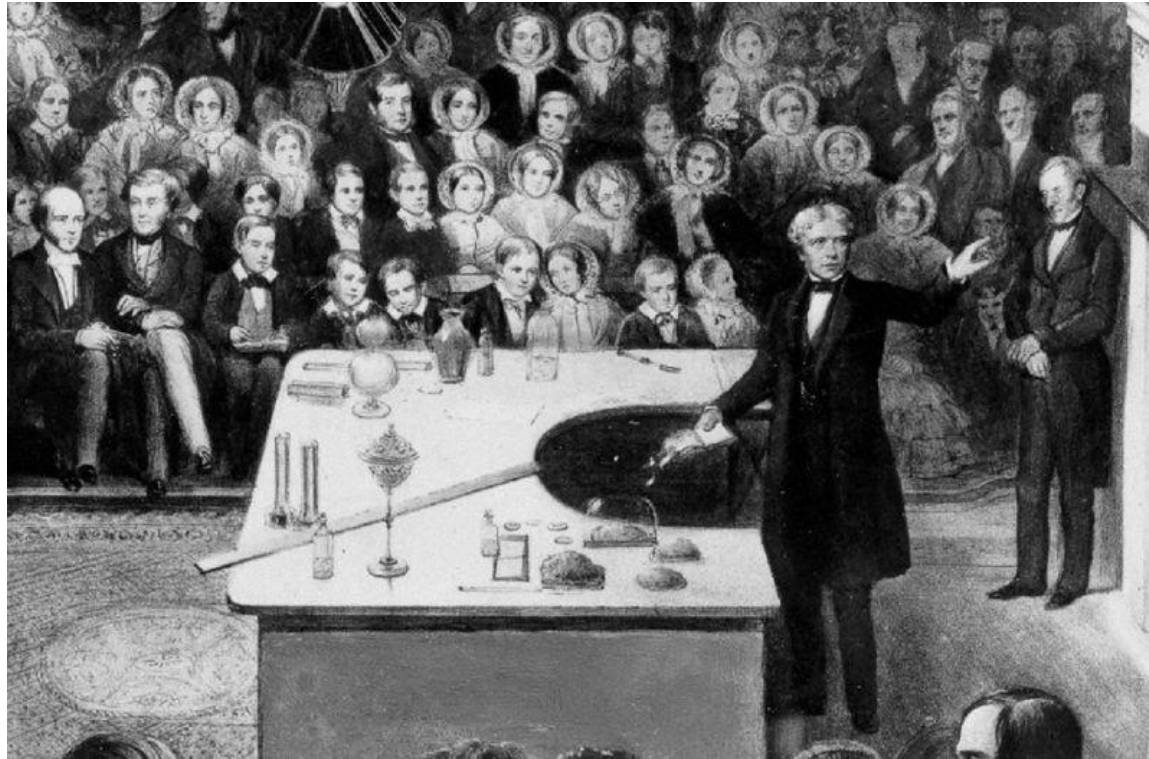


Ch 18 Electrochemistry

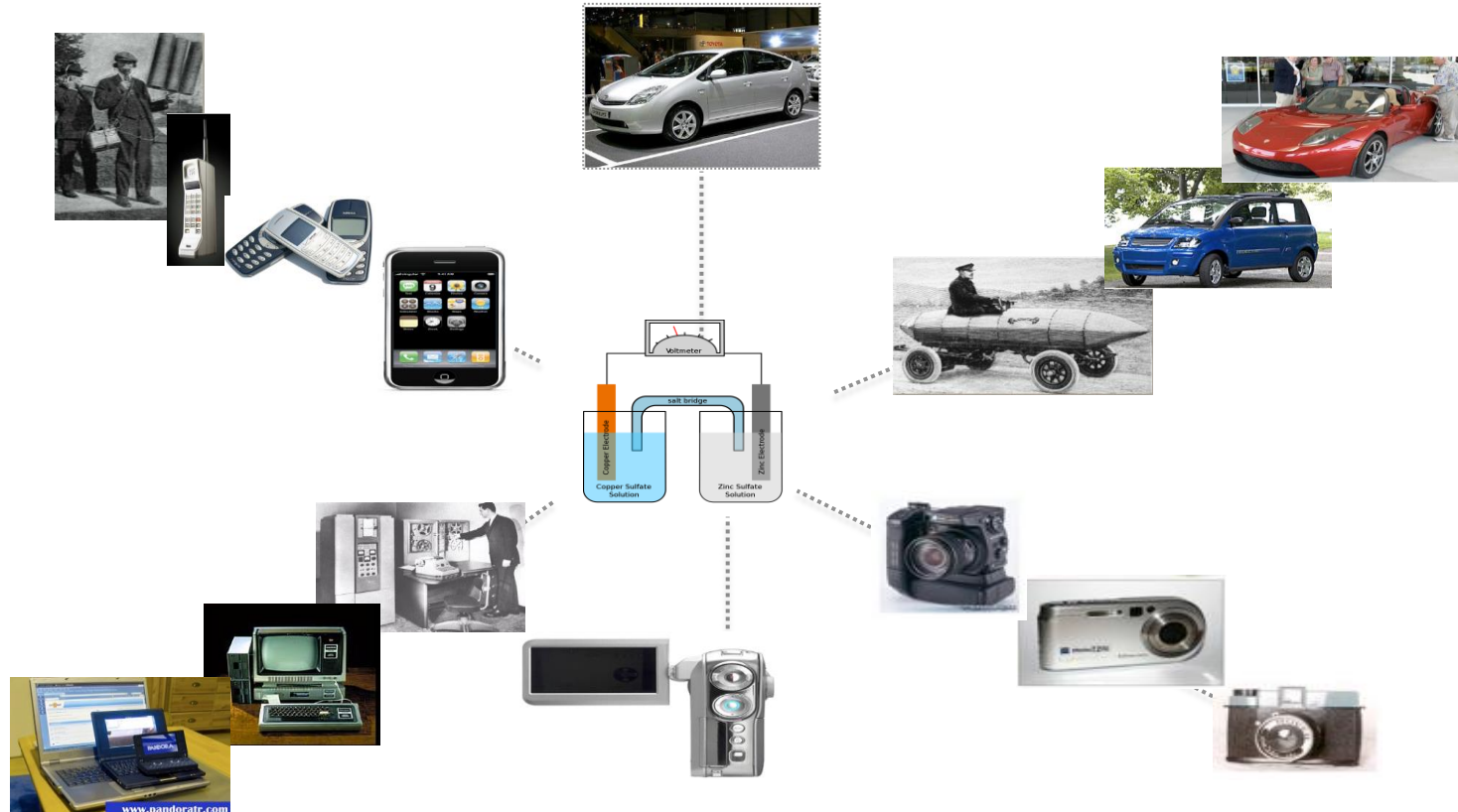
OIL-RIG Reactions



Alessandro Volta's Invention
Modified by Dr. Cheng-Yu Lai

Daily Electrochemistry Applications

Electrochemistry: The area of chemistry that examines the transformations between chemical and electrical energy.

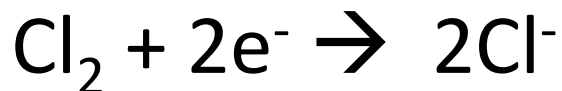


Electrochemistry Terminology #1

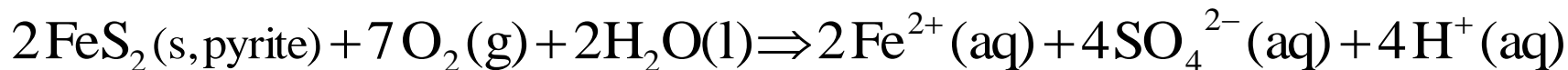
❖ **Oxidation** – A process in which an element attains a more positive oxidation state



❖ **Reduction** – A process in which an element attains a more negative oxidation state



In the following reaction, what is being oxidized, reduced?
What is the oxidizing agent, the reducing agent?



Electrochemistry Terminology #3

❑ ***Oxidizing agent***

The substance that is reduced is the oxidizing agent

❑ ***Reducing agent***

The substance that is oxidized is the reducing agent

You need to review the following terminology: oxidation, reduction, oxidizing agent, reducing agent and half-reaction (see CHEM 101).

Electrochemistry Terminology #4

➤ **Anode**

The electrode where oxidation occurs • *An ox*

➤ **Cathode**

The electrode where reduction occurs

Memory device:



Reduction
at the
Cathode

Redox Examples

1. In the reaction $2\text{Ca}(s) + \text{O}_2(g) \rightarrow 2\text{CaO}(s)$, calcium is _____
a. Reduced b. Electrolyzed c. synthesized d. oxidized e. none of these
2. In the reaction $\text{SiO}_2(s) + 2\text{C}(s) \rightarrow \text{Si}(s) + 2\text{CO}(g)$, which species is the oxidizing agent?
a. Si b. C c. O d. SiO_2 e. CO
3. In the reaction $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$, which element, if any, is oxidized?
a. zinc b. hydrogen c. sulfur d. oxygen e. none is oxidized

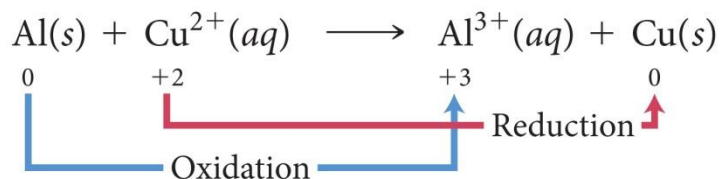
Example 18.1 Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution

Balance the redox equation:



General Procedure

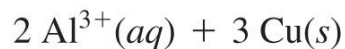
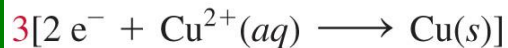
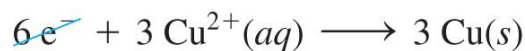
Step 1 Assign oxidation states to all atoms and identify the substances being oxidized and reduced.



Step 2 Separate the overall reaction into two half-reactions: one for oxidation and one for reduction.



Step 3



Reactants	Products
2 Al	2 Al
3 Cu	3 Cu
+6 charge	+6 charge

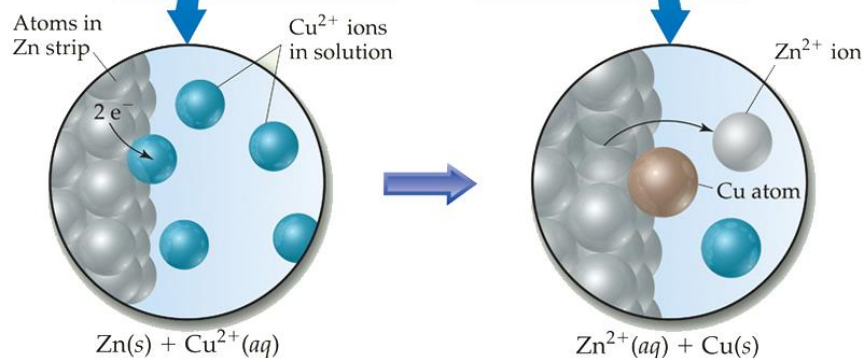
Redox Reactions and Current

- Redox reactions involve the transfer of electrons from one substance to another.
- Therefore, redox reactions have the potential to generate an electric current.
- To use that current, we need to separate the place where oxidation is occurring from the place where reduction is occurring.

Example - $\text{Zn (s)} + \text{Cu}^{2+} (\text{aq})$ Voltaic Cells



- $\text{Zn (s)} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu (s)}$
 - When run directly in a test tube
 - Cu metal plates out on surface of Zn metal
 - Zn metal enters solution as Zn^{2+} ions
 - Blue color of Cu^{2+} solution fades



In spontaneous oxidation-reduction (redox) reactions, **electrons are transferred and energy is released**. In order to harvest e^-/E ,

Voltaic Cells (aka Galvanic Cell)

Redox reactions have the potential to generate an electric current. To use that current, we need to separate the place where oxidation is occurring from the place where reduction is occurring.

