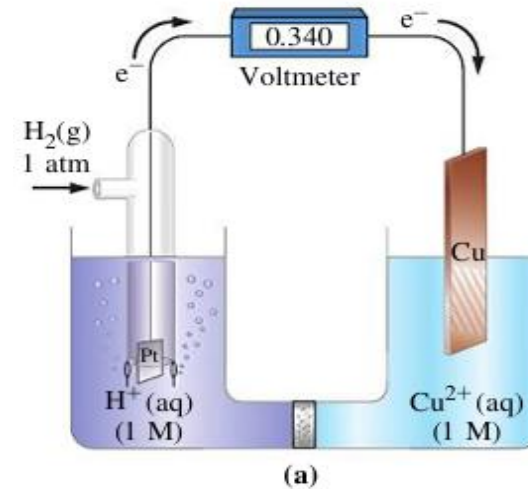
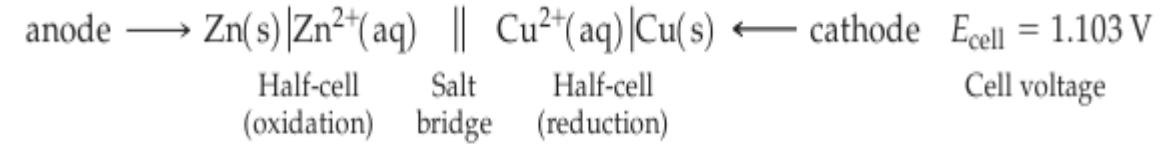
Comparisons of the standard copper and zinc electrodes to the standard hydrogen electrode are, Calculation of standard cell potentials for redox reactions E°_{cell} values from standard electrode potentials for half-cell reactions values E° .

Suppose for a reaction and cell diagram,



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ(\text{right}) - E^\circ(\text{left}) \\ &= E^\circ(\text{cathode}) - E^\circ(\text{anode}) \\ &= E^\circ(\text{reduction half-cell}) - E^\circ(\text{oxidation half-cell}) \\ &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.340\text{ V} - (-0.763\text{ V}) = 1.103\text{ V} \end{aligned}$$

Here, E°_{cell} for a new battery system with one known electrode potential and a measured E°_{cell} value to determine an unknown E° . E° values in this formulation are for a reduction half-reaction, regardless of whether oxidation or reduction occurs in the half-cell.



(a) A standard hydrogen electrode is the anode, and copper is the cathode. Contact between the half-cells occurs through a porous plate that prevents bulk flow of the solutions while allowing ions to pass. (b) This cell has the same connections as that in part (a), but with zinc substituting for copper. However, the electron flow is opposite that in (a), as noted by the negative voltage. (Zinc is the anode.)

Electrode potentials of metals with respect to SHE (Electrochemical series (or) EMF series)

When the various metals are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, the arrangement is called the electrochemical series.

Electrode	Electrode reaction	E ⁰ (V)	Nature
Li ⁺ /Li	$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	-3.01	Anodic ↑
Mg ²⁺ /Mg	$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	-2.37	
Pb ²⁺ /Pb	$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	-1.12	
Zn ²⁺ /Zn	$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0.76	
Fe ²⁺ /Fe	$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	-0.44	
Sn ²⁺ /Sn	$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	-0.136	Pt- Reference: ↓ Cathodic
H ⁺ /H ₂	$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	0.00	
Cu ²⁺ /Cu	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+0.34	
Ag ⁺ /Ag	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+0.80	
Au ⁺ /Au	$\text{Au}^+ + e^- \rightleftharpoons \text{Au}$	+1.50	
1/2 F ₂ /F ⁻	$1/2 \text{F}_2 + e^- \rightleftharpoons \text{F}^-$	+2.87	

Basic solution

$\text{O}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2e^- \longrightarrow \text{O}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	+1.246
$\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2e^- \longrightarrow \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	+0.890
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4e^- \longrightarrow 4\text{OH}^-(\text{aq})$	+0.401
$2\text{H}_2\text{O}(\text{l}) + 2e^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.828

Acidic solution

	E ⁰ , V
$\text{F}_2(\text{g}) + 2e^- \longrightarrow 2\text{F}^-(\text{aq})$	+2.866
$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+2.075
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2e^- \longrightarrow 2\text{SO}_4^{2-}(\text{aq})$	+2.01
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$	+1.763
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.455
$\text{Cl}_2(\text{g}) + 2e^- \longrightarrow 2\text{Cl}^-(\text{aq})$	+1.358
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$	+1.229
$2\text{IO}_3^-(\text{aq}) + 12\text{H}^+(\text{aq}) + 10e^- \longrightarrow \text{I}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l})$	+1.20
$\text{Br}_2(\text{l}) + 2e^- \longrightarrow 2\text{Br}^-(\text{aq})$	+1.065
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3e^- \longrightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.956
$\text{Ag}^+(\text{aq}) + e^- \longrightarrow \text{Ag}(\text{s})$	+0.800
$\text{Fe}^{3+}(\text{aq}) + e^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.771
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.695
$\text{I}_2(\text{s}) + 2e^- \longrightarrow 2\text{I}^-(\text{aq})$	+0.535
$\text{Cu}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cu}(\text{s})$	+0.340
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow 2\text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$	+0.17
$\text{Sn}^{4+}(\text{aq}) + 2e^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	+0.154
$\text{S}(\text{s}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2\text{S}(\text{g})$	+0.14
$2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Pb}(\text{s})$	-0.125
$\text{Sn}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Sn}(\text{s})$	-0.137
$\text{Fe}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Fe}(\text{s})$	-0.440
$\text{Zn}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Zn}(\text{s})$	-0.763
$\text{Al}^{3+}(\text{aq}) + 3e^- \longrightarrow \text{Al}(\text{s})$	-1.676
$\text{Mg}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Mg}(\text{s})$	-2.356
$\text{Na}^+(\text{aq}) + e^- \longrightarrow \text{Na}(\text{s})$	-2.713
$\text{Ca}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Ca}(\text{s})$	-2.84
$\text{K}^+(\text{aq}) + e^- \longrightarrow \text{K}(\text{s})$	-2.924
$\text{Li}^+(\text{aq}) + e^- \longrightarrow \text{Li}(\text{s})$	-3.040

Significance of emf series (or) Application of electrochemical series (or) Applications of Nernst equation

Calculation of standard emf of the cell

E^0 can be calculated if the standard electrode potential values are $E_{cell} = E_{right}^0 - E_{left}^0$

Relative ease of oxidation or reduction

Higher (+ve) value of standard reduction potential, greater is the tendency for reduction. Metals on the top (-ve) are more easily oxidized.

Fluorine has higher +ve value of standard reduction potential (+2.87V) and shows higher tendency for reduction.

Lithium has highest – ve value (-3.02V) and shows higher tendency towards oxidation.

Displacement of one element by the other

Metals which lie higher in the series can displace those which lie below them in the series. Copper will displace silver from its solution. Iron will displace copper from its solution.

Determination of equilibrium constant (K) for a reaction

From the value of E^0 , the equilibrium constant for the reaction can be obtained

$$\begin{aligned} -\Delta G^0 &= RT \ln K = 2.303RT \log K \\ \log K &= \frac{-\Delta G^0}{2.303RT} = \frac{nFE^0}{2.303RT} \quad \left[\because -\Delta G^0 = nFE^0 \right] \end{aligned}$$

Hydrogen displacement behavior

Metals with – ve reduction potential (metals placed above H_2) in emf series will displace hydrogen from acid solutions. Zn will displace H_2 from dilute acids whereas, silver cannot.

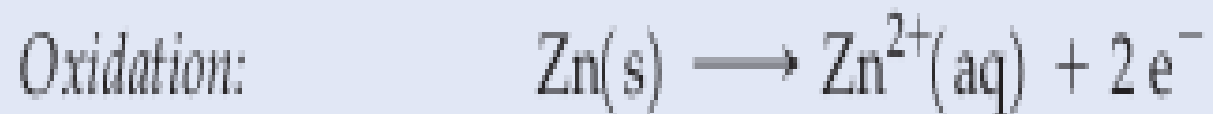
Predicting the spontaneity of redox reactions

If E^0 of a cell is +ve, the reaction is spontaneous. If E^0 of a cell is – ve, the reaction is not possible

Combining E° Values into E°_{cell} for a Reaction

A new battery system currently under study for possible use in electric vehicles is the zinc- chlorine battery. The overall reaction producing electricity in this cell is $\text{Zn(s)} + \text{Cl}_2(\text{g}) \longrightarrow \text{ZnCl}_2(\text{aq.})$. What is E°_{cell} of this voltaic cell?

The oxidation state of zinc changes from 0 to +2 and therefore is oxidized; consequently, the chlorine is reduced. The half-reactions are indicated below and are combined into the overall equation,



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ(\text{reduction half-cell}) - E^\circ(\text{oxidation half-cell}) \\ &= 1.358\text{ V} - (-0.763\text{ V}) = 2.121\text{ V} \end{aligned}$$

Determining an Unknown E° from an E° cell Measurement

Cadmium is found in small quantities wherever zinc is found. Unlike zinc, which in trace amounts is an essential element, cadmium is an environmental poison. To determine cadmium ion concentrations by electrical measurements, we need the standard electrode potential for the Cd^{2+}/Cd electrode. The voltage of the following voltaic cell is measured.



