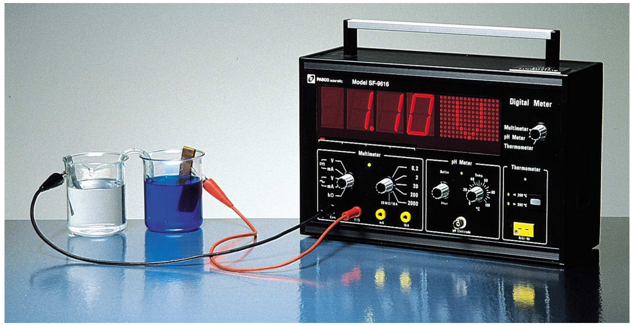


Chapter 17

Electrochemistry

Chapter 17 Preview

Electrochemistry

- Galvanic Cells

  Cell potential, Standard reduction potentials, Complete description of a galvanic cell, Electrical Work and Free Energy
- Dependence of cell potential on concentration

  Concentration cells, Nernst Equation, Ion-selective electrodes, Calculations of equilibrium constant for Redox reactions
- Applications: Batteries and Corrosion

  Lead storage battery, other batteries, fuel cells, Corrosion of iron, prevention of corrosion
- Electrolysis and commercial electrolytic processes

  Electrolysis of water and of mixtures of ions, production of Aluminum, electro-refining of metals and metal plating.

Introduction: Redox reaction

Electrochemical processes are oxidation-reduction (Redox) reactions in which:

- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur

$$2\overset{0}{\mathrm{Mg}}\ (s) + \overset{0}{\mathrm{O}_2}\ (g) \longrightarrow 2\overset{2+}{\mathrm{Mg}}\overset{2-}{\mathrm{O}}\ (s)$$

$2Mg \longrightarrow 2Mg^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$O_2 + 4e^- \longrightarrow 2O^{2-}$ ***Reduction*** half-reaction (gain e^-)

Review: Oxidation number

(Chapter 4)

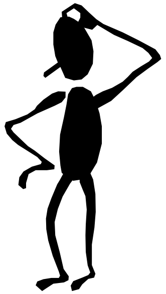
The charge on the atom in a molecule (or an ionic compound), if electrons were completely transferred.

1. Elements (uncombined state) have an oxidation number of zero.

$$Na, Be, K, Pb, H_2, O_2, P_4 = 0$$

2. In monatomic ions, the oxidation number is equal to the charge on the ion.

$$Li^+, Li = +1; Fe^{3+}, Fe = +3; O^{2-}, O = -2$$



Find the oxidation numbers of all the atoms in HCO_3^- ?

HCO_3^-

$O = -2 \quad H = +1$

$3x(-2) + 1 + ? = -1$

$C = +4$

Review: Balancing Redox Equations

The oxidation of Fe^{2+} to Fe^{3+} by $Cr_2O_7^{2-}$ in acid solution?

1. Write the unbalanced equation for the reaction ion ionic form.

$$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$$

2. Separate the equation into two half-reactions.

Oxidation: $\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$

Reduction: $\overset{+6}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}}$

3. Balance the atoms other than O and H in each half-reaction.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

Review: Balancing Redox Equations

4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.

$$Fe^{2+} \longrightarrow Fe^{3+} + \boxed{1e^-}$$

$$\boxed{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Review: Balancing Redox Equations

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

Oxidation: $6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^-}$

Reduction: $\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

8. Verify that the number of atoms and the charges are balanced.

$$14 \times 1 - 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3$$

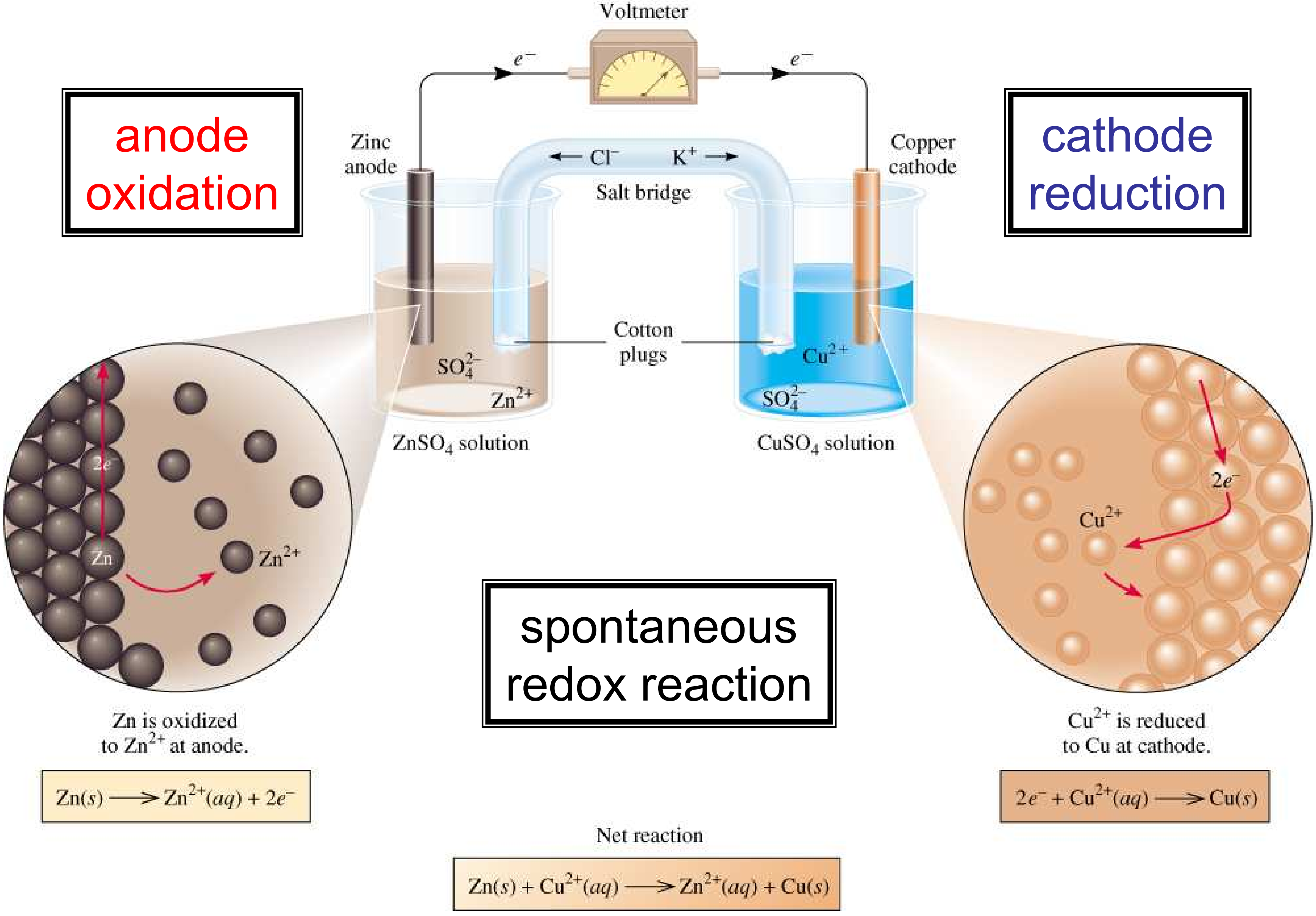
9. For reactions in basic solutions, add OH^- to **both sides** of the equation for every H^+ that appears in the final equation.