A typical **voltaic cell** looks like this.

The oxidation occurs at the **anode**.

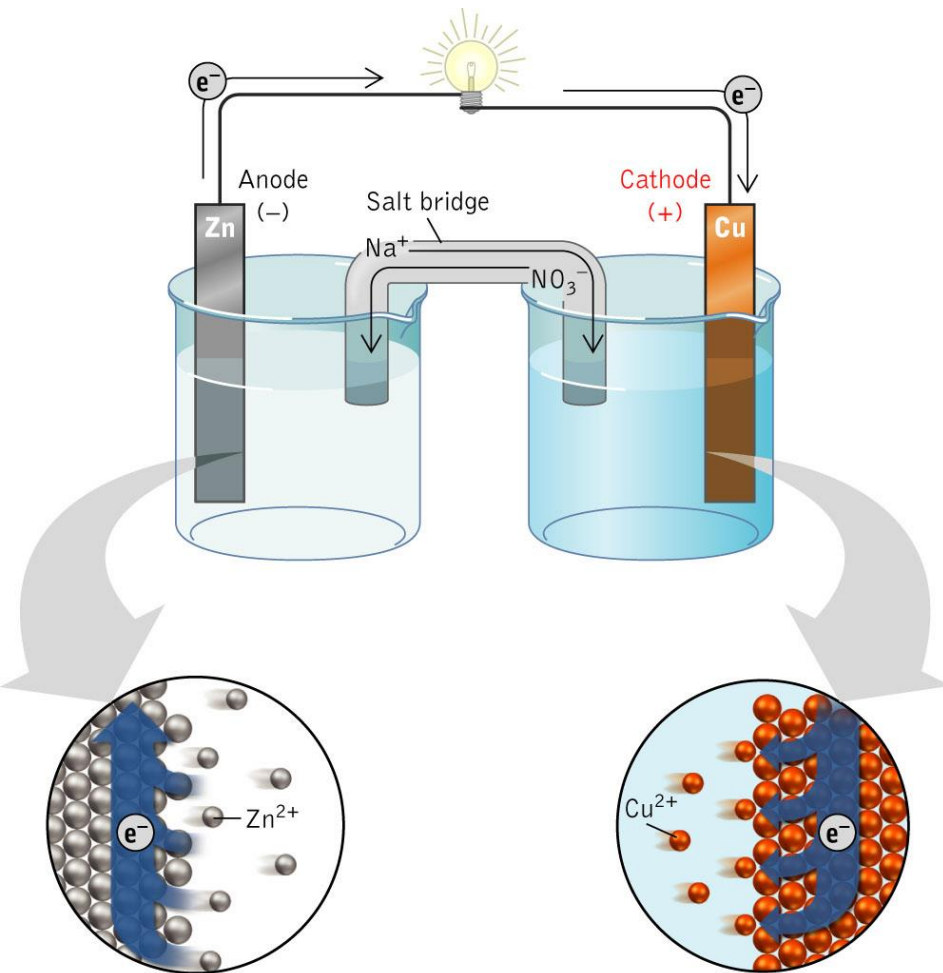
The reduction occurs at the **cathode**.

- We can use that energy to do work if we make the electrons flow through an external device.



Voltaic or Galvanic cell – chemical energy is used to produce electrical energy ($\Delta G < 0$) (i.e. a battery).

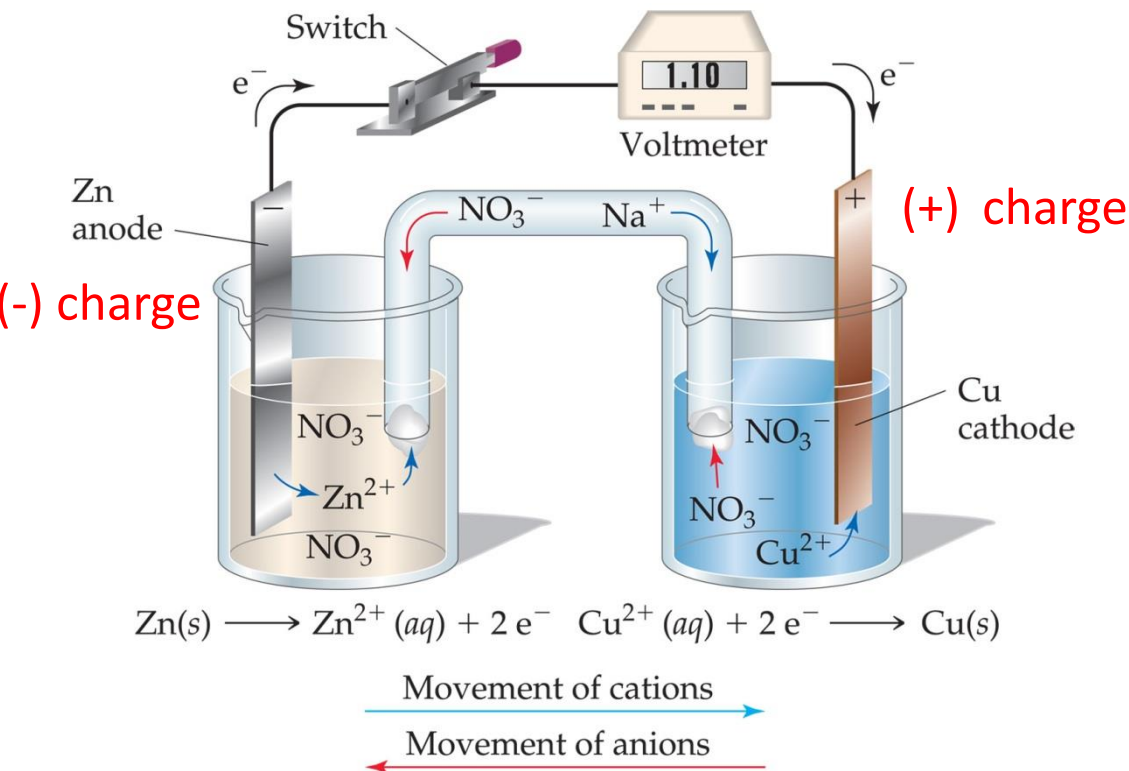
Electrolytic cell – an external source of electrical energy is used to do work on a chemical system (i.e. charging a car battery with the alternator after the car has started).



Cells Components :

An electrochemical cell is a reaction system in which oxidation and reduction reactions occur in separate compartments (or **2 half cells**) either consume or produce electrical energy. The cells are separated by a **salt bridge** or semi-permeable membrane that allows ions to migrate from one cell to the other. **Electrons move from anode (oxd) to cathode (red).**

Voltaic Cells



Once even one electron flows from the anode to the cathode, the charges in each beaker would not be balanced and the flow of electrons would stop.

As the half reactions occur

A surplus of positive ions builds up at the anode , (-) charge

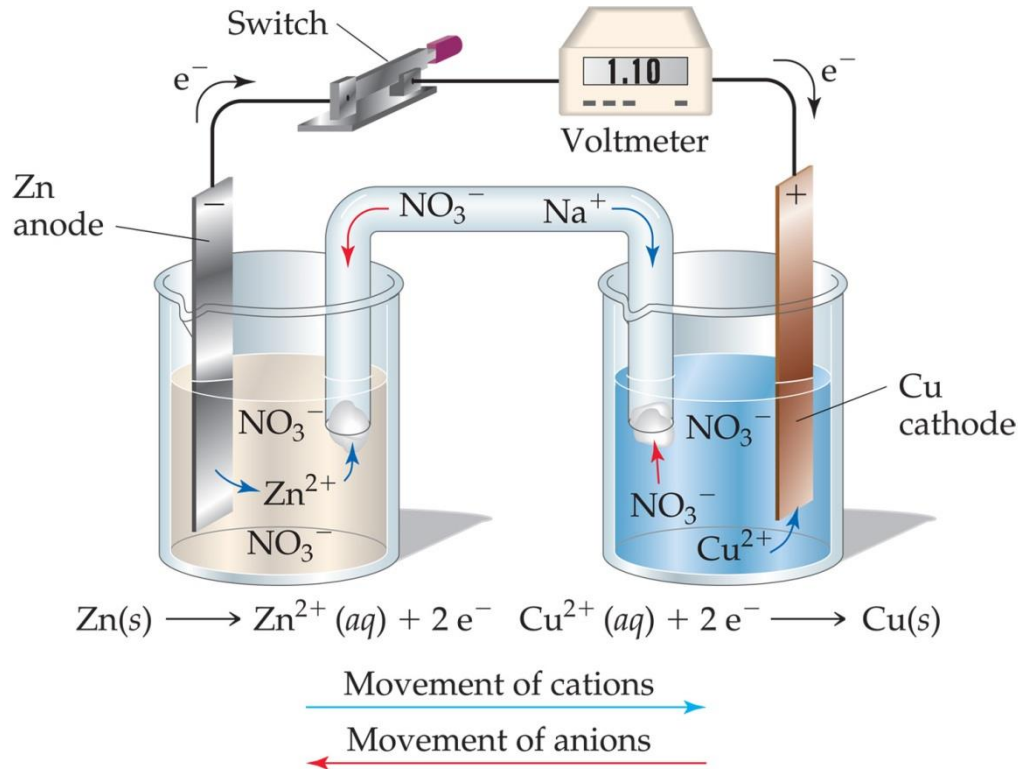
A surplus of negative ions builds up at the cathode, (+) charge

Anions and cations must flow to balance charge

Current is the number of electrons that flow through the system per second.

Unit = ampere

Salt Bridge



- Therefore, we use a salt bridge, usually a U-shaped tube that contains a salt solution, to keep the charges balanced.

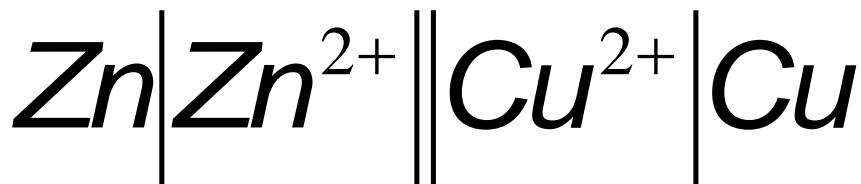
Na^+ Cations move toward the cathode. The sign of this electrode is (+)
 NO_3^- Anions move toward the anode. The sign of this electrode is (-)

Salt Bridges allows current to flow

- The salt bridge is a gel-filled U-tube with a solution of a salt containing ions *other than those involved in the redox reaction*
 - KNO_3 / NaNO_3 is frequently used
 - Na^+ Cations flow toward the cathode to neutralize the build-up of negative charge
 - NO_3^- Anions flow toward the anode to neutralize the build-up of positive charge

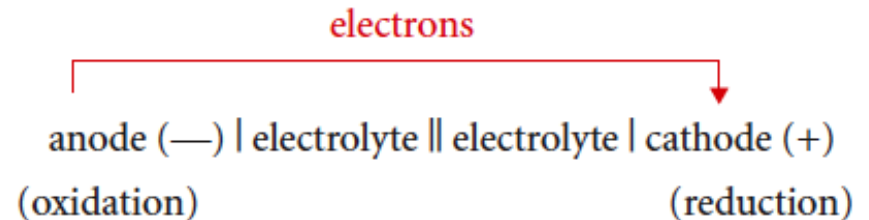
Shorthand Cell Notation

- Oxidation on the left
- Reduction on the right
- Single vertical line represents a phase boundary
 - Liquid-metal or liquid-gas, etc.
- Double line is the salt bridge



electrons flow

The single line represents a phase boundary (electrode to electrolyte) and the double line represents a physical boundary (porous boundary)



The difference in potential energy between the reactants and products is the **potential difference**.