What is the standard electrode potential for the Cd^{2+}/Cd electrode?

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ(\text{right}) - E^\circ(\text{left}) \\ 0.743\text{ V} &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Cd}^{2+}/\text{Cd}} \\ &= 0.340\text{ V} - E^\circ_{\text{Cd}^{2+}/\text{Cd}} \\ E^\circ_{\text{Cd}^{2+}/\text{Cd}} &= 0.340\text{ V} - 0.743\text{ V} = -0.403\text{ V} \end{aligned}$$

ΔG & ΔG°

The basic criterion for spontaneous change is that the entropy change of the universe, which is the sum of the entropy change of the system plus that of the surroundings must be greater than zero. This statement is known as the second law of thermodynamics.

An equivalent criterion applied to the system alone is based on a thermodynamic function known as the Gibbs energy.

Gibbs free energy is denoted by the symbol 'G'. Its value is usually expressed in Joules or Kilojoules. Gibbs free energy can be defined as the maximum amount of work that can be extracted from a closed system.

The Gibbs energy change, ΔG , is the enthalpy change for the system (ΔH) minus the product of the temperature and entropy change for the system ($T\Delta S$).

$$\Delta G = \Delta H - T \Delta S$$

The standard Gibbs energy change, ΔG° , is based on the conversion of reactants in their standard states to products in their standard states. Tabulated Gibbs energy data are usually standard Gibbs energies of formation, ΔG°_f , usually at 298.15 K. If $\Delta G^\circ < 0$ (negative), the process is spontaneous. If $\Delta G^\circ > 0$ (positive), the process is nonspontaneous. If $\Delta G^\circ = 0$ (zero), the process is at equilibrium.

The relationship between Gibbs free energy (ΔG), standard Gibbs free energy (ΔG°) and the equilibrium constant (K) is derived through the equation: $\Delta G = \Delta G^\circ + RT \ln(Q)$, where Q is the reaction quotient, and at equilibrium, Q becomes K, and ΔG is zero, leading to the final expression: $\Delta G^\circ = -RT \ln(K)$.

The constant, K, is called a thermodynamic equilibrium constant. It is based on the activities of reactants and products, but these activities can be related to solution molarities and gas partial pressures by means of a few simple conventions.

Interpretation of the equation:

- If ΔG° is negative, then $K > 1$, indicating that the reaction favors the products at equilibrium.
- If ΔG° is positive, then $K < 1$, indicating that the reaction favors the reactants at equilibrium.
- If ΔG° is zero, then $K = 1$, indicating that the reactants and products are present in equal amounts at equilibrium.

E_{cell} , ΔG , and K

When a reaction occurs in a voltaic cell, the cell does work- electrical work (the work of moving electric charges). The total work done is the product of three terms: (a) E_{cell} ; (b) z , the number of electrons transferred between the electrodes; and (c) the electric charge per mole of electrons, called the Faraday constant (F). The Faraday constant is equal to 96,485 coulombs per mole of electrons (96,485 C>mol). the unit of w_{elec} is joules (J). Because the product volt x coulomb = joule, the unit of w_{elec} is joules (J).

$$w_{\text{elec}} = zFE_{\text{cell}}$$

The Expression applies only if the cell operates reversibly

The amount of available energy (work) that can be derived from a process as equal to $-\Delta G$. In the special case in which the reactants and products are in their standard states.

$$\Delta G = -zFE_{\text{cell}}$$

$$\Delta G^{\circ} = -zFE_{\text{cell}}^{\circ}$$

The symbol z in equations is properly called the electron number of an electrochemical reaction and is occasionally referred to as the charge number. The electron number has no units; that is, it is simply a number.

For any given cell reaction, we can write the reaction with a charge number of one or two. Thus, the hydrogen electrode reaction can be written as either,



Considering an overall cell reaction, we must balance the electrons. For the cell,



The half-cell reactions can be written as



The electron number is two and the overall electrochemical reaction is,

The standard reduction potential for this reaction is,



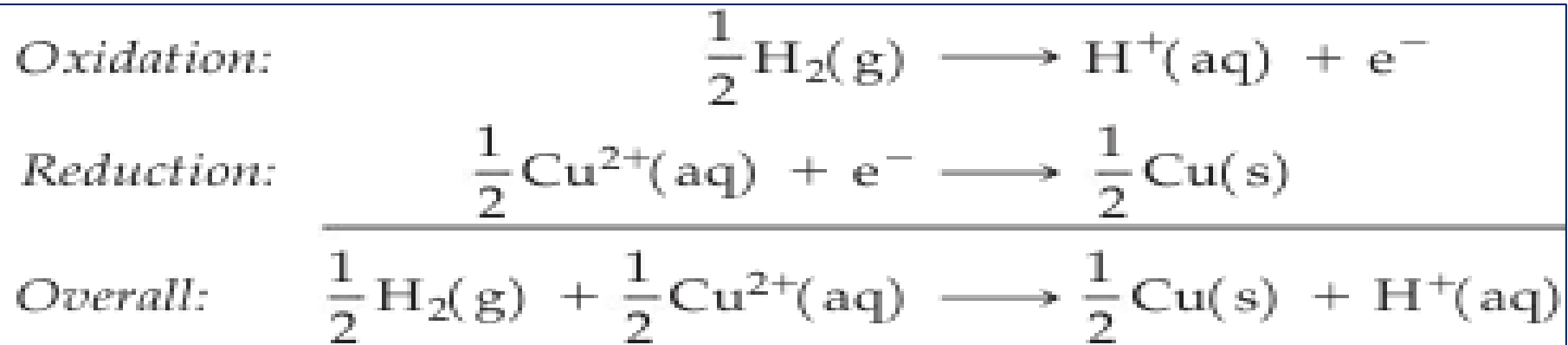
$$\begin{aligned} E_{\text{cell}}^{\circ} &= E^{\circ}(\text{right}) - E^{\circ}(\text{left}) \\ &= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - 0 \text{ V} = 0.340 \text{ V} \end{aligned}$$

E_{cell} , ΔG , and K

The standard Gibbs energy is given by,

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= -zFE_{\text{cell}}^{\circ} = 2 \times \frac{96485 \text{ C}}{\text{mol}} \times 0.340 \text{ V} \\ &= -6.5610 \times 10^4 \text{ J mol}^{-1} = -65.6 \text{ kJ mol}^{-1}\end{aligned}$$

That is, 65.6 kJ of energy is generated when 1 mole of Cu^{2+} ion is reduced, or 2 moles of H^{+} are produced. The process is accompanied by the passage of two moles of electrons around the outer circuit. We could also have written the reactions as



This reaction is represented by the same cell diagram given above, but the electron number is one; consequently, the Gibbs energy is one-half of that previously calculated, but the value of E° cell is the same. This result supports the fact that the standard reduction potential is an intensive property, but the Gibbs energy is an extensive property. Finally, the reaction tells us that when 0.5 mole of Cu^{2+} is reduced, 32.8 kJ of energy is released, and one mole of electrons passes from the anode to the cathode.

E°_{cell} , ΔG , and K

Determining a Gibbs Energy Change from a Cell Potential,

Use E° data to determine ΔG° for the reaction,

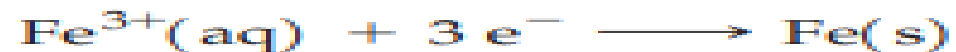


This reaction is cell reaction occurring in the voltaic cell. In this type of problem, the overall equation generally needs to be separated into two half-equations. Then the value of E°_{cell} and the number of moles of electrons (n) involved in the cell reaction can be determined. ($E^\circ_{\text{cell}} = 2.121 \text{ V}$, and $z = 2 \text{ moles } e^-$)

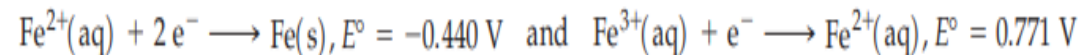
$$\begin{aligned} \Delta G^\circ &= -zFE^\circ_{\text{cell}} = -\left(2 \text{ mol } e^- \times \frac{96,485 \text{ C}}{1 \text{ mol } e^-} \times 2.121 \text{ V}\right) \\ &= -4.093 \times 10^5 \text{ J} = -409.3 \text{ kJ mol}^{-1} \end{aligned}$$

Combining Reduction Half-Equations (Determining E°_{cell} value from ΔG ,

Determination of E° for the following half-reaction,



Data for Fe (s) and its ions are available.



The half-equation is simply the sum of these two half equations, but the E° value is not the sum of -0.440 V , 0.771 V . We can add together, though, are the values for ΔG° the two known half-reactions.