17.1 Galvanic Cells

anode
oxidation

cathode
reduction

spontaneous
redox reaction



Zn is oxidized to Zn^{2+} at anode.

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

Cu^{2+} is reduced to Cu at cathode.

$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$

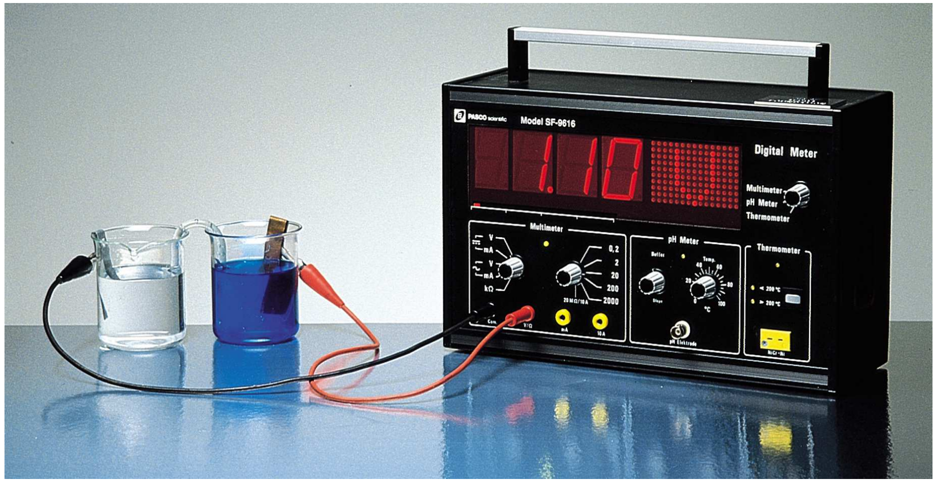
Net reaction

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

17.1 Galvanic Cells

The difference in electrical potential between the anode and cathode is called:

- ***cell voltage***
- ***electromotive force (emf)***
- ***cell potential***



Cell Diagram

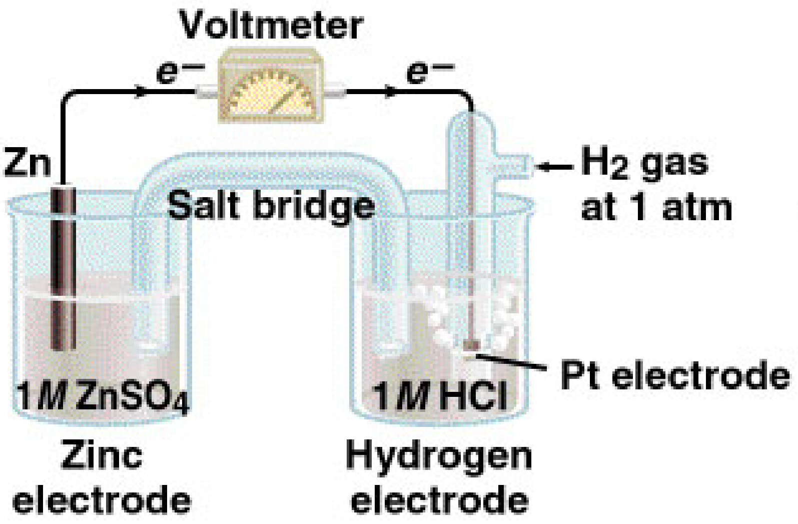
$$\text{Zn}\ (s) + \text{Cu}^{2+}\ (aq) \longrightarrow \text{Cu}\ (s) + \text{Zn}^{2+}\ (aq)$$

$$[\text{Cu}^{2+}] = 1\ M\ \&\ [\text{Zn}^{2+}] = 1\ M$$

$$\text{Zn}\ (s)\ |\ \text{Zn}^{2+}\ (1\ M)\ ||\ \text{Cu}^{2+}\ (1\ M)\ |\ \text{Cu}\ (s)$$

anode cathode

17.1 Galvanic Cells



$$\text{Zn}\ (s)\ |\ \text{Zn}^{2+}\ (1\ M)\ ||\ \text{H}^{+}\ (1\ M)\ |\ \text{H}_2\ (1\ \text{atm})\ |\ \text{Pt}\ (s)$$