Unit = volt

The amount of force pushing the electrons through the wire is called the **electromotive force, emf**.

EXAMPLE 17.1

When chlorine gas is bubbled through an aqueous solution of NaBr, chloride ions and liquid bromine are the products of the spontaneous reaction. For this cell,

- Draw a sketch of the cell, labeling the anode, the cathode, and the direction of electron flow.
- Write the half-reaction that takes place at the anode and at the cathode.
- Write a balanced equation for the cell reaction.
- Write an abbreviated notation for the cell.

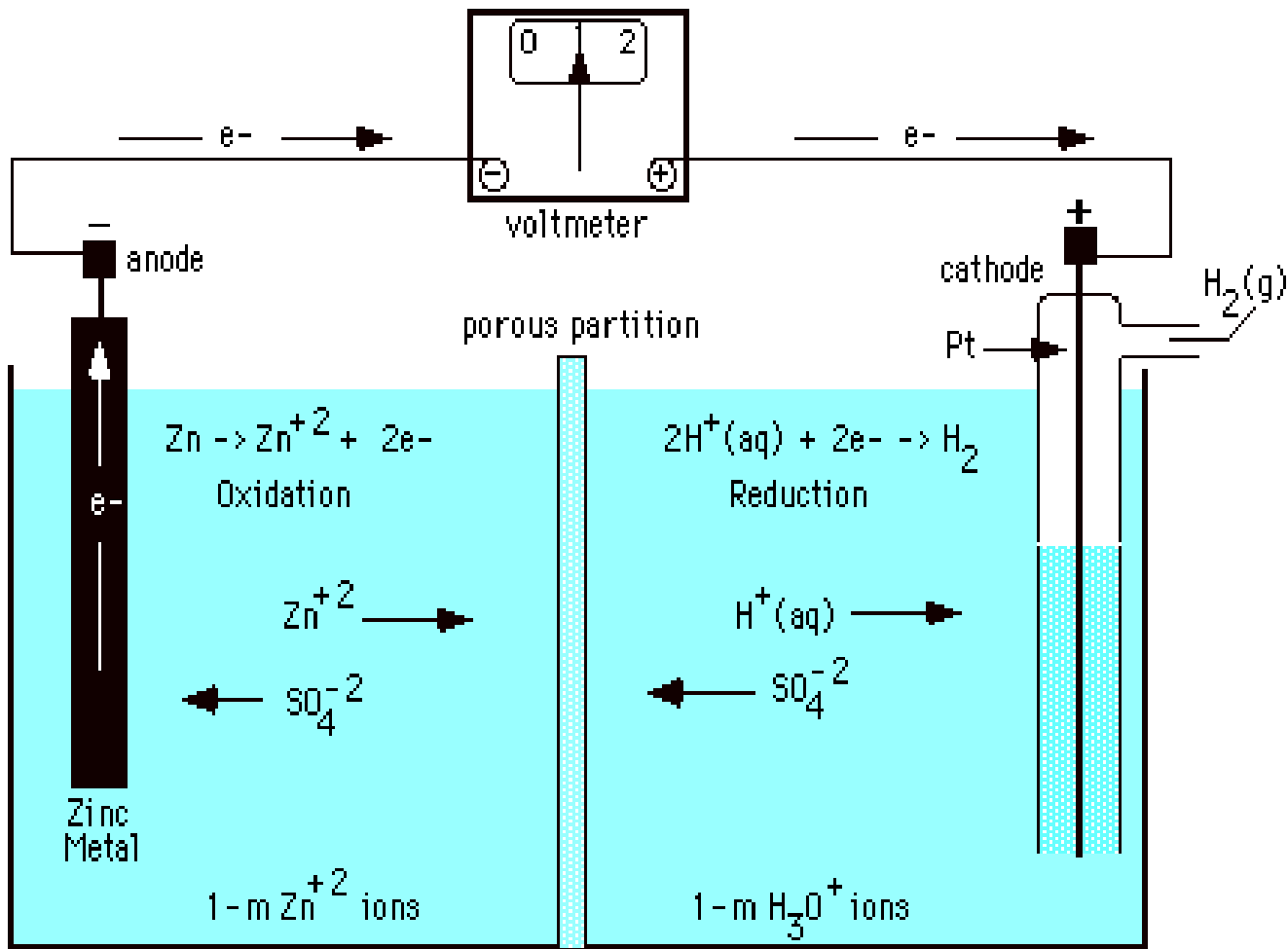
continued

STRATEGY

- Split the equation into two half-reactions.
- Recall that the anode
 - is where oxidation takes place.
 - is the electrode toward which anions move.
 - is where electrons are produced.
- The cathode
 - is where reduction takes place.
 - is the electrode toward which cations move.
 - is where electrons are released by the anode through an external circuit.

SOLUTION

- | | |
|-------------------------------|--|
| (a) Sketch of the cell | See Figure 17.4, where all the appropriate parts are labeled and the direction of electron flow is indicated. |
| (b) Half-reactions | cathode: $\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$ (reduction)
anode: $2\text{Br}^-(\text{aq}) \longrightarrow \text{Br}_2(\text{l}) + 2\text{e}^-$ (oxidation) |
| (c) Balanced equation | $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \longrightarrow 2\text{Cl}^-(\text{aq}) + \text{Br}_2(\text{l})$ |
| (d) Abbreviated cell notation | $\text{Pt} \mid \text{Br}_2, \text{Br}^- \parallel \text{Cl}^- \mid \text{Cl}_2 \mid \text{Pt}$ |



Measuring Electrode Potential

Measuring Standard Electrode Potential

Potentials are measured against a hydrogen ion reduction reaction, which is arbitrarily assigned a potential of **zero volts**.

**Standard
Potential (V)****Reduction Half-Reaction**

+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
-0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
-0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
-0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
-0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
-1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
-2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
-3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Table of
Reduction
PotentialsMeasured
against
the
Standard
Hydrogen
Electrode

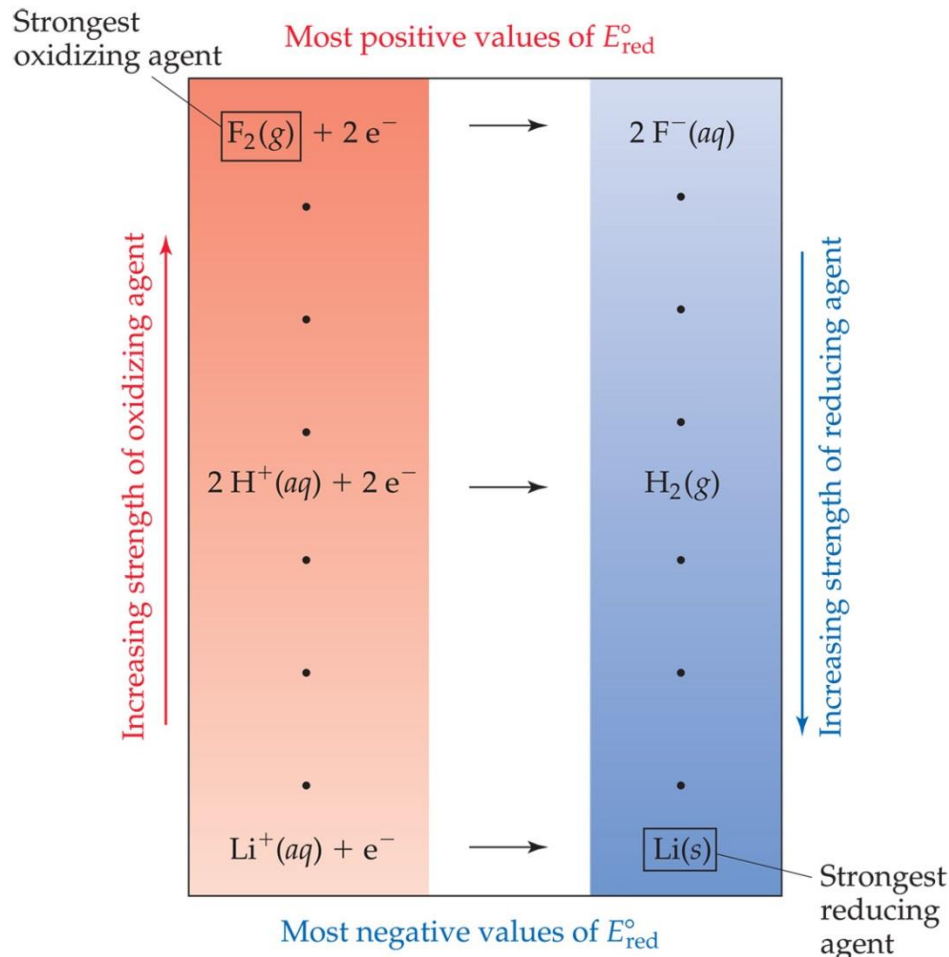
Consider the reduction potential chart. Find the reduction equations for $\text{Ag}^+ \rightarrow \text{Ag}^\circ$ and $\text{Pb}^{2+} \rightarrow \text{Pb}^\circ$.

1. Which metal ion has the greater reduction potential? _____ see table
2. If these two metals (and their solutions) were used to create a galvanic cell, which metal would be the anode? _____
3. Write the reaction at the anode: _____
4. Write the reaction at the cathode: _____
5. What is the overall reaction? _____
6. Write the cell notation for the cell: _____ | _____ || _____ | _____
7. How many moles of electrons are involved in this reaction?

Standard Potentials

- Once the hydrogen half cell has been assigned a voltage of 0.000 V, other half cells can be measured relative to it
 - Tables of ***standard potentials*** can be prepared
 - These are always ***reduction*** potentials, i.e., E_{red}°
 - To obtain the oxidation potential, simply reverse the sign:
 - $\text{Zn}^{2+} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn} (\text{s}) \quad E_{red}^{\circ} = -0.762\text{V}$
 - $\text{Zn} (\text{s}) \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^{-} \quad E_{ox}^{\circ} = +0.762\text{V}$
- 25 °C, 1 atm for gases, 1 M concentration of solution
- Standard voltages for oxidation and reduction are ***equal in magnitude and opposite in sign***

Oxidizing and Reducing Agents

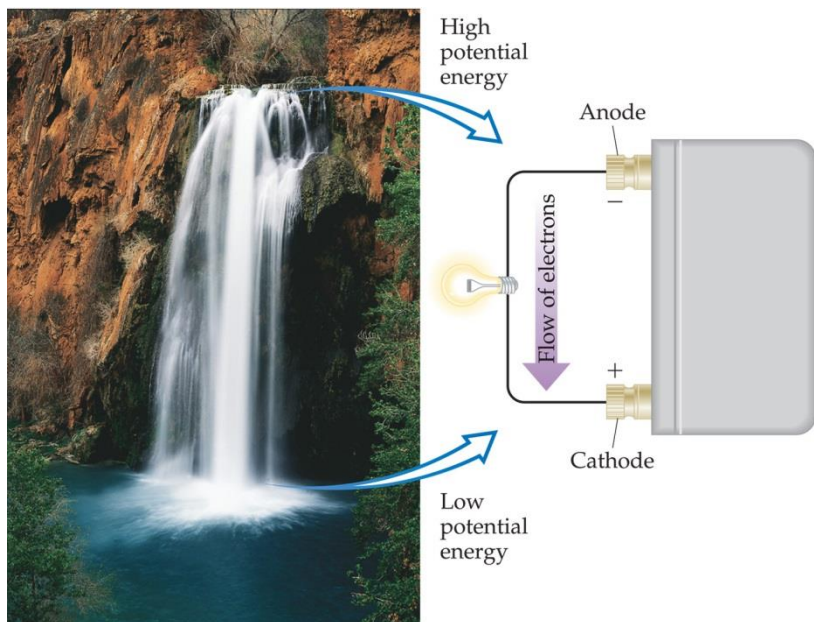


- The strongest oxidizers have the most positive reduction potentials.
- The strongest reducers have the most negative reduction potentials.