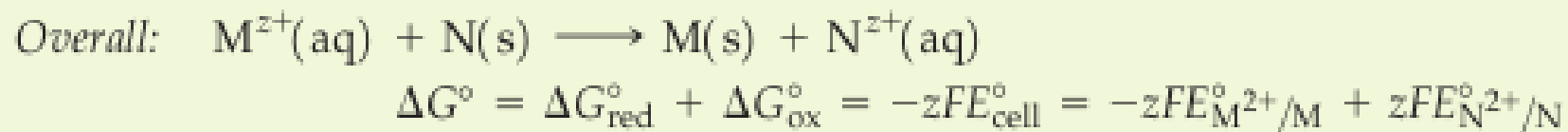
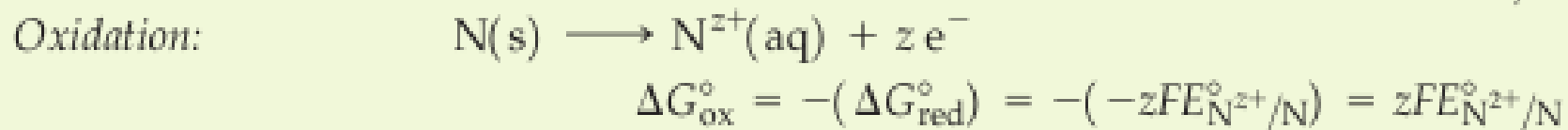
$$\begin{array}{ll} \text{Fe}^{2+}(\text{aq}) + 2 e^- \longrightarrow \text{Fe(s)}; & \Delta G^\circ = -2 \times F \times (-0.440 \text{ V}) \\ \text{Fe}^{3+}(\text{aq}) + e^- \longrightarrow \text{Fe}^{2+}(\text{aq}); & \Delta G^\circ = -1 \times F \times (0.771 \text{ V}) \\ \hline \text{Fe}^{3+}(\text{aq}) + 3 e^- \longrightarrow \text{Fe(s)}; & \Delta G^\circ = (0.880F) \text{ V} - (0.771F) \text{ V} = (0.109F) \text{ V} \end{array}$$

Now, to get $E^\circ_{\text{Fe}^{3+}/\text{Fe}}$, we can again use equation and solve for $E^\circ_{\text{Fe}^{3+}/\text{Fe}}$.

$$\begin{aligned} \Delta G^\circ &= -zFE^\circ_{\text{Fe}^{3+}/\text{Fe}} = -3FE^\circ_{\text{Fe}^{3+}/\text{Fe}} = (0.109F) \text{ V} \\ E^\circ_{\text{Fe}^{3+}/\text{Fe}} &= (-0.109F/3F) \text{ V} = -0.0363 \text{ V} \end{aligned}$$

Combining two E° values to obtain an unknown E°

An unknown E° from two known E° values of by working through the expression $\Delta G = -zFE^\circ$. For a hypothetical displacement reaction, we can similarly calculate an unknown E°_{cell} expression $\Delta G^\circ = -zFE^\circ_{\text{cell}}$. For the oxidation half-reaction, $\Delta G^\circ_{\text{ox}}$ simply the negative of the value for the reverse half-reaction $\Delta G^\circ_{\text{red}}$.



Dividing through the above equation by the term $-zF$, we obtain E°_{cell} as the familiar difference in two electrode potentials.

$$E^\circ_{\text{cell}} = E^\circ_{M^{2+}/M} - E^\circ_{N^{2+}/N}$$

$$E^\circ_{\text{cell}} = E^\circ(\text{reduction}) - E^\circ(\text{oxidation})$$

- If E_{cell} is positive, a reaction occurs spontaneously in the forward direction for the stated conditions.
- If E_{cell} is negative, the reaction occurs spontaneously in the reverse direction for the stated conditions.
- If $E_{\text{cell}} = 0$, reaction is at equilibrium for the stated conditions.
- If a cell reaction is reversed, E_{cell} changes sign.

Spontaneous Change in Oxidation Reduction Reactions

Will aluminum metal displace Cu^{2+} ion from aqueous solution? That is, will a spontaneous reaction occur in the forward direction for the following reaction?



The cell diagram corresponding to the reaction is $\text{Al}(s) | \text{Al}^{3+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(s)$, and E°_{cell} is

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ(\text{cathode}) - E^\circ(\text{anode}) \\ &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Al}^{3+}/\text{Al}} \\ &= 0.340 \text{ V} - (-1.676 \text{ V}) = 2.016 \text{ V} \end{aligned}$$

Because E°_{cell} is positive, the direction of spontaneous change is that of the forward reaction. **Al(s) will displace Cu^{2+} from aqueous solution under standard-state conditions.**

Relationship Between E°_{cell} & K

At equilibrium,

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

Also, $\Delta G^\circ = -zFE^\circ_{\text{cell}}$

Therefore, we can write

$$\Delta G^\circ = -RT \ln K = -zFE^\circ_{\text{cell}}$$

$$E^\circ_{\text{cell}} = \frac{RT}{zF} \ln K$$

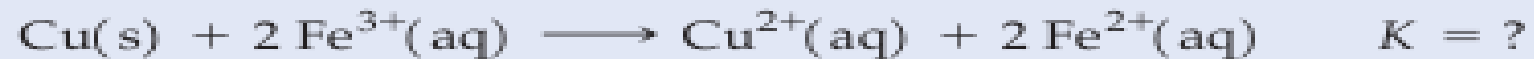
In the equation, R has a value of $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ and z represents the number of electrons involved in the reaction. If we then specify a temperature of $25^\circ\text{C} = 298.15^\circ\text{K}$ (the temperature at which electrode potentials are generally determined), the combined terms RT/F in equation can be replaced by a single constant. This constant has the value $0.025693 \text{ J/C} = 0.025693 \text{ V}$

$$E^\circ_{\text{cell}} = \frac{RT}{zF} \ln K = \frac{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{z \times 96485 \text{ C mol}^{-1}} \ln K$$

$$E^\circ_{\text{cell}} = \frac{0.025693 \text{ V}}{z} \ln K$$

Relationship Between E°_{cell} & K

What is the value of the equilibrium constant K for the reaction between copper metal and iron(III) ions in aqueous solution at 25 °C?



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ(\text{reduction half-cell}) - E^\circ(\text{oxidation half-cell}) \\ &= E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} \\ &= 0.771 \text{ V} - 0.340 \text{ V} = 0.431 \text{ V} \end{aligned}$$

$$E^\circ_{\text{cell}} = 0.431 \text{ V} = \frac{0.02569 \text{ V}}{2} \ln K$$

$$\ln K = \frac{2 \times 0.431 \cancel{\text{ V}}}{0.02569 \cancel{\text{ V}}} = 33.6$$

$$K = e^{33.6} = 4 \times 10^{14}$$

The charge number (z) for the cell reaction is 2.

E°_{cell} as a Function of Concentrations

Combining of standard electrode potentials, a standard E°_{cell} . For the following cell reaction at nonstandard conditions, however, the measured E_{cell} is not 1.103 V (E°_{cell})



Experimental measurements of cell potentials are often made for nonstandard conditions; these measurements have great significance, especially for performing chemical analyses. From Le Châtelier's principle, increasing the concentration of a reactant (Cu^{2+}) while decreasing the concentration of a product (Zn^{2+}) should favor the forward reaction. Zn(s) should displace $\text{Cu}^{2+}(\text{aq.})$ even more readily than for standard-state conditions and $E_{\text{cell}} > 1.103 \text{ V}$. E_{cell} is found to vary linearly with $\log ([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$

The cell potential (E_{cell}), and the concentrations of reactants and products can be related as $\Delta G = \Delta G^\circ + RT \ln Q$

For ΔG and ΔG° , we can substitute $-zFE_{\text{cell}}$ and $-zFE^\circ_{\text{cell}}$, respectively, $-zFE_{\text{cell}} = -zFE^\circ_{\text{cell}} + RT \ln Q$

Dividing through by $-zF$ gives,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{zF} \ln Q$$

This equation was first proposed by Walther Nernst in 1889. It is commonly used by analytical chemists in the form in which Nernst expressed it. The Nernst equation can be obtained by switching from natural to common logarithms, ($\ln Q = 2.3026 \log Q$).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.3026 RT}{zF} \log Q$$

By specifying a temperature of 298.15 K and replacing RT/F by 0.025693 V. The term $2.3026 RT/F = 2.3026 \times 0.025693 \text{ V} = 0.059161 \text{ V}$, usually rounded off to 0.0592 V. The final form of the Nernst equation is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592 \text{ V}}{z} \log Q$$

Applying the Nernst Equation for Determining E_{cell}

What is the value of E_{cell} for the voltaic cell pictured in Figure and diagrammed as follows?