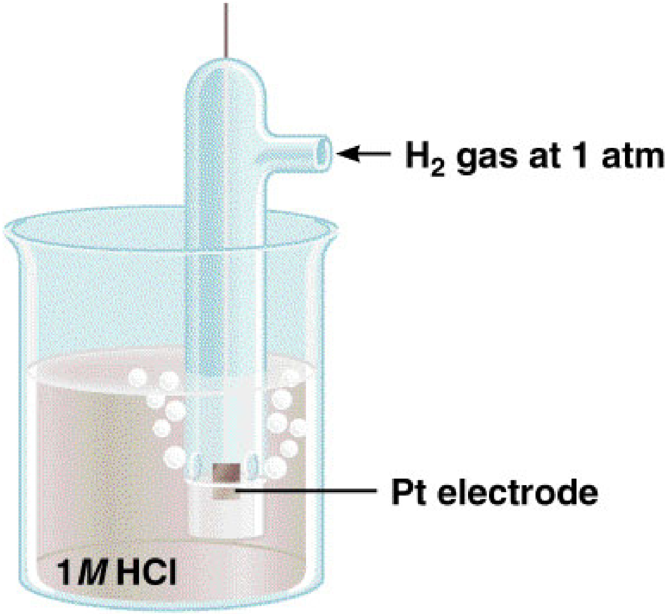
Anode (oxidation): $\text{Zn}\ (s) \longrightarrow \text{Zn}^{2+}\ (1\ M) + 2e^{-}$

Cathode (reduction): $2e^{-} + 2\text{H}^{+}\ (1\ M) \longrightarrow \text{H}_2\ (1\ atm)$

$$\text{Zn}\ (s) + 2\text{H}^{+}\ (1\ M) \longrightarrow \text{Zn}^{2+} + \text{H}_2\ (1\ atm)$$

17.2 Standard Electrode Potentials

Standard reduction potential (E^0) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.



Reduction Reaction

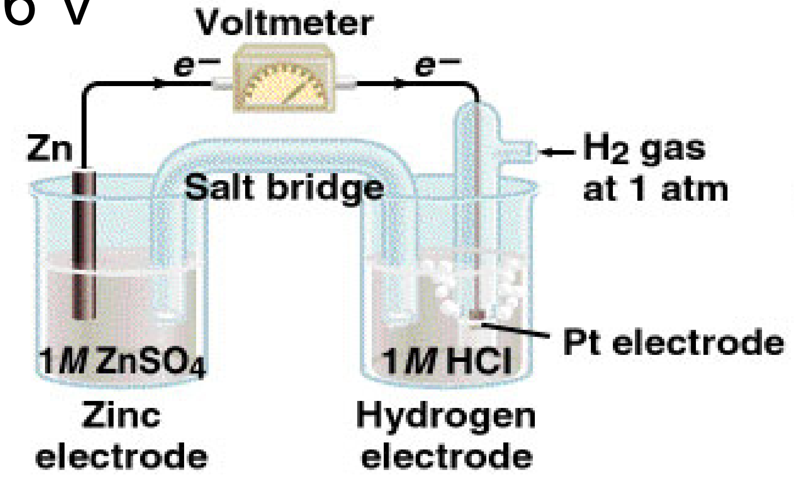
$$2e^- + 2H^+ (1\ M) \longrightarrow H_2\ (1\ atm)$$

$$E^0 = 0\ V$$

Standard hydrogen electrode (SHE)

17.2 Standard Electrode Potentials

$E^0_{cell} = 0.76\ V$



Standard emf (E^0_{cell})

$$\boxed{E^0_{cell} = E^0_{cathode} - E^0_{anode}}$$

Zn (s) | Zn^{2+} (1 M) || H^+ (1 M) | H_2 (1 atm) | Pt (s)