A **standard potential** (E°) is the electromotive force of a *half-reaction written as a reduction* reaction in which all reactants and products are in their standard states (see

The **standard cell potential** (E°_{cell}) is the potential of a cell when all reactants and products are in their standard states, i.e. the pressure of all gases are 1 atm, and the concentration of dissolved species are 1 molar.

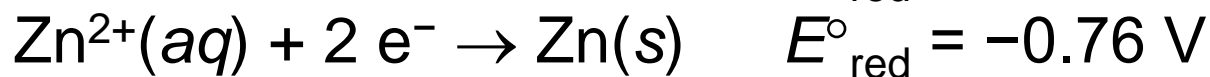
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad \text{or} \quad E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$$



Because cell potential is based on the potential energy per unit of charge, **it is an intensive property.**
(not numbers)

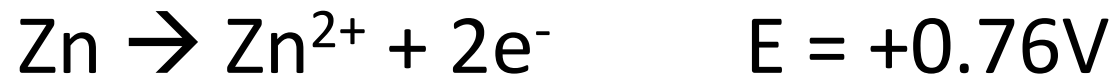
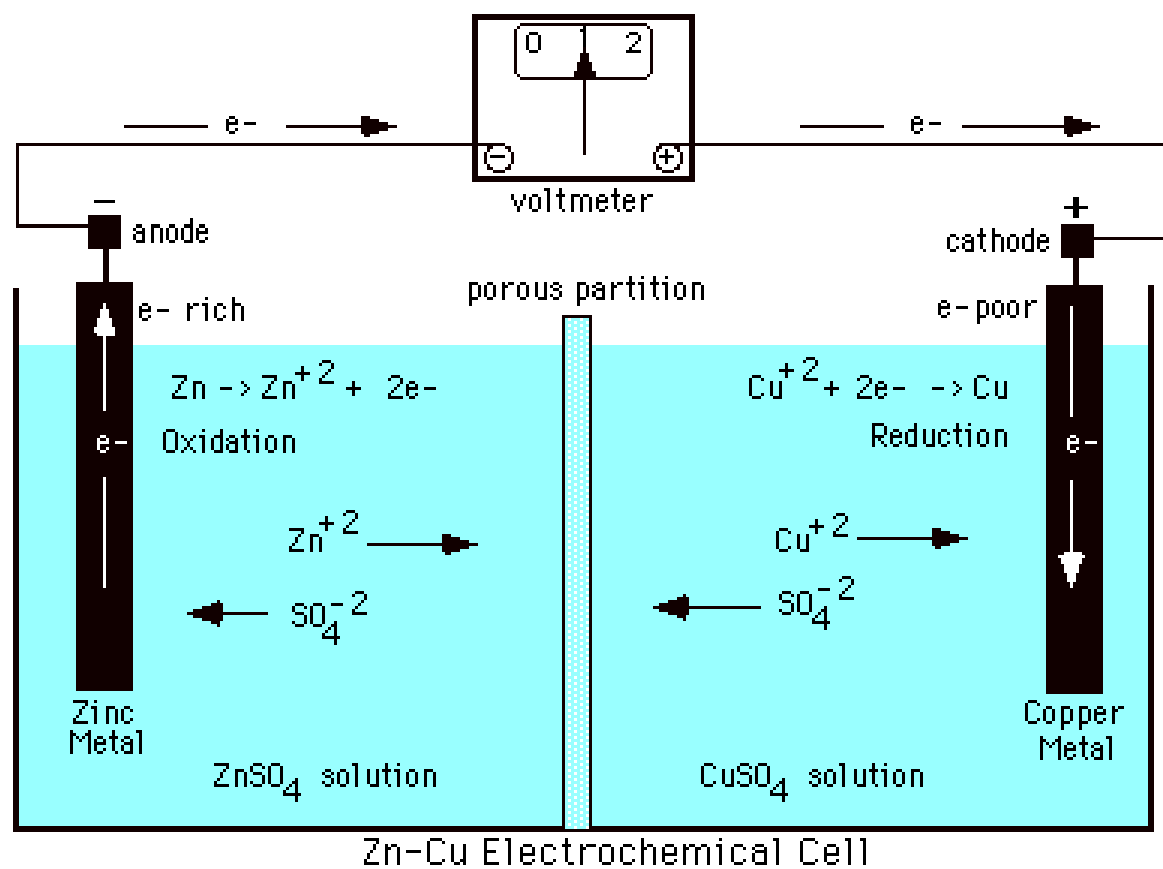
Predicting Spontaneity of Redox Reactions

- A spontaneous reaction will take place when a reduction half-reaction is paired with an oxidation half-reaction lower on the table.
- If paired the other way, the reverse reaction is spontaneous.



Zn - Cu Galvanic Cell

The less positive, or more negative reduction potential becomes the oxidation...

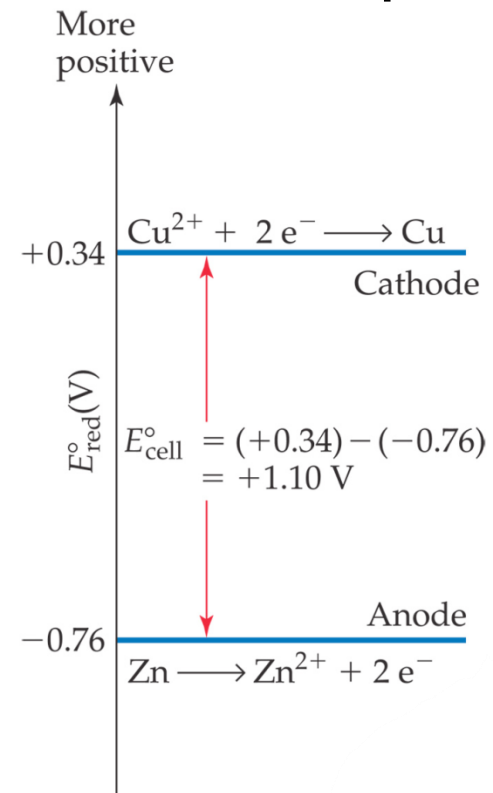


Calculating Cell Potentials under Standard Conditions

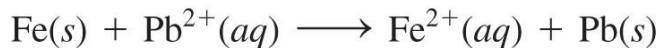
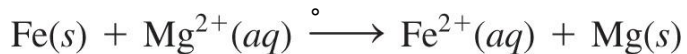
- $E^\circ_{\text{cell}} = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}}$
- When adding E° values for the half-cells, *do not multiply the half-cell E° values,* even if you need to multiply the half-reactions to balance the equation.

Oxidizing and Reducing Agents

The greater the difference between the two, the greater the voltage of the cell.



Example 18.5 Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells



Solution

a.



This reaction involves the reduction of Mg^{2+} :



and the oxidation of Fe:



b.



This reaction involves the reduction of Pb^{2+} :



and the oxidation of iron:



TABLE 18.1 Standard Electrode Potentials at 25 °C

Reduction Half-Reaction	E° (V)
$\text{F}_2(g) + 2 e^{-} \longrightarrow 2 \text{F}^{-}(aq)$	2.87
$\text{H}_2\text{O}_2(aq) + 2 \text{H}^{+}(aq) + 2 e^{-} \longrightarrow 2 \text{H}_2\text{O}(l)$	1.78
$\text{PbO}_2(s) + 4 \text{H}^{+}(aq) + \text{SO}_4^{2-}(aq) + 2 e^{-} \longrightarrow \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(l)$	1.69
$\text{MnO}_4^{-}(aq) + 4 \text{H}^{+}(aq) + 3 e^{-} \longrightarrow \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l)$	1.68
$\text{MnO}_4^{-}(aq) + 8 \text{H}^{+}(aq) + 5 e^{-} \longrightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l)$	1.51
$\text{Au}^{3+}(aq) + 3 e^{-} \longrightarrow \text{Au}(s)$	1.50
$\text{PbO}_2(s) + 4 \text{H}^{+}(aq) + 2 e^{-} \longrightarrow \text{Pb}^{2+}(aq) + 2 \text{H}_2\text{O}(l)$	1.46
$\text{Cl}_2(g) + 2 e^{-} \longrightarrow 2 \text{Cl}^{-}(aq)$	1.36
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^{+}(aq) + 6 e^{-} \longrightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33
$\text{O}_2(g) + 4 \text{H}^{+}(aq) + 4 e^{-} \longrightarrow 2 \text{H}_2\text{O}(l)$	1.23
$\text{MnO}_2(s) + 4 \text{H}^{+}(aq) + 2 e^{-} \longrightarrow \text{Mn}^{2+}(aq) + 2 \text{H}_2\text{O}(l)$	1.21
$\text{IO}_3^{-}(aq) + 6 \text{H}^{+}(aq) + 5 e^{-} \longrightarrow \frac{1}{2} \text{I}_2(aq) + 3 \text{H}_2\text{O}(l)$	1.20
$\text{Br}_2(l) + 2 e^{-} \longrightarrow 2 \text{Br}^{-}(aq)$	1.09
$\text{VO}_2^{+}(aq) + 2 \text{H}^{+}(aq) + e^{-} \longrightarrow \text{VO}^{2+}(aq) + \text{H}_2\text{O}(l)$	1.00
$\text{NO}_3^{-}(aq) + 4 \text{H}^{+}(aq) + 3 e^{-} \longrightarrow \text{NO}(g) + 2 \text{H}_2\text{O}(l)$	0.96
$\text{ClO}_2(g) + e^{-} \longrightarrow \text{ClO}_2^{-}(aq)$	0.95
$\text{Ag}^{+}(aq) + e^{-} \longrightarrow \text{Ag}(s)$	0.80
$\text{Fe}^{3+}(aq) + e^{-} \longrightarrow \text{Fe}^{2+}(aq)$	0.77
$\text{O}_2(g) + 2 \text{H}^{+}(aq) + 2 e^{-} \longrightarrow \text{H}_2\text{O}_2(aq)$	0.70
$\text{MnO}_4^{-}(aq) + e^{-} \longrightarrow \text{MnO}_4^{2-}(aq)$	0.56
$\text{I}_2(s) + 2 e^{-} \longrightarrow 2 \text{I}^{-}(aq)$	0.54
$\text{Cu}^{+}(aq) + e^{-} \longrightarrow \text{Cu}(s)$	0.52
$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 e^{-} \longrightarrow 4 \text{OH}^{-}(aq)$	0.40
$\text{Cu}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Cu}(s)$	0.34
$\text{SO}_4^{2-}(aq) + 4 \text{H}^{+}(aq) + 2 e^{-} \longrightarrow \text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l)$	0.20
$\text{Cu}^{2+}(aq) + e^{-} \longrightarrow \text{Cu}^{+}(aq)$	0.16
$\text{Sn}^{4+}(aq) + 2 e^{-} \longrightarrow \text{Sn}^{2+}(aq)$	0.15
$2 \text{H}^{+}(aq) + 2 e^{-} \longrightarrow \text{H}_2(g)$	0
$\text{Fe}^{3+}(aq) + 3 e^{-} \longrightarrow \text{Fe}(s)$	-0.036
$\text{Pb}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Pb}(s)$	-0.13
$\text{Sn}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Sn}(s)$	-0.14
$\text{Ni}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Ni}(s)$	-0.23
$\text{Cd}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Cd}(s)$	-0.40
$\text{Fe}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Fe}(s)$	-0.45
$\text{Cr}^{3+}(aq) + e^{-} \longrightarrow \text{Cr}^{2+}(aq)$	-0.50
$\text{Cr}^{3+}(aq) + 3 e^{-} \longrightarrow \text{Cr}(s)$	-0.73
$\text{Zn}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Zn}(s)$	-0.76
$2 \text{H}_2\text{O}(l) + 2 e^{-} \longrightarrow \text{H}_2(g) + 2 \text{OH}^{-}(aq)$	-0.83
$\text{Mn}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Mn}(s)$	-1.18
$\text{Al}^{3+}(aq) + 3 e^{-} \longrightarrow \text{Al}(s)$	-1.66
$\text{Mg}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Mg}(s)$	-2.37
$\text{Na}^{+}(aq) + e^{-} \longrightarrow \text{Na}(s)$	-2.71
$\text{Ca}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Ca}(s)$	-2.76
$\text{Ba}^{2+}(aq) + 2 e^{-} \longrightarrow \text{Ba}(s)$	-2.90
$\text{K}^{+}(aq) + e^{-} \longrightarrow \text{K}(s)$	-2.92
$\text{Li}^{+}(aq) + e^{-} \longrightarrow \text{Li}(s)$	-3.04