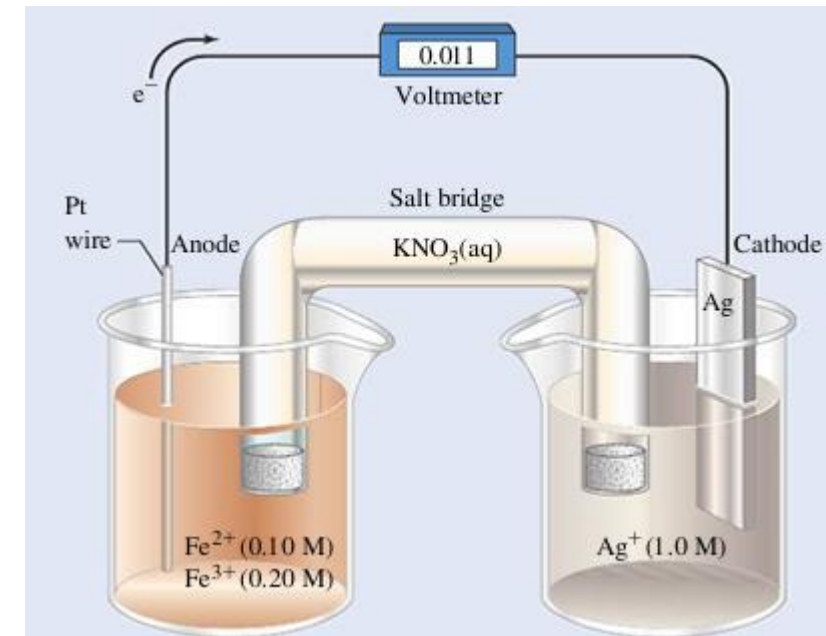


$$\begin{aligned} E_{\text{cell}}^{\circ} &= E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) \\ &= E_{\text{Ag}^{+}/\text{Ag}}^{\circ} - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} \\ &= 0.800\text{ V} - 0.771\text{ V} = 0.029\text{ V} \end{aligned}$$



$$E_{\text{cell}} = 0.029\text{ V} - \frac{0.0592\text{ V}}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]}$$

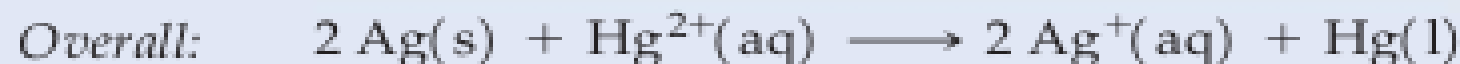
$$\begin{aligned} E_{\text{cell}} &= 0.029\text{ V} - 0.0592\text{ V} \times \log \frac{0.20}{0.10 \times 1.0} \\ &= 0.029\text{ V} - 0.0592\text{ V} \times \log 2 = 0.029\text{ V} - 0.018\text{ V} \\ &= 0.011\text{ V} \end{aligned}$$



Applying the Nernst Equation for Determining E_{cell}

2. Will the cell reaction proceed spontaneously as written for the following cell? $\text{Ag(s)}|\text{Ag}^+(0.075\text{ M})||\text{Hg}^{2+}(0.85\text{ M})|\text{Hg(l)}$

To determine E_{cell}° from E° data we write



$$\begin{aligned} E_{\text{cell}}^\circ &= E^\circ(\text{reduction half-cell}) - E^\circ(\text{oxidation half-cell}) \\ &= 0.854 \text{ V} - (0.800 \text{ V}) = 0.054 \text{ V} \end{aligned}$$

The overall reaction that we have written has an electron number, $z = 2$, so that the Nernst equation is

$$E_{\text{cell}} = 0.054 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Ag}^+]^2}{[\text{Hg}^{2+}]}$$

By using the concentrations $[\text{Ag}^+] = 0.075 \text{ M}$ and $[\text{Hg}^{2+}] = 0.85 \text{ M}$ provided, we obtain

$$\begin{aligned} E_{\text{cell}} &= 0.054 \text{ V} - 0.0296 \text{ V} \log \frac{[0.075]^2}{[0.85]} \\ &= 0.054 \text{ V} - 0.0296 \text{ V} \log(0.0066) = 0.054 - 0.0296 \times (-2.179) \text{ V} \\ &= 0.054 + 0.065 \text{ V} = 0.119 \text{ V} \end{aligned}$$

Because $E_{\text{cell}} > 0$, we conclude that the reaction as written is **spontaneous**.

Alternative Standard Electrodes

The standard hydrogen electrode is not the most convenient to use because **it requires highly flammable hydrogen gas to be bubbled over the platinum electrode**. Other electrodes can be used as secondary standard electrodes, such as the silver- silver chloride electrode, in which a silver wire is covered with a layer of insoluble solid silver chloride. The silver-chloride-coated silver wire is immersed in a 1 M potassium chloride solution giving the electrode (a), $\text{Ag(s)}|\text{AgCl(s)}|\text{Cl}^-(1.0\text{ M})$ with a half-cell reaction of

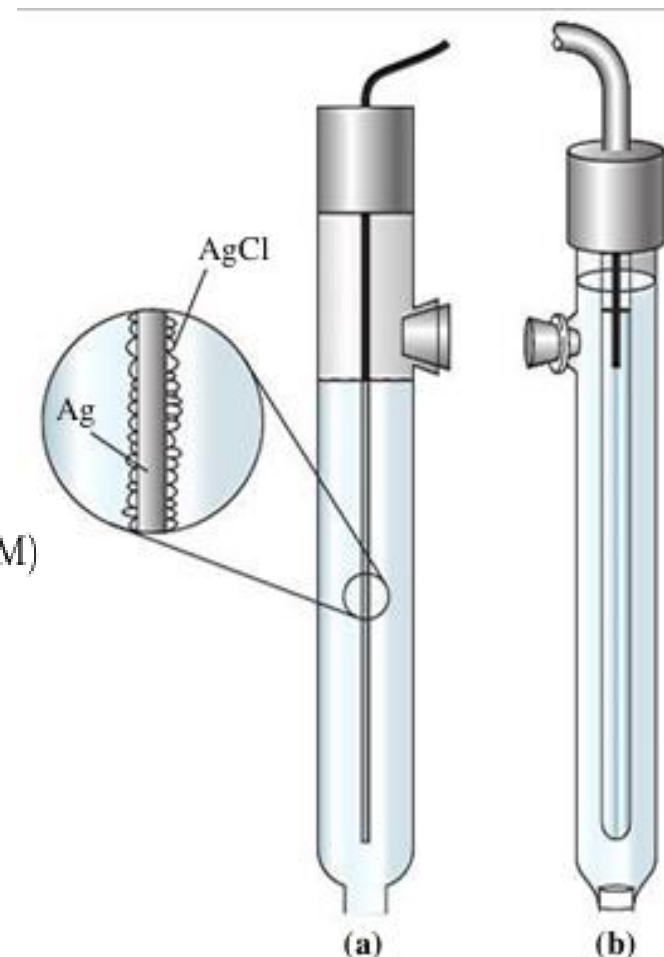


This electrode has been measured against the standard hydrogen electrode, and the electrode potential has been found to be 0.22233 V at 25 °C. Since all components of this electrode are in their standard states, the standard electrode potential of the silver-silver chloride electrode is 0.22233 V at 25 °C.

An alternative electrode is the calomel electrode, illustrated in Figure (b). In this electrode, mercurous chloride (calomel, 25°C. Hg_2Cl_2) is mixed with mercury to form a paste, which is in contact with liquid mercury, Hg(l) , and the whole setup is immersed in either a 1.0 M solution of potassium chloride or a saturated solution of potassium chloride. The electrode is, $\text{Hg(l)}|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Cl}^-(1.0\text{ M})$ **and the half-cell reaction is,**



The standard electrode potential at 25 °C is 0.2680 V . If a saturated solution of KCl is used instead of 1 M, the reduction potential is 0.2412 V. This electrode is known as the saturated calomel electrode (SCE) and is often used as a reference.



Batteries: Producing Electricity Through Chemical Reactions

A battery is a device that stores chemical energy for later release as electricity. Some batteries consist of a single voltaic cell with two electrodes and the appropriate electrolyte(s); an example is a flashlight cell. **Other batteries consist of two or more voltaic cells joined in series fashion plus to minus to increase the total voltage; an example is an automobile battery.**

Three types of voltaic cells

Primary cells- The cell reaction in a primary cell is not reversible. When the reactants have been mostly converted to products, no more electricity is produced and a battery employing a primary cell(s) is dead.

Secondary cells- The cell reaction in a secondary cell can be reversed by passing electricity through the cell (charging). A battery employing secondary cells can be used through several hundred or more cycles of discharging followed by charging.

Flow batteries and fuel cells-

Materials (reactants, products, and electrolytes) pass through the battery, which is simply a converter of chemical energy to electric energy. These types of batteries can be run indefinitely as long as they are supplied by electrolytes.

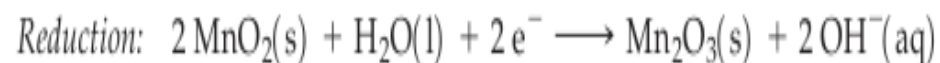
The Leclanché (Dry) Cell

The most common form of voltaic cell (Galvanic cell) is the Leclanché cell, invented by the French chemist Georges Leclanché (1839 1882) in the 1860s. Popularly called a **dry cell**, because no free liquid is present, or **flashlight battery**, the Leclanché cell is diagrammed in Figure. In this cell, oxidation occurs at a zinc anode and reduction at an inert carbon (graphite) cathode. The electrolyte is a moist paste of MnO_2 , ZnCl_2 , NH_4Cl , and carbon black (soot). The maximum cell voltage is 1.55 V. The anode (oxidation) half-reaction is simple.

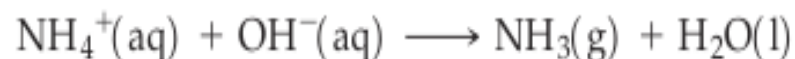
The reduction is more complex. Essentially, it involves the reduction of MnO_2



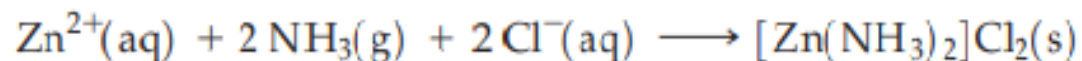
to compounds having Mn in a +3-oxidation state, for example,



An acid base reaction occurs between NH_4^+ (from NH_4Cl) and OH^- .