$$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}$$

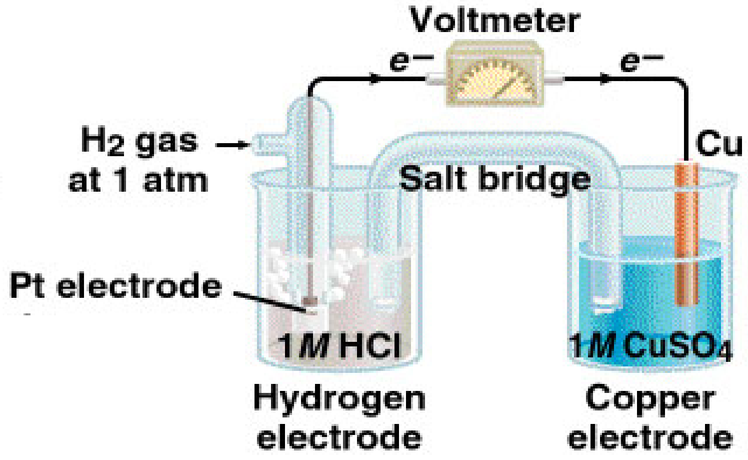
$$0.76\ V = 0 - E^0_{Zn^{2+}/Zn}$$

$$E^0_{Zn^{2+}/Zn} = -0.76\ V$$

$$Zn^{2+}\ (1\ M) + 2e^- \longrightarrow Zn \qquad E^0 = -0.76\ V$$

17.2 Standard Electrode Potentials

$E^0_{cell} = 0.34$ V



$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{H^+/H_2}$$

$$0.34 = E^0_{Cu^{2+}/Cu} - 0$$

$$E^0_{Cu^{2+}/Cu} = 0.34 \text{ V}$$

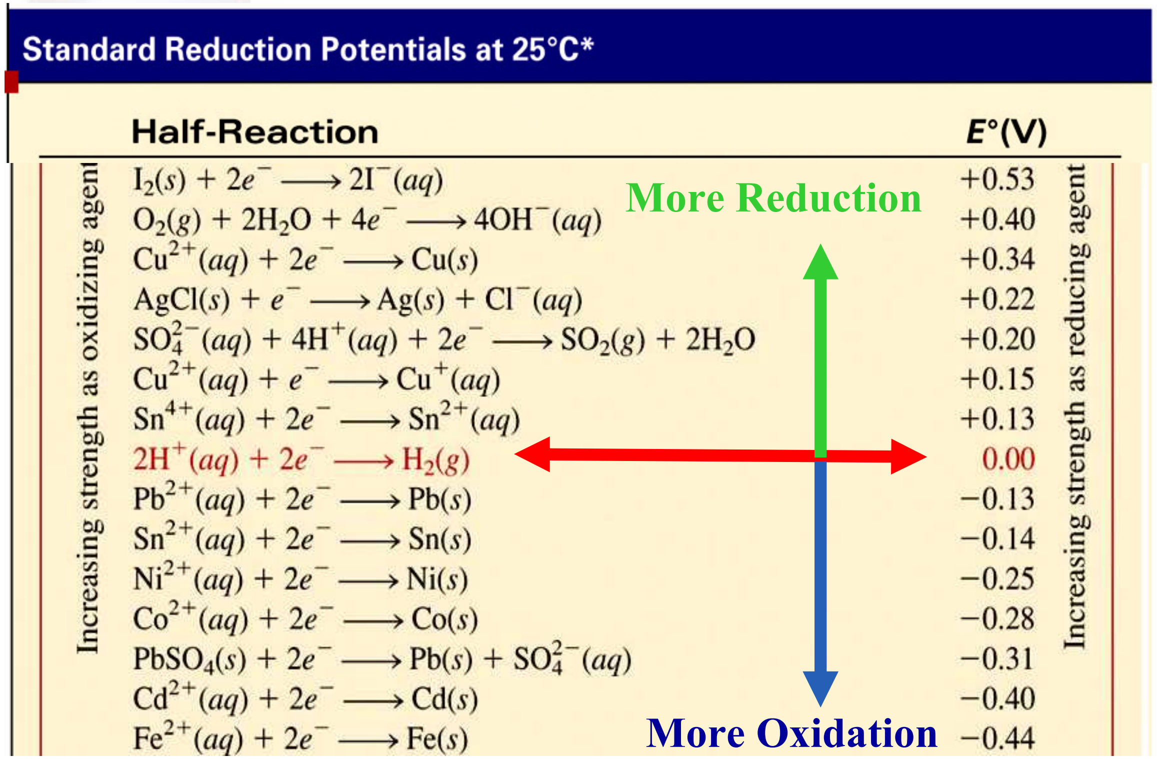
Pt (s) | H_2 (1 atm) | H^+ (1 M) || Cu^{2+} (1 M) | Cu (s)

Anode (oxidation): $H_2 \text{ (1 } atm) \longrightarrow 2H^+ \text{ (1 } M) + 2e^-$

Cathode (reduction): $2e^- + Cu^{2+} \text{ (1 } M) \longrightarrow Cu \text{ (s)}$

$$H_2 \text{ (1 } atm) + Cu^{2+} \text{ (1 } M) \longrightarrow Cu\ (s) + 2H^+ \text{ (1 } M)$$

17.2 Standard Electrode Potentials

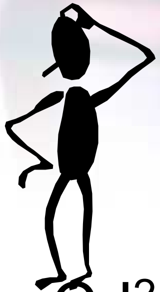


Standard Reduction Potentials at 25°C*

Half-Reaction	$E°$(V)
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44

- *E^0* is for the reaction as written
- The more positive *E^0* the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of *E^0* changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of *E^0*

Review Exercise



What is the standard emf of an electrochemical cell made of a Cd electrode in a 1.0 *M* $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 *M* $Cr(NO_3)_3$ solution?

$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s) \quad E^0 = -0.40\text{ V}$ Cd is the stronger oxidizer

$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s) \quad E^0 = -0.74\text{ V}$ Cd will oxidize Cr

Anode (oxidation): $Cr(s) \longrightarrow Cr^{3+}(1\,M) + \boxed{3e^-} \quad \times 2$

Cathode (reduction): $\boxed{2e^-} + Cd^{2+}(1\,M) \longrightarrow Cd(s) \quad \times 3$

$$2Cr(s) + 3Cd^{2+}(1\,M) \longrightarrow 3Cd(s) + 2Cr^{3+}(1\,M)$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.40 - (-0.74)$$

$$E^0_{cell} = 0.34\text{ V}$$

QUESTION

Choice 3 The standard reduction potentials listed in the table for each metal will have to be reversed since the question concerns the metal being oxidized while H+ is being reduced. Then the determined voltage for the oxidation would be added to the reduction potential for $2\ H^+ + 2e^- \rightarrow H_2\ (g)$. Only two metals produce a positive voltage (which would indicate a spontaneous reaction) – Al and Sn.