Stronger oxidizing agent

Weaker reducing agent

Weaker oxidizing agent

Stronger reducing agent

EXAMPLE 17.3 GRADED

Consider the voltaic cell in which the reaction is



- a Use Table 17.1 to calculate E° for the voltaic cell.
- ~~b If the value zero is arbitrarily assigned to the standard voltage for the reduction of Ag^+ ions to Ag , what is E°_{red} for the reduction of Cd^{2+} ions to Cd ?~~

continued

a

STRATEGY

1. Assign oxidation numbers to each element so you can decide which element is reduced and which one is oxidized.
2. Write the oxidation and reduction half-reactions together with the corresponding E°_{ox} and E°_{red} . Recall that $E^\circ_{\text{ox}} = -(E^\circ_{\text{red}})$.
3. Add both half-reactions (make sure you cancel electrons) and take the sum of E°_{ox} and E°_{red} to obtain E° for the cell.

SOLUTION

- | | | |
|----------------------|--|---|
| 1. Oxidation numbers | $\text{Ag}: +1 \longrightarrow 0$ (reduction)
$\text{Cd}: 0 \longrightarrow +2$ (oxidation) | $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag} \quad E_{\text{red}} = +0.799 \text{ V}$
Why $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Ag} \quad E_{\text{red}} = +0.799 \text{ V}$ |
| 2. Half-reactions | $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Ag}(\text{s}) \quad E^\circ_{\text{red}} = +0.799 \text{ V}$
$\text{Cd}(\text{s}) \longrightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \quad E^\circ_{\text{ox}} = -(E^\circ_{\text{red}}) = -(-0.402 \text{ V}) = +0.402 \text{ V}$ | |
| 3. E° | $\text{Cd}(\text{s}) + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{Ag}(\text{s}) \quad E^\circ = 0.799 \text{ V} + 0.402 \text{ V} = 1.201 \text{ V}$ | |



b

STRATEGY AND SOLUTION

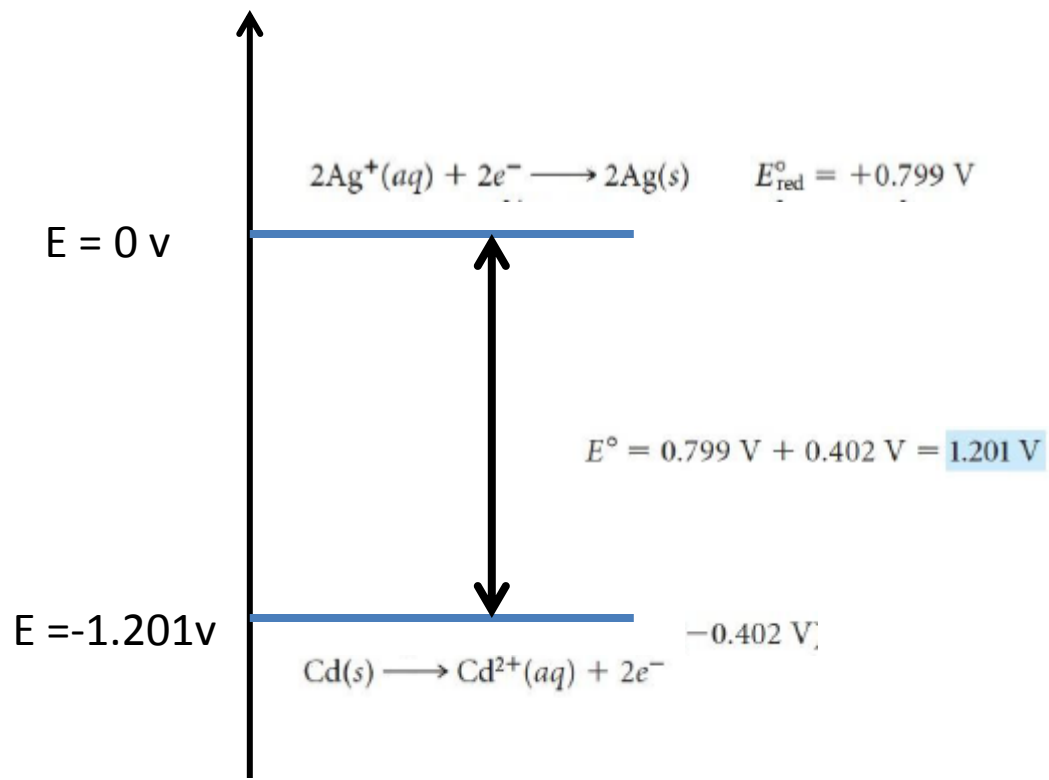
E° for the cell does not change. It does not matter what you choose to be E_{red}° of the half-reaction. Naturally, E_{ox}° will also change and you cannot choose to change that.

If you choose E_{red}° to be zero, then

$$E_{\text{red}}^\circ + E_{\text{ox}}^\circ = 1.201 \text{ V}$$

$$0 + E_{\text{ox}}^\circ = 1.201 \text{ V}; E_{\text{ox}}^\circ \text{ for the half-reaction } \text{Cd}(s) \longrightarrow \text{Cd}^{2+}(aq) + 2e^- = 1.201 \text{ V}$$

Since E_{red}° for Cd^{2+} is asked for, then $E_{\text{red}}^\circ = -(E_{\text{ox}}^\circ) = -1.201 \text{ V}$



Free Energy

ΔG for a redox reaction can be found by using the equation

$$\Delta G = -nFE$$

where n is the number of moles of electrons transferred, and F is a constant, the Faraday.

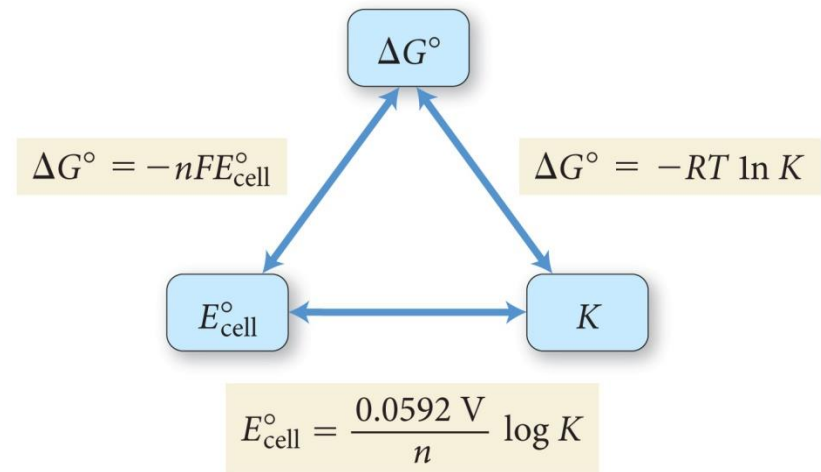
$$1 F = 96,485 \text{ C/mol} = 96,485 \text{ J/V-mol}$$

Under standard conditions,

$$\Delta G^\circ = -nFE^\circ$$

E°_{cell} , ΔG° , and K

- For a spontaneous reaction
 - one that proceeds in the forward direction with the chemicals in their standard states
 - $\Delta G^\circ < 0$ (negative)
 - $E^\circ > 0$ (positive)
 - $K > 1$
- $\Delta G^\circ = -RT \ln K = -nFE^\circ_{\text{cell}}$
 - n = the number of electrons
 - F = Faraday's constant = 96,485 C/mol e^-



Calculating ΔG^0 for a Cell

$$\Delta G^0 = -nFE^0$$

n = moles of electrons in balanced redox equation

F = Faraday constant = 96,485 coulombs/mol e^-



$$\Delta G^0 = -(2 \text{ mol } e^-)(96485 \frac{\text{coulombs}}{\text{mol } e^-})(1.10 \frac{\text{Joules}}{\text{Coulomb}})$$

$$\Delta G^0 = -212267 \text{ Joules} = -212 \text{ kJ}$$

Example 18.6 Relating ΔG° and E°_{cell}

Use the tabulated electrode potentials to calculate ΔG° for the reaction.



Is the reaction spontaneous?

Sort

You are given a redox reaction and asked to find ΔG° .

Given: $\text{I}_2(\text{s}) + 2 \text{Br}^-(\text{aq}) \longrightarrow 2 \text{I}^-(\text{aq}) + \text{Br}_2(\text{l})$

Find: ΔG°

Strategize

Refer to the values of electrode potentials in Table 18.1 to calculate E°_{cell} . Then use Equation 18.3 to calculate G from E°_{cell} .

Conceptual Plan

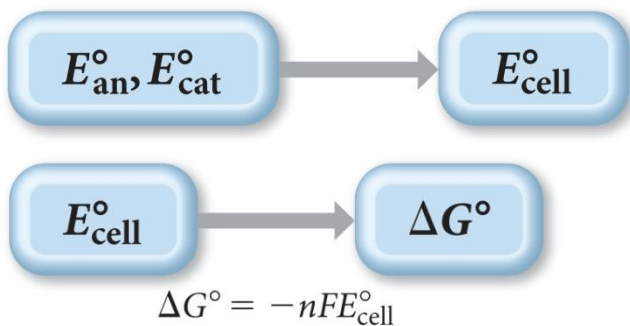


TABLE 18.1 Standard Electrode Potentials at 25 °C

Reduction Half-Reaction	E° (V)
$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$	2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.78
$\text{PbO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$	1.69
$\text{MnO}_4^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$	1.68
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	1.51
$\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Au}(\text{s})$	1.50
$\text{PbO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	1.46
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$	1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	1.33
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.23
$\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	1.21
$\text{IO}_3^-(\text{aq}) + 6 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \frac{1}{2} \text{I}_2(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$	1.20
$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$	1.09
$\text{VO}_2^+(\text{aq}) + 2 \text{H}^+(\text{aq}) + \text{e}^- \longrightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	1.00
$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	0.96
$\text{ClO}_2(\text{g}) + \text{e}^- \longrightarrow \text{ClO}_2^-(\text{aq})$	0.95
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70
$\text{MnO}_4^-(\text{aq}) + \text{e}^- \longrightarrow \text{MnO}_4^{2-}(\text{aq})$	0.56
$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$	0.54
$\text{Cu}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}(\text{s})$	0.52
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$	0.40
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$	0.34
$\text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.20
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}^+(\text{aq})$	0.16
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0
$\text{Fe}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.036
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.23
$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.45
$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Cr}^{2+}(\text{aq})$	-0.50
$\text{Cr}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Cr}(\text{s})$	-0.73
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.76
$\text{Ba}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ba}(\text{s})$	-2.90
$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.92
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.04

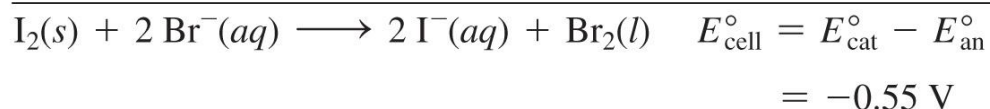
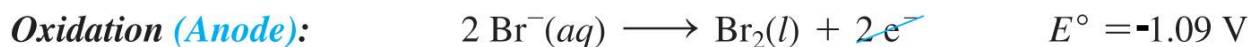
Example 18.6 Relating ΔG° and E_{cell}°

Continued

Solve

Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Determine E_{cell}° by subtracting E_{an} from E_{cat} .