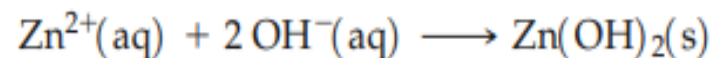
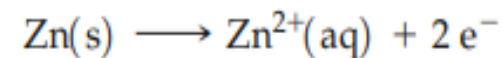


A buildup of $\text{NH}_3(\text{g})$ around the cathode would disrupt the current because the $\text{NH}_3(\text{g})$ adheres to the cathode. That buildup is prevented by a reaction between Zn^{2+} and to form the complex ion $[\text{Zn}(\text{NH}_3)_2]^{2+}$ which crystallizes as the chloride salt.



The Leclanché cell is a primary cell; it cannot be recharged. This cell is cheap to make, but it has some drawbacks. When current is drawn rapidly from the cell, products, such as build up on the electrodes, causing the voltage to drop. Also, because the electrolyte medium is acidic, zinc metal slowly dissolves.

A superior form of the Leclanché cell is the alkaline cell, which uses NaOH or KOH in place of NH_4Cl as the electrolyte. The oxidation half-reaction is the same as that shown above, but the reduction half-reaction involves the formation of $\text{Zn(OH)}_2(\text{s})$ which can be thought of as occurring in two steps.



The advantages of the alkaline cell are that zinc does not dissolve as readily in a basic (alkaline) medium as in an acidic medium, and the cell does a better job of maintaining its voltage as current is drawn from it

Electrochemical cells (Daniel cell)

Cell device (construction)

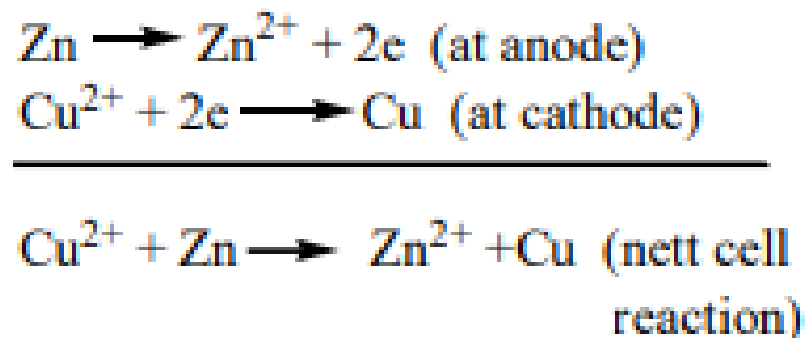
Consists of Zn electrode dipped in 1M ZnSO_4 solution and a Cu electrode dipped in 1M CuSO_4 solution. Each electrode is a half cell. The solutions are inter- connected by salt bridge and the two electrodes are connected by wire.

At anode: oxidation takes place with the liberation of e^- .

At cathode: Reduction

takes place by the acceptance of e^- .

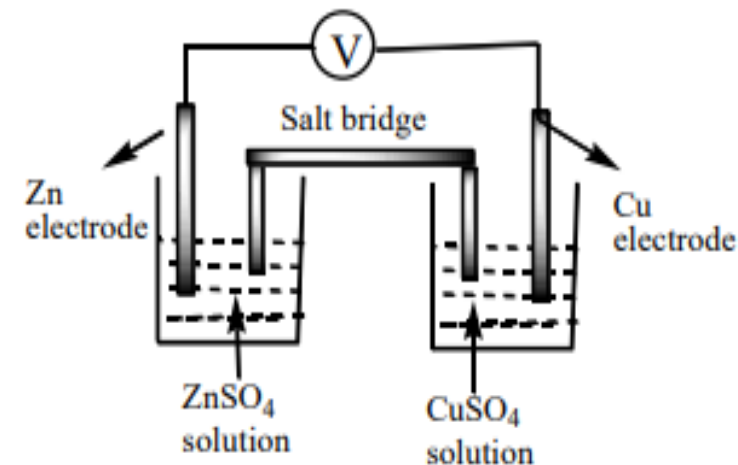
The electrons liberated in oxidation reaction flow through external wire and are consumed by the copper ions at the cathode.



Salt bridge: It consists of a U-tube containing a saturated solution of KCl or $(\text{NH}_4)_2\text{NO}_3$ in agar – agar gel. It connects the two half cells.

Functions-

- Eliminates liquid junction potential
- Provides a path for the flow of electrons between two half cells



Representation of a galvanic cell (Cell diagram)

Galvanic cell consists of two electrodes, anode and cathode. Anode is written on the LHS and cathode on RHS.

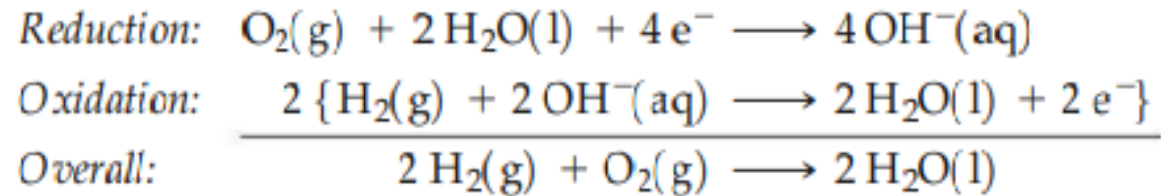
The anode is written with the metal first and then the electrolyte which are separated by a vertical line
Example: Zn/Zn^{2+} (or) Zn/ZnSO_4 iv. The cathode is written with the electrolyte first and then the metal
Example : Cu^{2+}/Cu (or) CuSO_4/Cu

The two half cells are separated by a salt bridge, which is indicated by two vertical lines. Using the above representation, the galvanic cell is represented as $\text{Zn}/\text{ZnSO}_4 (1\text{M}) // \text{CuSO}_4 (1\text{M}) / \text{Cu}$

Fuel Cells-Converting the Chemical Energy of Fuels Directly to Electricity

The first fuel cells were based on the reaction of hydrogen and oxygen. Figure represents such a fuel cell. The overall change is that $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ in an alkaline medium produce $\text{H}_2\text{O}(\text{l})$.

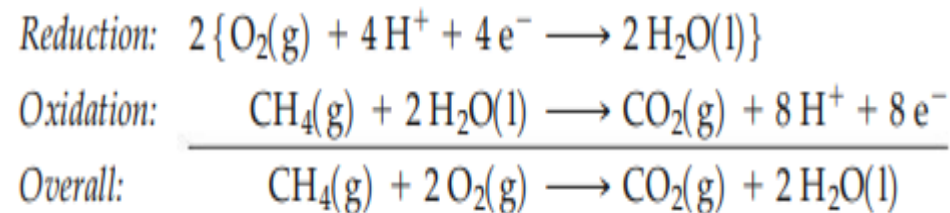
The theoretical maximum energy available as electric energy in any electrochemical cell is the Gibbs energy change for the cell reaction, ΔG° .



$$E_{\text{cell}}^\circ = E_{\text{O}_2/\text{OH}^-}^\circ - E_{\text{H}_2\text{O}/\text{H}_2}^\circ = 0.401 \text{ V} - (-0.828 \text{ V}) = 1.229 \text{ V}$$

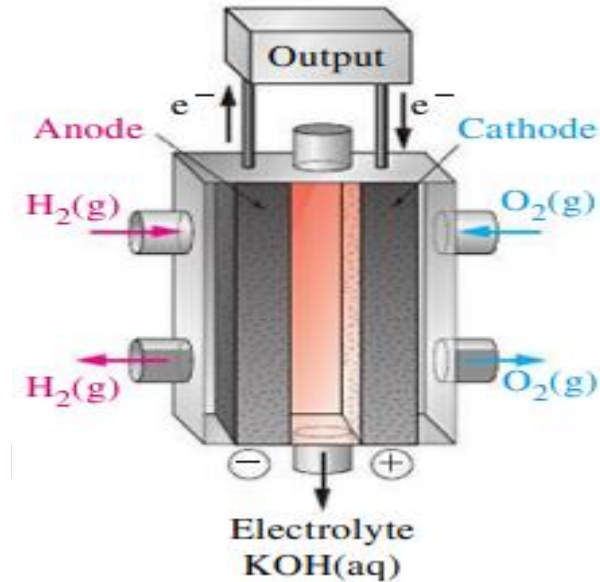
The maximum energy release when a fuel is burned is the enthalpy change, ΔH° . One of the measures used to evaluate a fuel cell is the efficiency value, $\varepsilon = \Delta G^\circ / \Delta H^\circ$. fuel cell, $\varepsilon = -474.4 \text{ kJ} / -571.6 \text{ kJ} = 0.83$. Now, Fuel cells based on the direct oxidation of common fuels will become a reality. For example, the half-reaction and cell

reaction for a fuel cell using methane (natural gas) are,



$$\Delta H^\circ = -890 \text{ kJ} \quad \Delta G^\circ = -818 \text{ kJ} \quad \varepsilon = 0.92$$

A fuel cell should actually be called an energy converter rather than a battery. As long as fuel and are available, the cell will produce electricity. It does not have the limited capacity of a primary battery or the fixed storage capacity of a secondary battery. Fuel cells based on reaction between hydrogen and oxygen have had their most notable successes as energy sources in space vehicles. (Water produced in the cell reaction is also a valuable product of the fuel cell.)