Ag; Cu; Sn; Al

1. All would react
2. Ag; Sn; Al would react
3. Only Sn and Al would react
4. Only Ag and Cu would react

QUESTION

A galvanic cell made with the two half cells $Au^{3+} + 3e^- \rightarrow Au$ ($E° = 1.50$ V) and $IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2} I_2 + 3H_2O$ ($E° = 1.20$V). When the total reaction is put together and balanced, how many gold atoms would be involved and what would be the predicted $E°$ for the cell?

1. 1 gold atom; $E° = 0.30$ V
2. 3 gold atoms; $E° = 1.50$ V
3. 15 gold atoms; $E° = 3.90$ V
4. 5 gold atoms; $E° = 0.30$ V

Choice 4: This can be obtained by finding a common multiple (15) and multiplying each half-reaction appropriately to reach 15. The gold reaction is slightly more positive (at standard conditions) so the iodate reaction must be reversed before combining their $E°$ values to determine the cell $E°$.

17.3 Cell Potential, Work, and Free Energy

Relationships among $\Delta G°$, K, and $E°_{cell}$

$\Delta G°$	K	$E°_{cell}$	Reaction under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

$$\text{potential difference (V)} = E_{cell} = \frac{work(J)}{charge(C)} = \frac{-w}{q}$$

E and *w* have opposite signs (work by motor) and *q* is the charge of 1 mole of electrons, i.e., Faraday (*F*) constant, thus the w_{max}

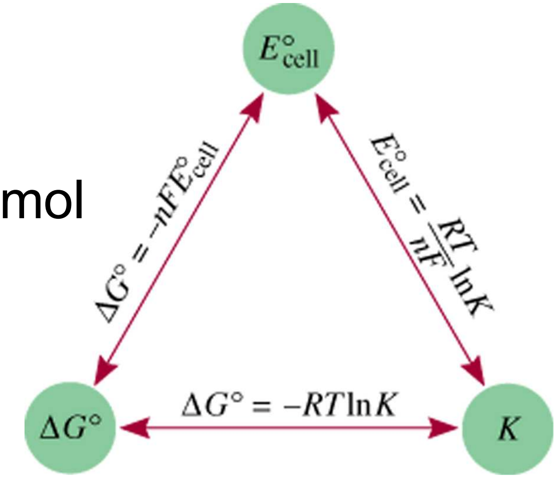
$$w_{max} = \Delta G = -qE = -nFE_{cell}$$

n = number of moles of electrons in reaction and

$$F = 96{,}500 \ \frac{\text{J}}{\text{V} \cdot \text{mol}} = 96{,}500 \text{ C/mol}$$

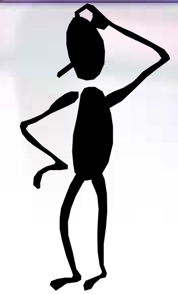
For standard condition: $\Delta G^0 = -nFE^0_{cell}$

$$\Delta G^0 = -RT \ln K = -nFE^0_{cell}$$



$$E^0_{cell} = \frac{RT}{nF}\ln K = \frac{(8.314 \cancel{\text{J}}/\cancel{\text{K}}\cdot\cancel{\text{mol}})(298\ \cancel{\text{K}})}{n\ (96{,}500\ \cancel{\text{J}}/\text{V}\cdot\cancel{\text{mol}})} \ln K = \frac{0.0592\ \text{V}}{n} \log K$$

Review Exercise



What is the equilibrium constant for the following reaction at 25^0C? $Fe^{2+}\ (aq) + 2Ag\ (s) \rightleftharpoons Fe\ (s) + 2Ag^+\ (aq)$

$$E^0_{cell} = \frac{0.0257\ V}{n} \ln K$$

Oxidation: $2Ag \longrightarrow 2Ag^+ + \boxed{2e^-}$

Reduction: $\boxed{2e^-} + Fe^{2+} \longrightarrow Fe$

$n = 2$

$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Ag^+/Ag}$

$E^0 = -0.44 - (0.80)$

$E^0 = -1.24\ V$

$$K = \exp\left[\frac{E^0_{cell} \times n}{0.0257\ V}\right] = \exp\left[\frac{-1.24\ V \times 2}{0.0257\ V}\right]$$

$K = 1.23 \times 10^{-42}$

QUESTION

Using the Standard Reduction Potential table, determine the free energy change for the reaction in a cell made from the following:

$$\mathrm{Zn}\ (s)|\ \mathrm{Zn}^{2+}\ (aq)\ ||\ \mathrm{Cr}^{3+}\ (aq)\ |\ \mathrm{Cr}\ (s)$$

1. –17 000 J
2. –2 900 J
3. 8 700 J
4. –830 000 J

Choice 1 Combining the two half-cell voltages produces 0.03 V. To account for the stoichiometry, the Cr^{3+} half-cell will have to be multiplied by 2 while the Zn^{2+} half-cell will have to be multiplied by 3. Therefore, the total moles of e^{-} will be six for this reaction.