Solution



Calculate ΔG° from E_{cell}° . The value of n (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions. Remember that $1 \text{ V} = 1 \text{ J/C}$.

$$\begin{aligned}\Delta G^\circ &= -nFE_{\text{cell}}^\circ \\ &= -2 \text{ mol e}^- \left(\frac{96,485 \text{ C}}{\text{mol e}^-} \right) \left(-0.55 \frac{\text{J}}{\text{C}} \right) \\ &= +1.1 \times 10^5 \text{ J}\end{aligned}$$

Since ΔG° is positive, the reaction is not spontaneous under standard conditions.

Nernst Equation

- Remember that Ch 17

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- This means

$$-nFE = -nFE^\circ + RT \ln Q$$

Nernst Equation

- Remember that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE = -nFE^\circ + RT \ln Q$$

We can combine R (8.31 J/mol-K), T (25 °C = 298 K), and F (96480 J/mol-V) to give 0.0257V

Dividing both sides by $-nF$, we get the **Nernst equation**:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = E^\circ - \frac{0.0257V}{n} \ln Q$$

If concentration can gives voltage, then from voltage we can tell concentration

Nernst Equation

EXAMPLE 17.7

Consider a voltaic cell at 25°C in which the reaction is



It is found that the voltage is +0.560 V when $[\text{Zn}^{2+}] = 0.85 \text{ M}$ and $P_{\text{H}_2} = 0.988 \text{ atm}$. What is the pH in the H₂-H half-cell?

ANALYSIS

Information given:

reaction: $(\text{Zn}(s) + 2\text{H}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g))$
 E (0.560 V); T (25°C)
 P_{H_2} (0.988 atm); $[\text{Zn}^{2+}]$ (0.85 M)
temperature (25°C)

Information implied:

Table 17.1 (standard reduction potentials)

Asked for:

pH

STRATEGY

1. Assign oxidation numbers, write oxidation and reduction half-reactions, and cancel electrons to find n .
2. Find E° . ($E^\circ_{\text{red}} + E^\circ_{\text{ox}}$)
3. Substitute into the Nernst equation (Equation 17.4) for $T = 25^\circ\text{C}$ and find Q .
4. Write the Q expression and substitute given concentrations and pressures to find $[\text{H}^+]$. Change $[\text{H}^+]$ to pH.

continued

Nernst Equation

SOLUTION

1. Oxidation numbers

Zn: 0 \longrightarrow +2 oxidation; H⁺: +1 \longrightarrow 0 reduction

Half-reactions



n

2 electrons cancel out so $n = 2$.

2. E°

$$E^\circ = E^\circ_{\text{ox Zn}} + E^\circ_{\text{red H}^+} = 0.762 \text{ V} + 0 \text{ V} = 0.762 \text{ V}$$

3. Q

$$E = E^\circ - \frac{0.0257}{n} \ln Q; 0.560 \text{ V} = 0.762 \text{ V} - \frac{0.0257}{2} \ln Q$$

$$\frac{0.0257}{2} \ln Q = 0.762 \text{ V} - 0.560 \text{ V}; \ln Q = 15.7; Q = 6.7 \times 10^6$$

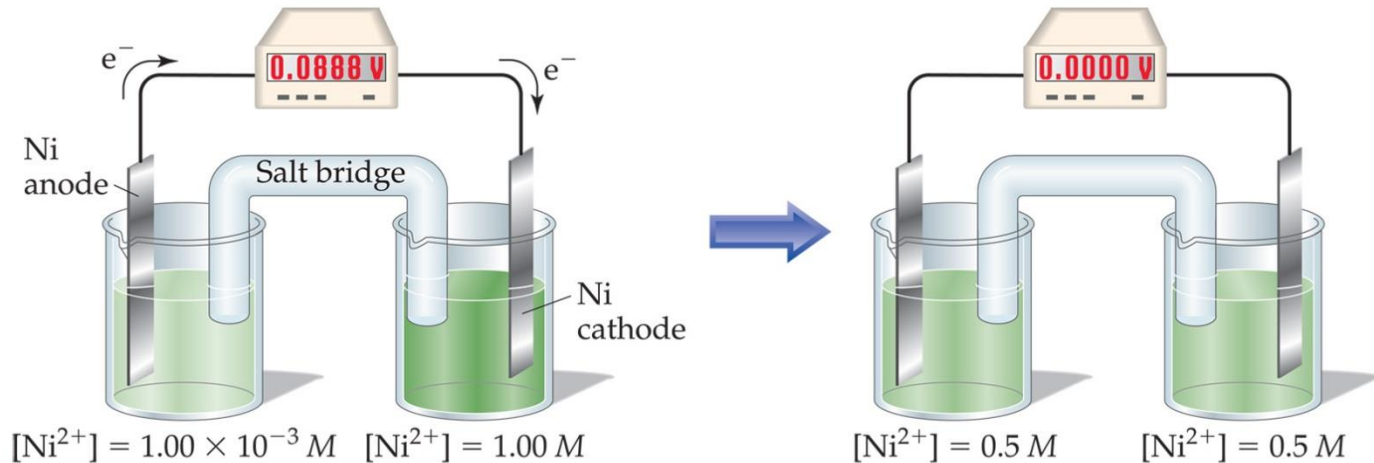
4. [H⁺]

$$Q = \frac{[\text{Zn}^{2+}](P_{\text{H}_2})}{[\text{H}^+]^2}; [\text{H}^+] = \left[\frac{(0.85)(0.988)}{6.7 \times 10^6} \right]^{\frac{1}{2}} = 3.5 \times 10^{-4}$$

pH

$$\text{pH} = -\log_{10} (3.5 \times 10^{-4}) = 3.45$$

Application- Concentration Cells



- Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes.
- For such a cell, E_{cell}° would be 0, but Q would not.
- Therefore, as long as the concentrations are different, E will not be 0.

Cell Potential When Ion Concentrations Are Not 1 M

- We know there is a relationship between the reaction quotient, Q ; the equilibrium constant, K ; and the free energy change, ΔG° .
- Changing the concentrations of the reactants and products so they are not 1 M will affect the standard free energy change, ΔG° .
- Because ΔG° determines the cell potential, E_{cell} , the voltage for the cell will be different when the ion concentrations are not 1 M.

Nernst Concentration Cells Calculations



$$E = E^0 - \frac{0.0591}{n} \log(Q)$$

$$E^0 = 0.0 \text{ Volts} \quad n = 2 \quad Q = \frac{(0.10)}{(1.0)}$$

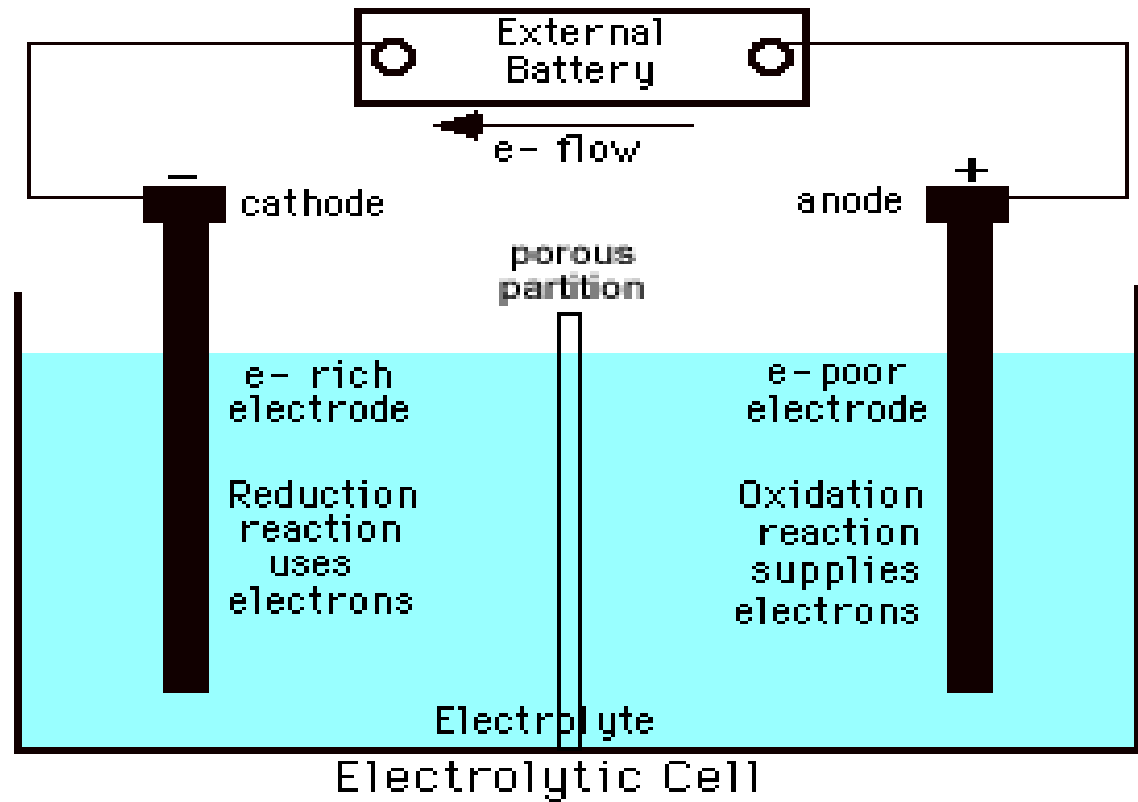
$$E = 0.0 - \frac{0.0591}{2} \log\left(\frac{0.10}{1.0}\right) = 0.030 \text{ Volts}$$

Electrolytic Processes

Electrolytic processes are **NOT** spontaneous. They have:

A negative cell potential, ($-E^0$)

A positive free energy change, ($+\Delta G$)