A hydrogen oxygen fuel cell
Porous electrodes that allow for easy access of the gaseous reactants to the electrolyte. The electrodes chosen should also catalyze the electrode reaction

Methane fuel cells are still in the research stage with several as

- A liquid hydrocarbon is vaporized
- The vaporized fuel is partially oxidized to $\text{CO}(\text{g})$;
- In the presence of catalyst, steam converts $\text{CO}(\text{g})$ to $\text{CO}_2(\text{g})$ and $\text{H}_2(\text{g})$.
- $\text{H}_2(\text{g})$ and air are fed through a fuel cell to producing electric energy.

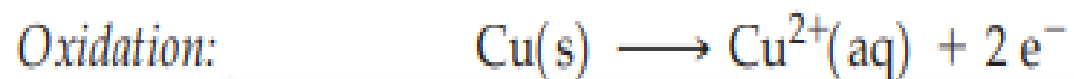
Electrolysis

Electrochemical cell, the electrolytic cell uses electricity to produce a nonspontaneous reaction. **The process in which a nonspontaneous reaction is driven by the application of electric energy is called electrolysis.**

Suppose in a voltaic cell, electrons flow from the zinc to the copper and the overall chemical change in the voltaic cell is,

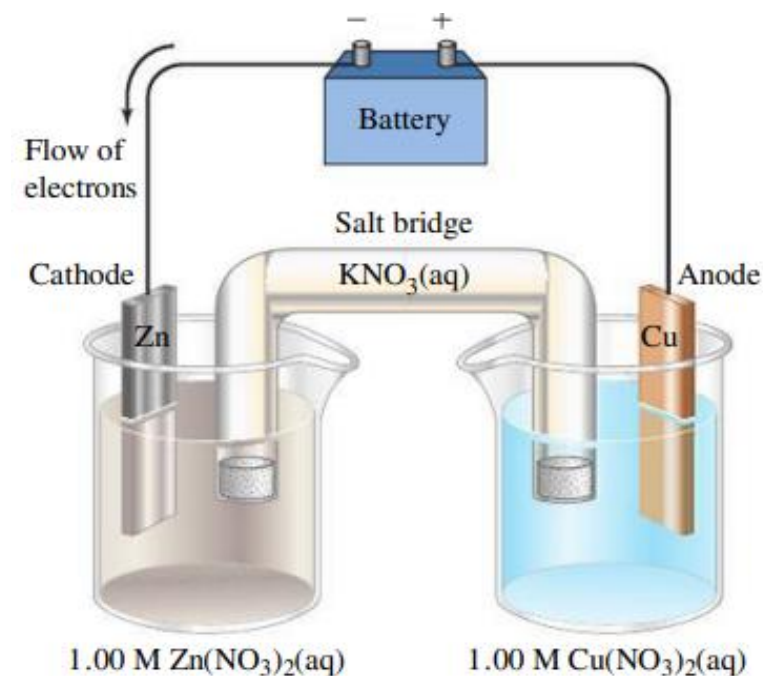


Suppose the same cell is connected to an external electric source of voltage greater than 1.103 V. That is, the connection is made so that electrons are forced into the zinc electrode (now the cathode) and removed from the copper electrode (now the anode). The overall reaction in this case is the reverse of the voltaic cell



$$E_{\text{cell}}^{\circ} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} - E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = -0.763 \text{ V} - 0.340 \text{ V} = -1.103 \text{ V}$$

reaction, and is negative. Reversing the direction of the electron flow changes the voltaic cell into an electrolytic cell.



Electrolytic Cell

The anode is (+) ve in an electrolytic cell but (-) ve in a voltaic cell

Anode and cathode is not based on the electrode charges; it is based on the half-reactions at the electrode surfaces.

Oxidation always occurs at the anode of an electrochemical cell. Because of the buildup of electrons freed in the oxidation half-reaction, the anode of a voltaic cell is (-) ve. Because electrons are withdrawn from it, the anode in an electrolytic cell is (+) ve. For both cell types, the anode is the electrode from which electrons exit the cell.

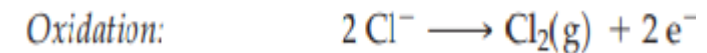
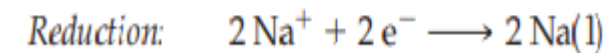
Reduction always occurs at the cathode of an electrochemical cell. Because of the removal of electrons by the reduction half-reaction, the cathode of a voltaic cell is (+) ve. Because of the electrons forced onto it, the cathode of an electrolytic cell is (-) ve. For both cell types, the cathode is the electrode at which electrons enter the cell. Table summarizes the relationship between a voltaic cell and an electrolytic cell.

Voltaic Cell			Electrolytic Cell		
<i>Oxidation:</i>	$A \longrightarrow A^+ + e^-$	Anode (negative)	<i>Oxidation:</i>	$B \longrightarrow B^+ + e^-$	Anode (positive)
<i>Reduction:</i>	$B^+ + e^- \longrightarrow B$	Cathode (positive)	<i>Reduction:</i>	$A^+ + e^- \longrightarrow A$	Cathode (negative)
<i>Overall:</i>	$A + B^+ \longrightarrow A^+ + B$ $\Delta G < 0$ Spontaneous redox reaction releases energy The system (the cell) does work on the surroundings		<i>Overall:</i>	$A^+ + B \longrightarrow A + B^+$ $\Delta G > 0$ Nonspontaneous redox reaction absorbs energy to drive it The surroundings (the source of energy) do work on the system	

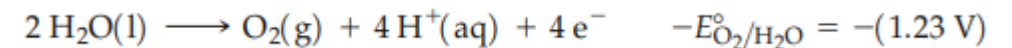
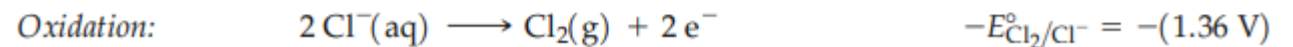
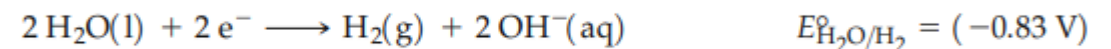
Electrolysis

For electrolysis, Four complicating factors must be considered:

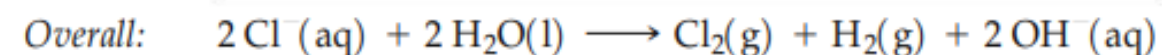
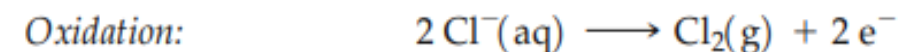
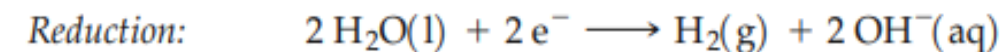
- A voltage significantly in excess of the calculated value, an overpotential, may be necessary to cause a particular electrode reaction to occur. Overpotentials are needed to overcome interactions at the electrode surface and are particularly common when gases are involved. For example, the overpotential for the discharge of at a mercury cathode is approximately 1.5 V; the overpotential on a platinum cathode is practically zero.
- Competing electrode reactions may occur. In the electrolysis of molten sodium chloride with inert electrodes, only one oxidation and one reduction are possible.



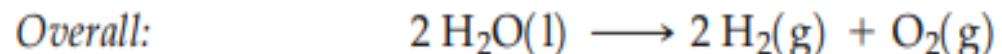
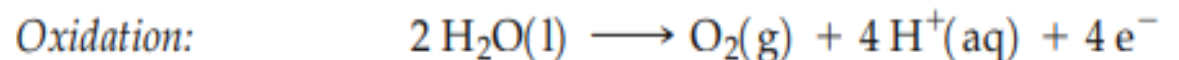
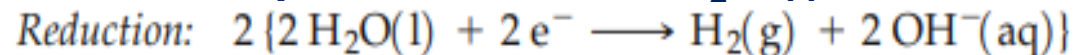
In the electrolysis of aqueous sodium chloride with inert electrodes, there are two possible reduction half-reactions and two possible oxidation half-reactions.



1st reaction can be eliminated as a possible reduction half-reaction: unless the overpotential for H₂(g) is unusually high, the reduction of Na⁺ is far more difficult to accomplish than that of H₂O (l). This leaves two possibilities for the cell reaction



$$E_{\text{cell}}^\circ = E_{\text{H}_2\text{O}/\text{H}_2}^\circ - E_{\text{Cl}_2/\text{Cl}^-}^\circ = -0.83 \text{ V} - (1.36 \text{ V}) = -2.19 \text{ V}$$



$$E_{\text{cell}}^\circ = E_{\text{H}_2\text{O}/\text{H}_2}^\circ - E_{\text{O}_2/\text{H}_2\text{O}}^\circ = -0.83 \text{ V} - (1.23 \text{ V}) = -2.06 \text{ V}$$

Electrolysis

In the electrolysis of NaCl (aq.), H_2 (g) is the product expected at the cathode. Because cell reactions have E°_{cell} values that are so similar, a mixture of Cl_2 (g) and O_2 (g) would be the expected product at the anode. Actually, because of the high overpotential of O_2 (g) compared to Cl_2 (g) cell reaction predominates; Cl_2 (g) is essentially the only product at the anode.