17.4 Dependence of Cell Emf On Concentration

$\Delta G = \Delta G^0 + RT \ln Q$ $\Delta G = -nFE$ $\Delta G^0 = -nFE^0$

$$-nFE = -nFE^0 + RT \ln Q$$

Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln Q$$

At 298

$$E = E^0 - \frac{0.0257\text{ V}}{n} \ln Q \qquad E = E^0 - \frac{0.0592\text{ V}}{n} \log Q$$

Review Exercise

Will the following reaction occur spontaneously at 25^0C if $[Fe^{2+}] = 0.60\ M$ and $[Cd^{2+}] = 0.010\ M$?

$$Fe^{2+}\ (aq) + Cd\ (s) \rightleftharpoons Fe\ (s) + Cd^{2+}\ (aq)$$

Oxidation: $Cd \longrightarrow Cd^{2+} + \boxed{2e^-}$

Reduction: $\boxed{2e^-} + Fe^{2+} \longrightarrow 2Fe$

$n = 2$

$$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Cd^{2+}/Cd}$$

$$E^0 = -0.44 - (-0.40)$$

$$E^0 = -0.04\ V$$

$$E = E^0 - \frac{0.0257\ V}{n} \ln Q$$

$$E = -0.04\ V - \frac{0.0257\ V}{2} \ln \frac{0.010}{0.60}$$

$$E = 0.013$$

$E > 0$ Spontaneous

QUESTION

Cells in which both compartments of the galvanic cell contain the same ion are called <u>concentration cells</u>. If such a cell were constructed with the $[Ag^+]$ in one cell at 0.050 M and the other at .0050 M, what would be the predicted voltage at 25°C?

$$E° \text{ for } Ag^+ + e^- \rightarrow Ag\ (s) = 0.80 \text{ V}$$

1. 0.0591 V
2. 0.94 V
3. 0.66 V

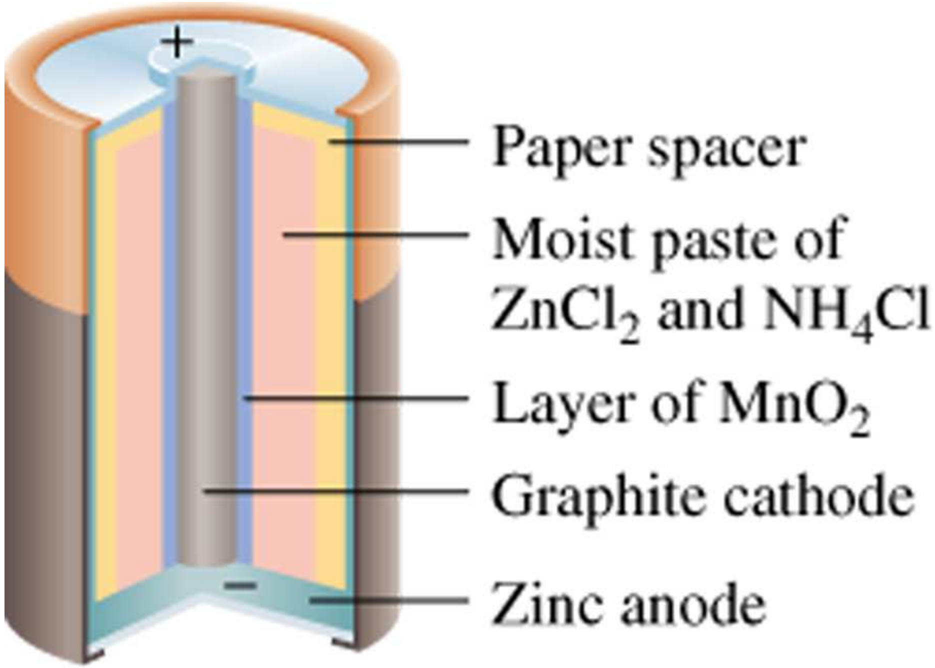
Choice 1: Recall that the flow of electrons from reactant to product will be from the lower to the higher ion concentration. Applying the Nernst equation to this one electron change reaction with the *P*/*R* ratio of 0.005 0/0.050 will produce 0.059 1 V.

$$(E = 0 - 0.059\,1 \log (0.005\,0/0.050))$$

17.5 Batteries

Dry cell

Leclanché cell



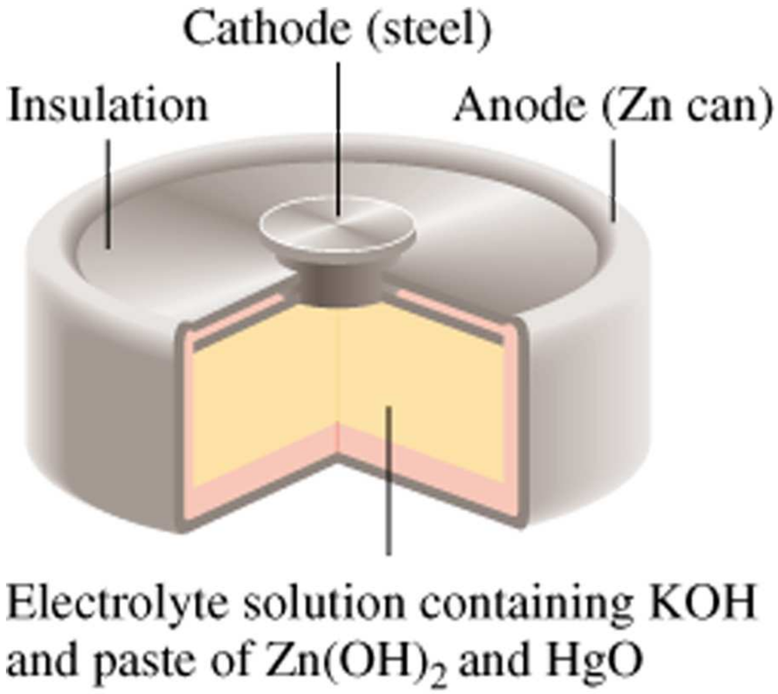
Anode: $Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-$