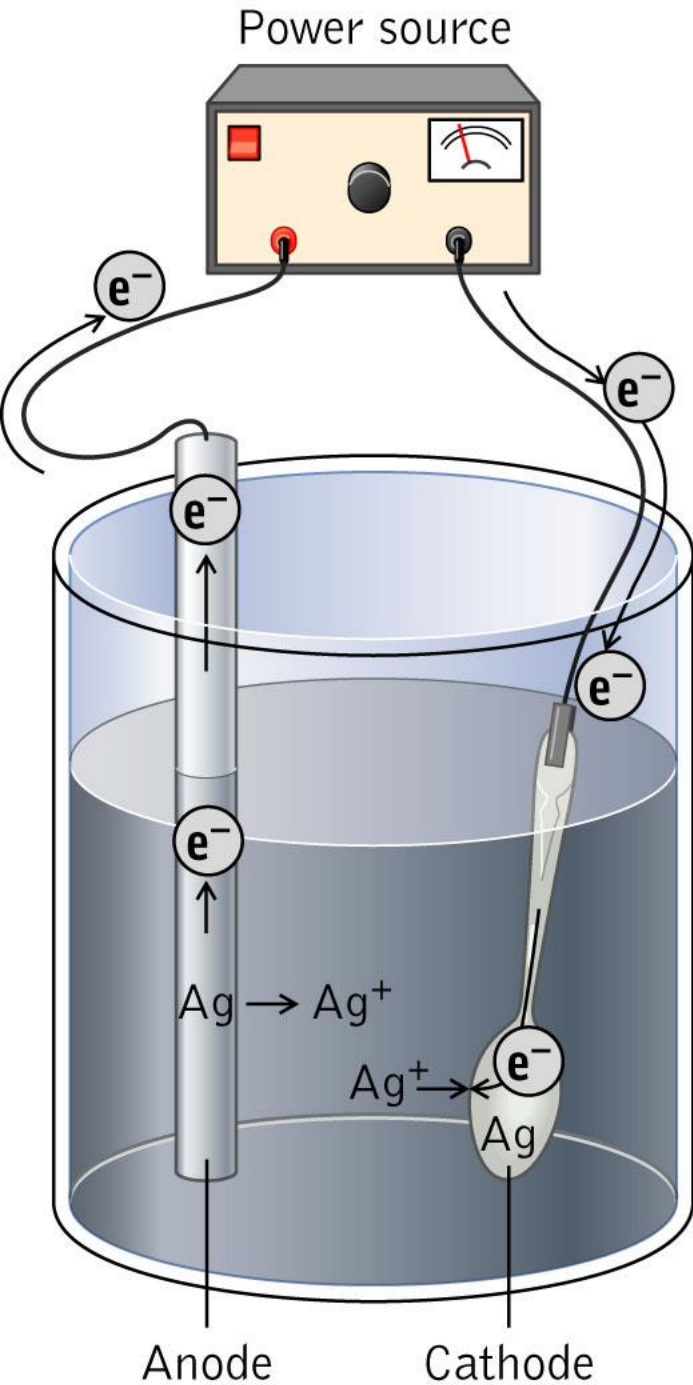


Electrolysis

- In electrolysis we use electrical energy to overcome the energy barrier of a nonspontaneous reaction, allowing it to occur.
- The reaction that takes place is the opposite of the spontaneous process.



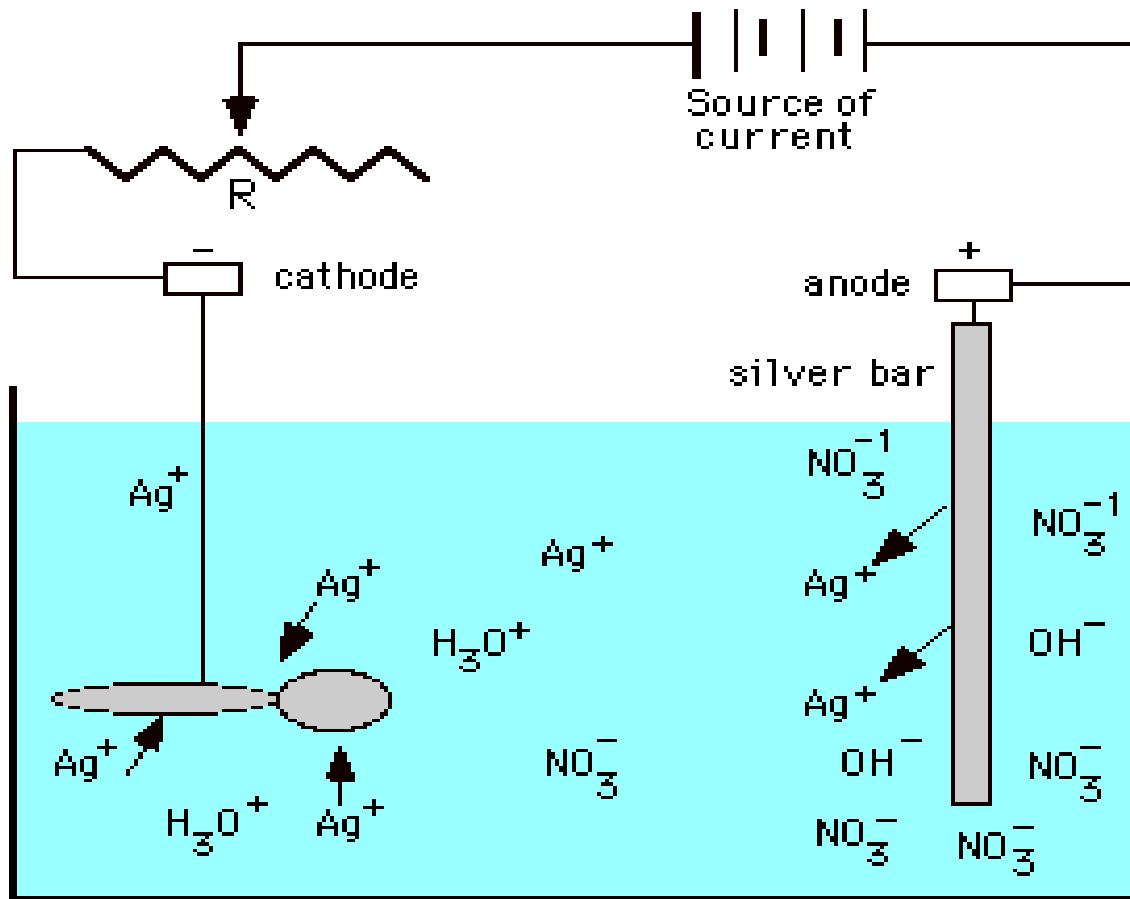
- Some applications are (1) metal extraction from minerals and purification, (2) production of H_2 for fuel cells, and (3) metal plating.



Electrolysis

- Running a galvanic cell backwards.
- Put a voltage bigger than the potential and reverse the direction of the redox reaction.
- Used for electroplating.

Thin coatings of metals can be applied using electrolytic reactions.



Electroplating of Silver

Anode reaction:



Cathode reaction:



Electroplating requirements:

1. Solution of the plating metal
2. Anode made of the plating metal
3. **Cathode with the object to be plated**
4. Source of current

Electrical Units

- Charge
 - 1 mol electrons = 96,480 coulombs (of charge)
- Current
 - 1 *ampere* = 1 coulomb/sec
- Electrical energy
 - 1 joule = 1 C·V
 - 1 kWh = 3.600×10^6 J = 3.600×10^3 kJ

Calculating plating

- Have to count charge.
- Measure current I (in amperes)
- 1 amp = 1 coulomb of charge per second
- $q = I \times t$
- $q/nF = \text{moles of metal}$
- Mass of plated metal

Solving an Electroplating Problem

Q: How many seconds will it take to plate out 5.0 grams of silver from a solution of AgNO_3 using a 20.0 Ampere current?

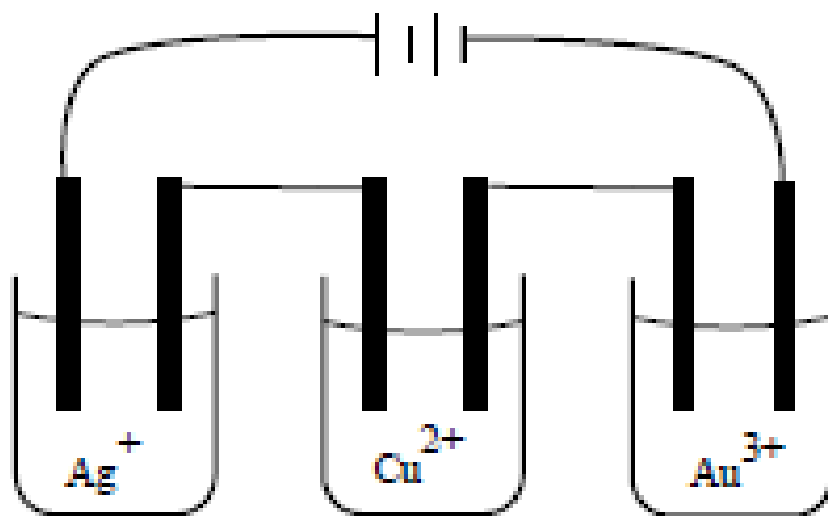


$$\frac{5.0 \text{ g}}{107.87 \text{ g}} \times \frac{1 \text{ mol Ag}}{1 \text{ mol Ag}} \times \frac{1 \text{ mol e}^-}{1 \text{ mol e}^-} \times \frac{96\,485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{20.0 \text{ C}}$$

$$= 2.2 \times 10^2 \text{ s}$$

Electrolysis

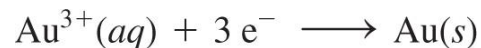
1.0 M aqueous solutions of AgNO_3 , $\text{Cu}(\text{NO}_3)_2$ and $\text{Au}(\text{NO}_3)_3$ are electrolyzed in the apparatus shown, so the same amount of electricity passes through each solution. If 0.10 moles of solid Cu are formed how many moles of Ag and Au are formed?



- (A) 0.10 moles Ag, 0.10 moles Au
- (B) 0.05 moles Ag, 0.075 moles Au
- (C) 0.05 moles Ag, 0.15 moles Au
- (D) 0.20 moles Ag, 0.067 moles Au

Example 18.10 Stoichiometry of Electrolysis

Gold can be plated out of a solution containing Au^{3+} according to the half-reaction:



What mass of gold (in grams) is plated by a 25-minute flow of 5.5 A current?

Sort

You are given the half-reaction for the plating of gold, which shows the stoichiometric relationship between moles of electrons and moles of gold. You are also given the current and duration. You must find the mass of gold that will be deposited in that time.

Given: 3 mol e^{-} : 1 mol Au
5.5 amps
25 min

Find: g Au

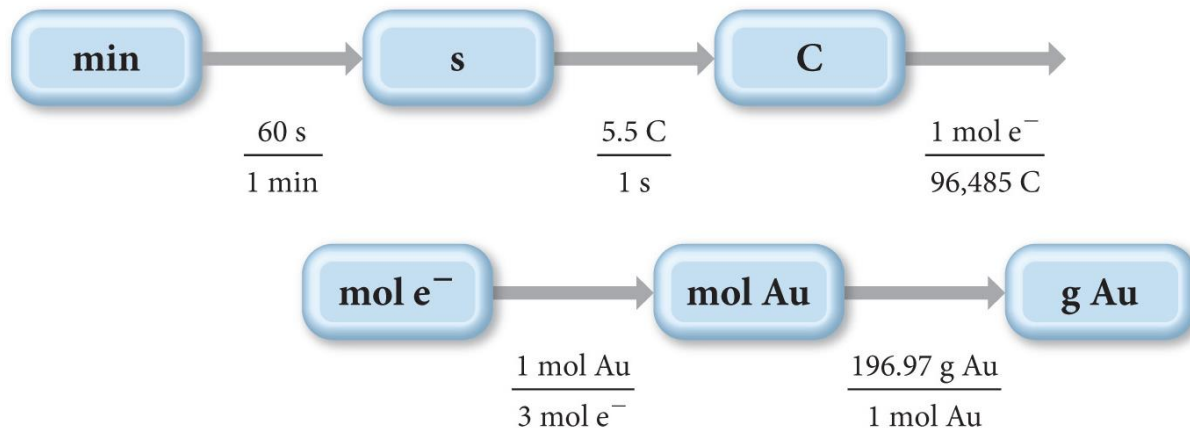
Strategize

You need to find the amount of gold, which is related stoichiometrically to the number of electrons that have flowed through the cell. Begin with time in minutes and convert to seconds. Then, since current is a measure of charge per unit time, use the given current and the time to find the number of coulombs. You can use Faraday's constant to calculate the number of moles of electrons and the stoichiometry of the reaction to find the number of moles of gold. Finally, use the molar mass of gold to convert to mass of gold.