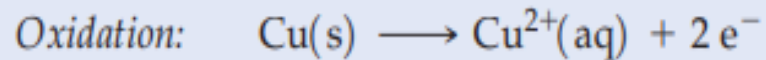
- The reactants very often are in non-standard state. In the industrial electrolysis of NaCl(aq.), $[\text{Cl}^-] \sim 5.5 \text{ M}$ not the unit activity ($[\text{Cl}^-] \sim 1 \text{ M}$) implied in half-reaction; therefore $E_{\text{Cl}_2/\text{Cl}^-} = 1.31 \text{ V}$ (not 1.36 V).
- Also, the pH in the anode half-cell is adjusted to 4, not the unit activity ($[\text{H}_2\text{O}^+] \sim 1 \text{ M}$) implied in half-reaction; hence $E_{\text{O}_2/\text{H}_2\text{O}} = 0.99 \text{ V}$ (not 1.23 V). The net effect of these nonstandard conditions is to favor the production of at the anode. In practice, however, the Cl_2 (g) obtained contains less than 1% O_2 (g) indicating the overpowering effect of the high overpotential of O_2 (g). Not surprisingly, the proportion of O_2 (g) increases significantly in the electrolysis of very dilute NaCl(aq.).
- The nature of the electrodes matters. An inert electrode, such as platinum, provides a surface on which an electrolysis half-reaction occurs, but the reactants themselves must come from the electrolyte solution. An active electrode is one that can itself participate in the oxidation or reduction half- reaction.

Predicting Electrode Half-Reactions and Overall Reactions in Electrolysis

Predict the electrode reactions and the overall reaction when the anode is made of (a) copper and (b) platinum considering the Figure.



(a) At the cathode we have the reduction of $\text{Cu}^{2+}(\text{aq})$. At the anode, $\text{Cu}(\text{s})$ can be oxidized to $\text{Cu}^{2+}(\text{aq})$, as represented by

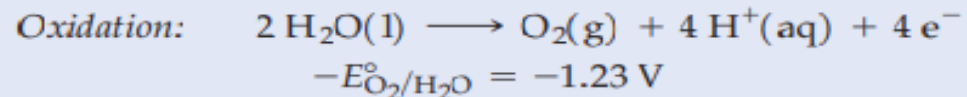


If the oxidation and reduction half-equations are added, $\text{Cu}^{2+}(\text{aq})$ cancels out. The electrolysis reaction is simply

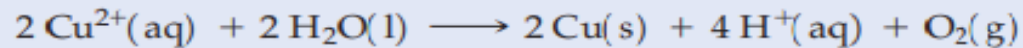


$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.340\text{ V} - 0.340\text{ V} = 0$$

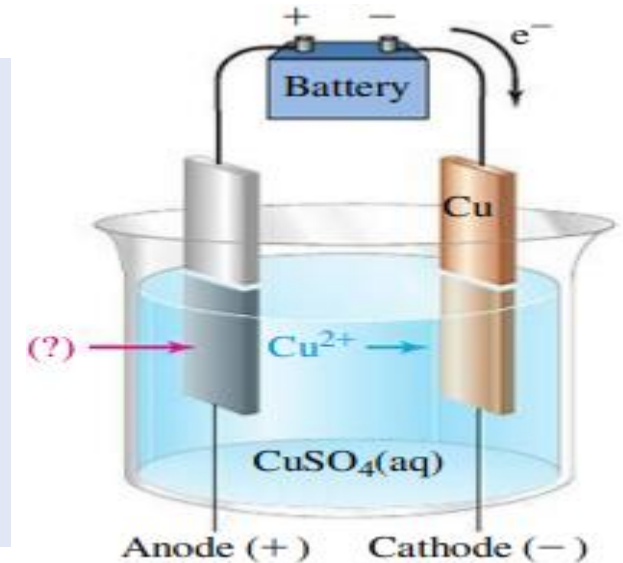
The oxidation that occurs most readily is that of H_2O shown in reaction.



The electrolysis reaction and its E_{cell}° are



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E^{\circ}(\text{reduction half-cell}) - E^{\circ}(\text{oxidation half-cell}) \\ &= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{O}_2/\text{H}_2\text{O}}^{\circ} \\ &= 0.340\text{ V} - 1.23\text{ V} = -0.89\text{ V} \end{aligned}$$



Predicting electrode reactions in electrolysis
 Electrons are forced onto the copper cathode by the external source (battery). Ions are attracted to the cathode and are reduced to $\text{Cu}(\text{s})$. The oxidation half-reaction depends on the metal used for the anode.

Quantitative Aspects of Electrolysis

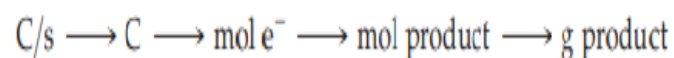
Calculation of the theoretical voltage required for electrolysis. Equally important are calculations of the quantities of reactants consumed and products formed in an electrolysis. For these calculations, we will continue to use stoichiometric factors from the chemical equation and the quantity of electric charge associated with one mole of electrons. This factor is provided by the Faraday constant. $1 \text{ mol e}^- = 96,485 \text{ C}$

Electric charge is not measured directly; instead, electric current is measured. One ampere (A) of electric current represents the passage of 1 coulomb of charge per second (C/s). The product of current and time yields the total quantity of charge transferred. $\text{charge (C)} = \text{current (C/s)} \times \text{time (s)}$

To determine the number of moles of electrons involved in an electrolysis reaction, we can write,

To determine the mass of a product in an electrolysis reaction, follow this conversion pathway.

$$\text{number of mol e}^- = \text{current} \left(\frac{\text{C}}{\text{s}} \right) \times \text{time (s)} \times \frac{1 \text{ mol e}^-}{96,485 \text{ C}}$$



The electrodeposition of copper can be used to determine the copper content of a sample. The sample is dissolved to produce $\text{Cu}^{2+}(\text{aq})$, which is electrolyzed. At the cathode, the reduction half-reaction is $\text{Cu}^{2+}(\text{aq}) + 2 \text{ e}^- \longrightarrow \text{Cu}(\text{s})$. What mass of copper can be deposited in 1.00 hour by a current of 1.62 A?

First, we determine the number of moles of electrons involved in the electrolysis in the manner outlined above:

$$1.00 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1.62 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^-}{96,485 \text{ C}} = 0.0604 \text{ mol e}^-$$

The mass of Cu(s) produced at the cathode by this number of moles of electrons is calculated as follows:

$$\text{mass of Cu} = 0.0604 \text{ mol e}^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \times \frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} = 1.92 \text{ g Cu}$$

Electroplating

In electroplating, one metal is plated onto another, often less expensive, metal by electrolysis. This procedure is done for decorative purposes or to protect the underlying metal from corrosion. Silver-plated flatware, for example, consists of a thin coating of metallic silver on an underlying base of iron.

In electroplating, the item to be plated is the cathode in an electrolytic cell. The electrolyte contains ions of the metal to be plated, which are attracted to the cathode, where they are reduced to metal atoms.

In copper plating, the electrolyte is usually copper sulfate. In silver plating, $\text{K}[\text{Ag}(\text{CN})_2]$ (aq.). The concentration of free silver ion in a solution of the complex ion $[\text{Ag}(\text{CN})_2]^-$ is very low, and electroplating under these conditions promotes a strongly adherent microcrystalline deposit of the metal.

Chromium plating is useful for its resistance to corrosion as well as its appearance. Steel can be chromium-plated from an aqueous solution of CrO_3 and H_2SO_4 . The plating obtained, however, is thin and porous and tends to develop cracks. In practice, the steel is first plated with a thin coat of copper or nickel, and then the chromium plating is applied. Chromium plating or cadmium plating is used to weatherproof machine parts.

Metal plating can even be applied to some plastics. The plastic must first be made electrically conductive for example, by coating it with graphite powder. Copper plating of plastics has been used to improve the quality of some microelectronic circuit boards.

Electroplating is even used to coat coin.

Check List

1. From the observations listed, estimate the value of E° for the half-reaction, $M^{2+}(aq) + 2e^- \longrightarrow M(s)$.
 - (a) The metal M reacts with $HNO_3(aq)$ not with $HCl(aq)$; M displaces $Ag^+(aq)$, but not $Cu^{2+}(aq)$.
 - (b) The metal reacts with $HCl(aq)$, producing $H_2(g)$ but neither displacing $Zn^{2+}(aq)$ or $Fe^{2+}(aq)$.
2. $E^\circ_{cell} = 0.201\text{ V}$ for the reaction,

$$3\text{Pt}(s) + 12\text{Cl}^-(aq) + 2\text{NO}_3^-(aq) + 8\text{H}^+(aq) \longrightarrow 3[\text{PtCl}_4]^{2-}(aq) + 2\text{NO}(g) + 4\text{H}_2\text{O}(l)$$

What is E° for the reduction of $[\text{PtCl}_4]^{2-}$ to Pt in acidic solution?