Cathode: $2NH_4^+\ (aq) + 2MnO_2\ (s) + 2e^- \longrightarrow Mn_2O_3\ (s) + 2NH_3\ (aq) + H_2O\ (l)$

$Zn\ (s) + 2NH_4\ (aq) + 2MnO_2\ (s) \longrightarrow Zn^{2+}\ (aq) + 2NH_3\ (aq) + H_2O\ (l) + Mn_2O_3\ (s)$

17.5 Batteries

Mercury Battery



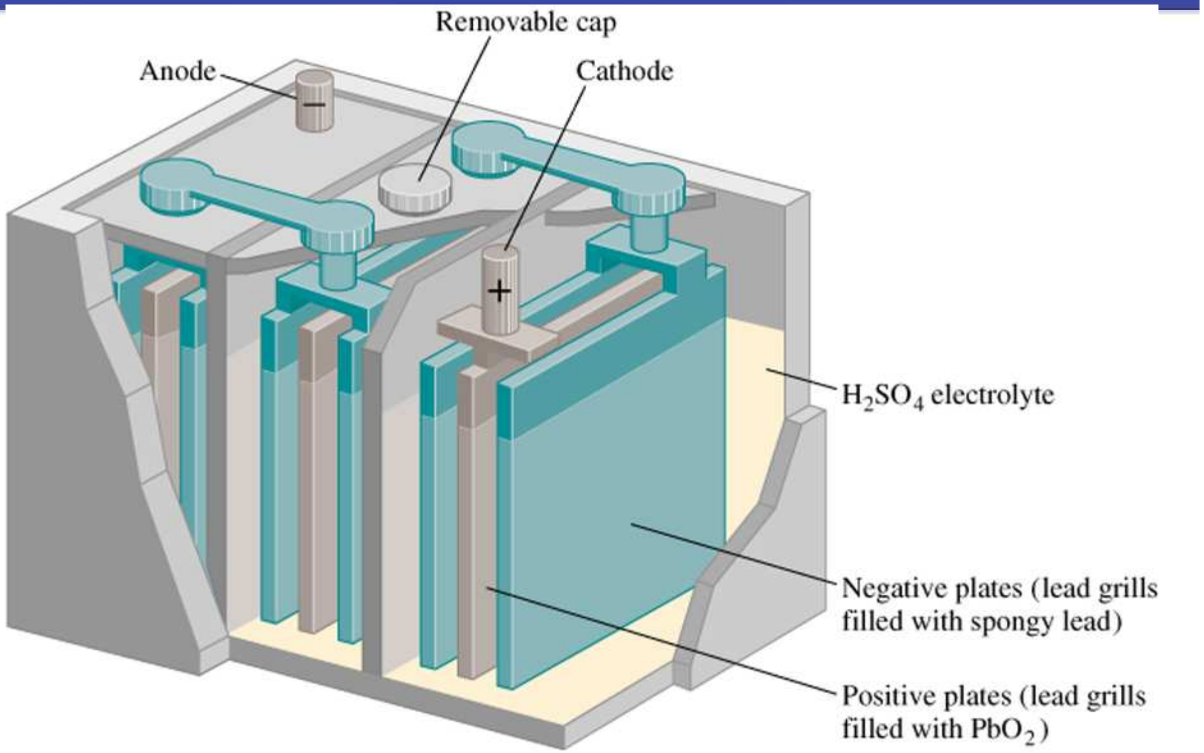
Anode: $Zn(Hg) + 2OH^- (aq) \longrightarrow ZnO (s) + H_2O (l) + 2e^-$