Example 18.10 Stoichiometry of Electrolysis

Continued

Conceptual Plan



Solve

Follow the conceptual plan to solve the problem, canceling units to arrive at the mass of gold.

Solution

$$25 \text{ min} \times \frac{60 \cancel{\text{ s}}}{1 \cancel{\text{ min}}} \times \frac{5.5 \cancel{\text{ C}}}{1 \cancel{\text{ s}}} \times \frac{1 \cancel{\text{ mol e}^-}}{96,485 \cancel{\text{ C}}} \times \frac{1 \cancel{\text{ mol Au}}}{3 \cancel{\text{ mol e}^-}} \times \frac{196.97 \text{ g Au}}{1 \cancel{\text{ mol Au}}} = 5.6 \text{ g Au}$$

Check

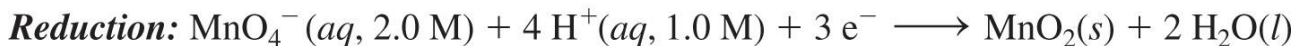
The answer has the correct units (g Au). The magnitude of the answer is reasonable if we consider that 10 amps of current for 1 hour is the equivalent of about 1/3 mol of electrons (check for yourself), which would produce 1/9 mol (or about 20 g) of gold.

Other uses

- Electrolysis of water.
- Separating mixtures of ions.
- More positive reduction potential means the reaction proceeds forward.
- We want the reverse.
- Most negative reduction potential is easiest to plate out of solution.

Example 18.8 Calculating E_{cell} under Nonstandard Conditions

Determine the cell potential for an electrochemical cell based on the following two half-reactions:



Sort

You are given the half-reactions for a redox reaction and the concentrations of the aqueous reactants and products. You are asked to find the cell potential.

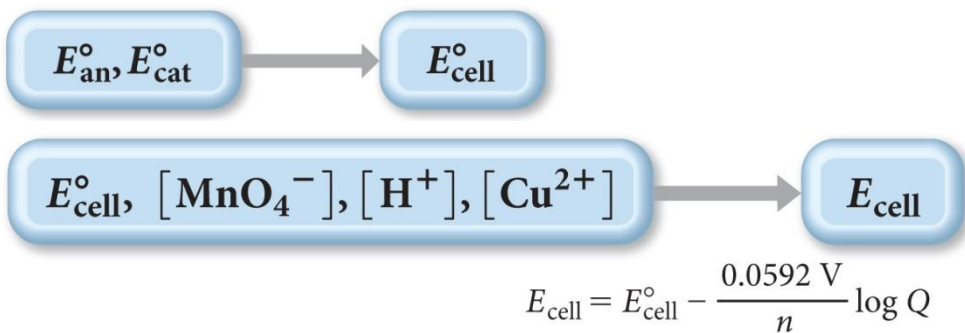
Given: $[\text{MnO}_4^{-}] = 2.0 \text{ M}$; $[\text{H}^{+}] = 1.0 \text{ M}$; $[\text{Cu}^{2+}] = 0.010 \text{ M}$

Find: E_{cell}

Strategize

Use the tabulated values of electrode potentials to calculate E_{cell}° . Then use Equation 18.9 to calculate E_{cell} .

Conceptual Plan



Example 18.8 Calculating E_{cell} under Nonstandard Conditions

Continued

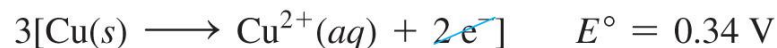
Solve

Write the oxidation and reduction half-reactions, multiplying by the appropriate coefficients to cancel the electrons. Find the standard electrode potentials for each. Find E_{cell}° .

Solution

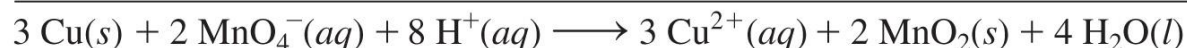
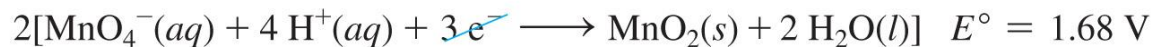
Oxidation

(Anode):



Reduction

(Cathode):



$$E_{\text{cell}}^{\circ} = E_{\text{cat}}^{\circ} - E_{\text{an}}^{\circ} = 1.34 \text{ V}$$

Calculate E_{cell} from E_{cell}° . The value of n (the number of moles of electrons) corresponds to the number of electrons (6 in this case) canceled in the half-reactions. Determine Q based on the overall balanced equation and the given concentrations of the reactants and products. (Note that pure liquid water, solid MnO_2 , and solid copper are omitted from the expression for Q .)

Example 18.8 Calculating E_{cell} under Nonstandard Conditions

Continued

$$\begin{aligned}E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\&= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log \frac{[\text{Cu}^{2+}]^3}{[\text{MnO}_4^-]^2[\text{H}^+]^8} \\&= 1.34 \text{ V} - \frac{0.0592 \text{ V}}{6} \log \frac{(0.010)^3}{(2.0)^2(1.0)^8} \\&= 1.34 \text{ V} - (-0.065 \text{ V}) \\&= 1.41 \text{ V}\end{aligned}$$

Check

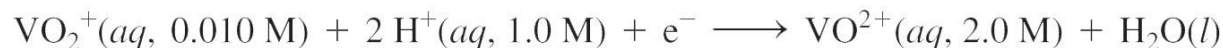
The answer has the correct units (V). The value of E_{cell} is larger than E_{cell}° , as expected based on Le Châtelier's principle because one of the aqueous reactants has a concentration greater than standard conditions and the one aqueous product has a concentration less than standard conditions. Therefore, the reaction has a greater tendency to proceed toward products and has a greater cell potential.

For Practice 18.8

Determine the cell potential of an electrochemical cell based on the following two half-reactions:



Reduction:



Electrolysis

EXAMPLE 17.8

Chromium metal can be electroplated from an aqueous solution of potassium dichromate. The reduction half-reaction is



A current of 6.00 A and a voltage of 4.5 V are used in the electroplating.

- How many grams of chromium can be plated if the current is run for 48 minutes?
- How long will it take to completely convert 215 mL of 1.25 M $\text{K}_2\text{Cr}_2\text{O}_7$ to elemental chromium?
- How many kilowatt-hours of electrical energy are required to plate 1.00 g of chromium?

a

ANALYSIS

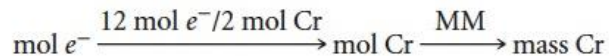
Information given:	reduction half-reaction: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 12\text{e}^- \longrightarrow 2\text{Cr}(\text{s}) + 7\text{H}_2\text{O}$ current (6.00 A); voltage (4.5 V); time in s (48×60)
Information implied:	$1\text{ C} = 1\text{ A} \cdot \text{s}$; MM Cr
Asked for:	mass Cr plated

STRATEGY

- Since mass is asked for, you may assume that you have all the information to convert the amount of electricity to moles of electrons. Moles of electrons provide the bridge that connects the amount of electricity to the stoichiometry of the chemical reaction. Use the following plan:

$$\text{amperes (A)} \xrightarrow{\times \text{ time (s)}} \text{coulomb (C)} \xrightarrow{1 \text{ mol } \text{e}^- = 9.648 \times 10^4 \text{ C}} \text{mol } \text{e}^-$$

- Convert mol e^- to mass of Cr using the stoichiometry of the reaction.



Electrolysis

SOLUTION

1. mol e^-

$$6.00 \text{ A} = 6.00 \text{ C/s}$$

$$6.00 \frac{\text{C}}{\text{s}} \times (48 \times 60)\text{s} \times \frac{1 \text{ mol } e^-}{9.648 \times 10^4 \text{ C}} = 0.179 \text{ mol } e^-$$

2. Mass Cr

$$0.179 \text{ mol } e^- \times \frac{2 \text{ mol Cr}}{12 \text{ mol } e^-} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 1.55 \text{ g}$$

b

ANALYSIS

Information given:

reduction half-reaction: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 12e^- \longrightarrow 2\text{Cr}(\text{s}) + 7\text{H}_2\text{O}$
current (6.00 A); voltage (4.5 V)
 $\text{K}_2\text{Cr}_2\text{O}_7$: V (0.215 L); M (1.25)

Information implied:

$$1 \text{ C} = 1\text{A} \cdot \text{s}$$

Asked for:

time

continued

Electrolysis

STRATEGY

1. Since V and M are given for $K_2Cr_2O_7$ (thus for $Cr_2O_7^{2-}$), you have enough information to convert to mole e^- using the stoichiometry of the reaction.

$$V \times M \longrightarrow \text{mol } Cr_2O_7^{2-} \xrightarrow{12 \text{ mol } e^- / 1 \text{ mol } Cr_2O_7^{2-}} \text{mol } e^-$$

2. Convert mol e^- to coulombs.

$$\text{mol } e^- \xrightarrow{9.648 \times 10^4 \text{ C} / 1 \text{ mol } e^-} \text{coulombs}$$

3. Convert coulomb to time. Recall $1 \text{ A} = 1 \text{ C/s}$.

SOLUTION

1. mol e^-

$$(0.215 \text{ L})(1.25 \text{ mol/L})(12 \text{ mol } e^- / \text{mol } Cr_2O_7^{2-}) = 3.225 \text{ mol } e^-$$

2. C

$$3.225 \text{ mol } e^- \times \frac{9.648 \times 10^4 \text{ C}}{1 \text{ mol } e^-} = 3.11 \times 10^5 \text{ C}$$

3. Time

$$\text{time} = \frac{3.11 \times 10^5 \text{ C}}{6.00 \text{ C/s}} = 5.16 \times 10^4 \text{ s} = 14.4 \text{ h}$$

Electrolysis

ANALYSIS	
Information given:	reduction half-reaction: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 12 e^- \longrightarrow 2\text{Cr}(\text{s}) + 7\text{H}_2\text{O}$ current (6.00 A); voltage (4.5 V) mass Cr (1.00 g)
Information implied:	1 A = 1 C/s; 1 kWh = 3.600×10^6 J; 1 J = 1 C · V MM for Cr
Asked for:	kilowatt-hours
STRATEGY	
1. Convert the mass of Cr to mol e^- using stoichiometry	
$\text{mass Cr} \xrightarrow{\text{MM}} \text{mol Cr} \xrightarrow{2 \text{ mol Cr}/12 \text{ mol } e^-} \text{mol } e^-$	
2. Find kWh by finding the energy in joules ($C \times V$) and then convert to kWh ($3.600 \times 10^6 \text{ J} = 1 \text{ kWh}$)	
$\text{mol } e^- \xrightarrow{1 \text{ mol } e^- = 9.648 \times 10^4 \text{ C}} \text{coulomb (C)} \xrightarrow{\text{V}} \text{C} \cdot \text{V} \longrightarrow \text{J} \longrightarrow \text{kWh}$	
SOLUTION	
1. mol e^-	$1.00 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g}} \times \frac{12 \text{ mol } e^-}{2 \text{ mol Cr}} = 0.115$
2. kWh	$0.115 \text{ mol } e^- \times \frac{9.648 \times 10^4 \text{ C}}{1 \text{ mol } e^-} \times 4.5 \text{ V} \times \frac{1 \text{ J}}{1 \text{ C} \cdot \text{V}} \times \frac{1 \text{ kWh}}{3.600 \times 10^6 \text{ J}} = 0.014 \text{ kWh}$
END POINTS	
1. Note that whether you are given data to determine the moles of a species in a reaction or the coulombs of electricity, you can get to moles of electrons.	
2. The value given for the voltage used is irrelevant for parts (a) and (b). You only need it to find the number of kilowatt hours.	