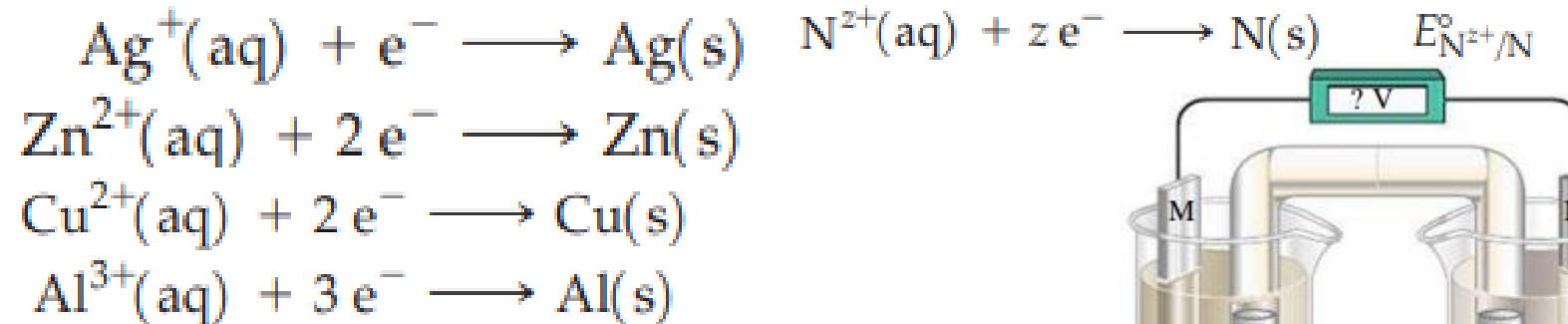
3. Given that $E^\circ_{cell} = 3.20\text{ V}$ for the reaction

$$2\text{Na}(\text{in Hg}) + \text{Cl}_2(g) \longrightarrow 2\text{Na}^+(aq) + 2\text{Cl}^-(aq)$$

What is E° for the reduction $2\text{Na}^+(aq) + 2e^- \longrightarrow 2\text{Na}(\text{Hg})$?

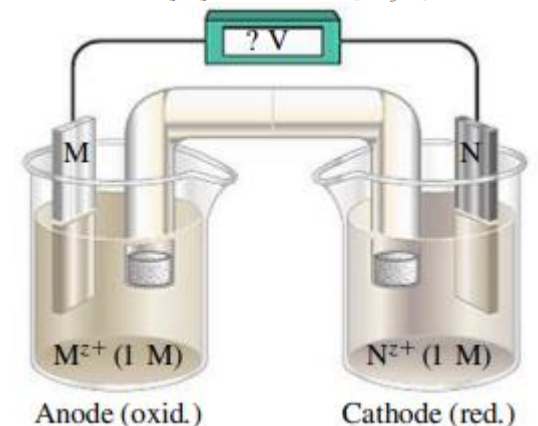
4. The following sketch is of a voltaic cell consisting of two standard electrodes for two metals, M and N

Use the standard reduction potentials of these half-reactions to answer the questions that follow:



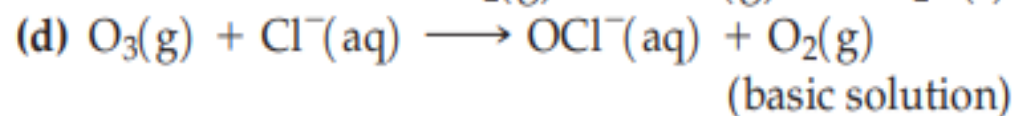
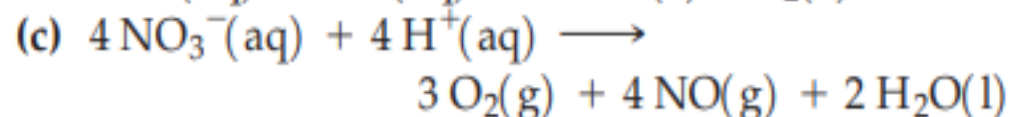
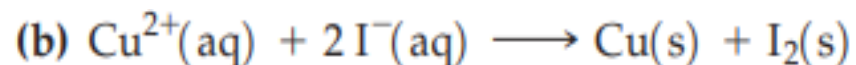
- (a) Determine which pair of these half-cell reactions leads to a cell reaction with the largest positive cell potential, and calculate its value. Which couple is at the anode and which at the cathode?

- (b) Determine which pair of these half-cell reactions leads to the cell with the smallest positive cell potential, and calculate its value. Which couple is at the anode and which is at the cathode?

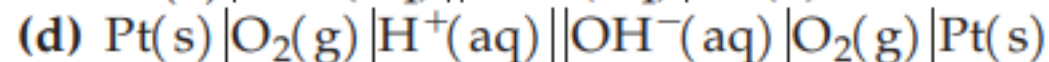
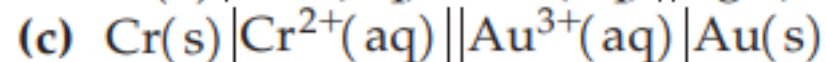
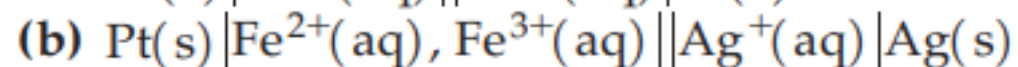
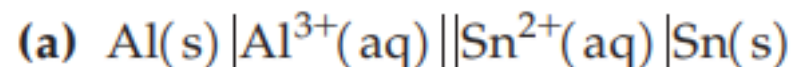


Check List

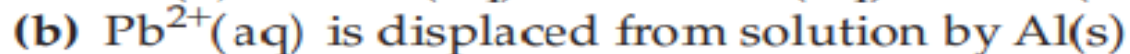
5. Assume that all reactants and products are in their standard states, and use data (from table of standard reduction potential, slide 15) to predict whether a spontaneous reaction will occur in the forward direction in each case?



6. Write cell reactions for the electrochemical cells diagrammed here, and use data (from slide 15) to calculate E°_{cell} for each reaction.

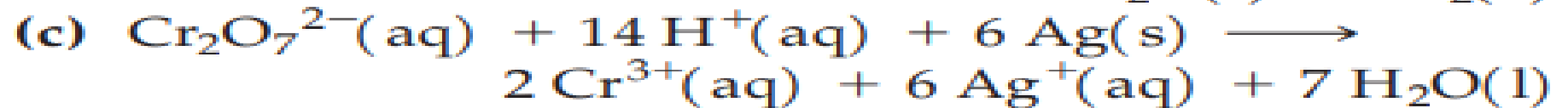
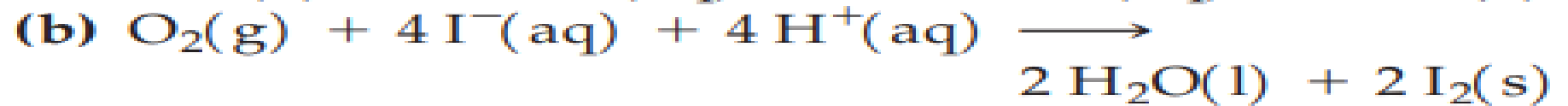


7. In each of the following examples, sketch a voltaic cell that uses the given reaction. Label the anode and cathode, indicate the direction of electron flow, write a balanced equation for the cell reaction; and calculate E°_{cell}

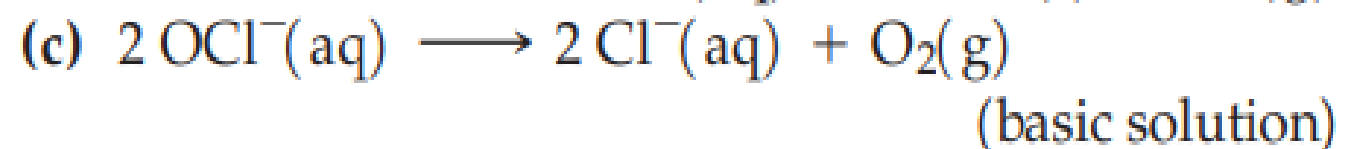
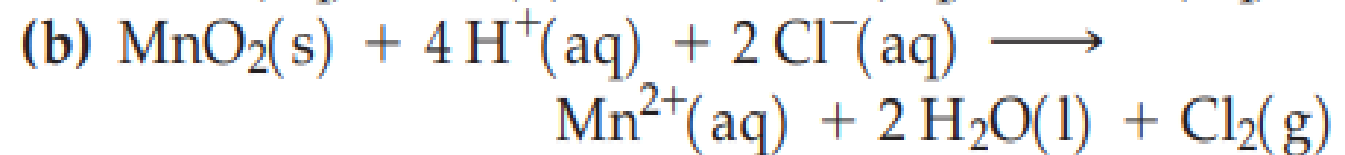


Check List

8. Determine the values of ΔG° for the following reactions carried out in voltaic cells.



9. Write the equilibrium constant expression for each of the following reactions, and determine the value of K at 25 °C (Use data from table, slide 15)



10. A voltaic cell represented by following cell diagram has $E_{\text{cell}} = 1.250 \text{ V}$. What must be $[\text{Ag}^{+}]$ in the cell?



11. Use the Nernst equation and Table (slide 15) to calculate

E_{cel} for each of the following cells.