Cathode: $HgO (s) + H_2O (l) + 2e^- \longrightarrow Hg (l) + 2OH^- (aq)$

$Zn(Hg) + HgO (s) \longrightarrow ZnO (s) + Hg (l)$

17.5 Batteries

Lead storage battery

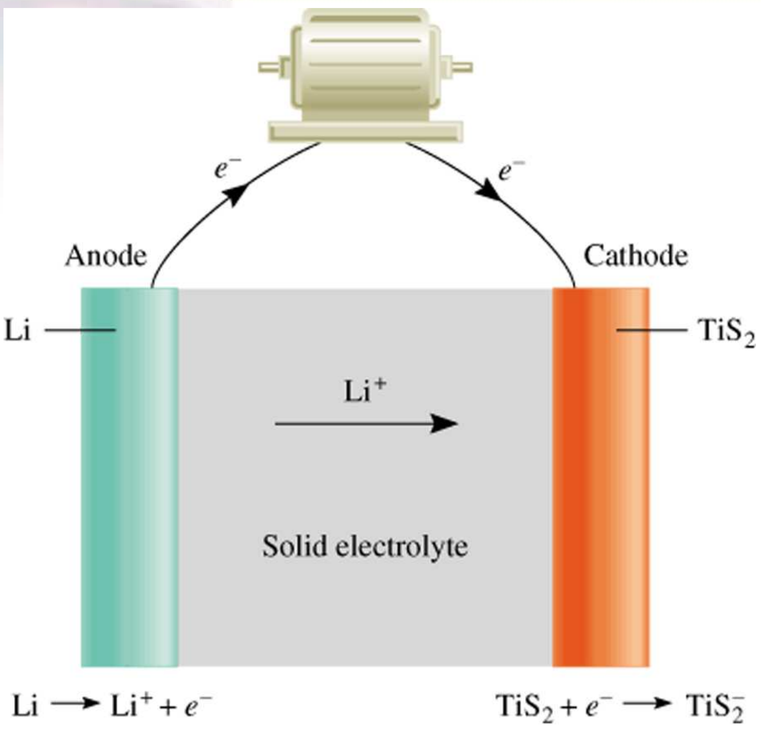


Anode: $Pb\ (s) + SO_4^{2-}\ (aq) \longrightarrow PbSO_4\ (s) + 2e^-$

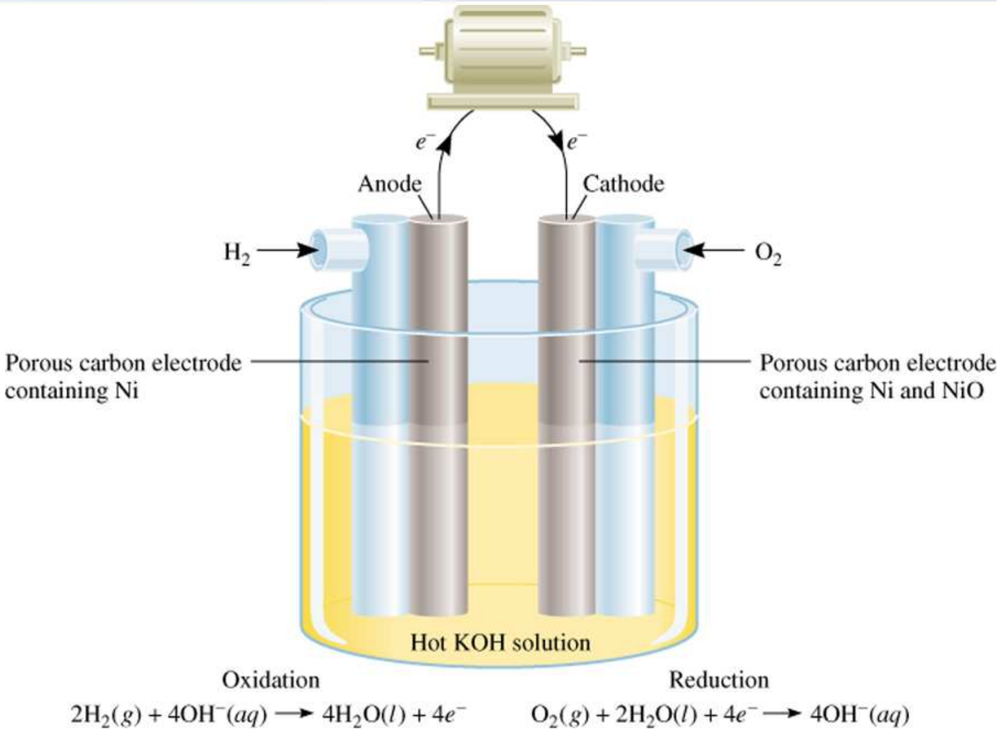
Cathode: $PbO_2\ (s) + 4H^+\ (aq) + SO_4^{2-}\ (aq) + 2e^- \longrightarrow PbSO_4\ (s) + 2H_2O\ (l)$

$$Pb\ (s) + PbO_2\ (s) + 4H^+\ (aq) + 2SO_4^{2-}\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$$

17.5 Batteries



Solid State Lithium Battery



fuel cell requires a continuous supply of reactants to keep functioning

fuel cell

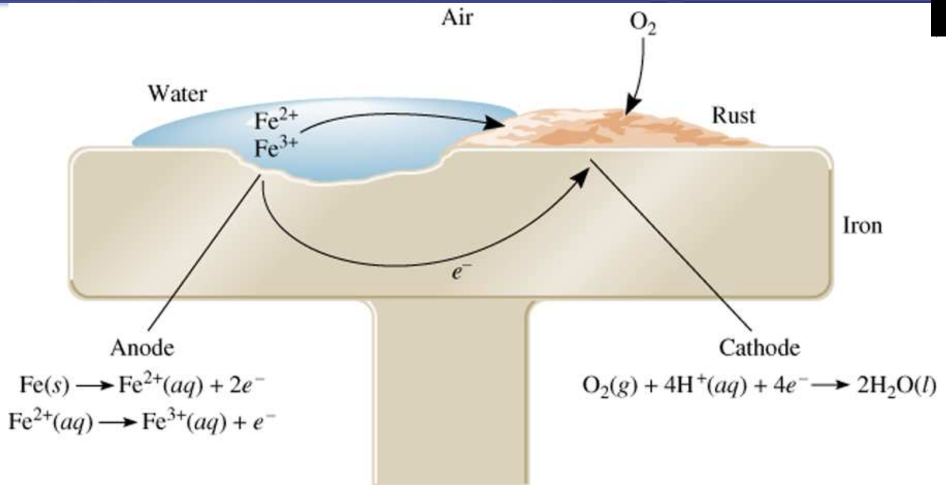
Anode: $2H_2\ (g) + 4OH^-\ (aq) \longrightarrow 4H_2O\ (l) + 4e^-$

Cathode: $O_2\ (g) + 2H_2O\ (l) + 4e^- \longrightarrow 4OH^-\ (aq)$

$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l)$

17.6 Corrosion

Iron Corrosion



But where's the rust?

As the iron corrodes, the pH in the droplet rises. Hydroxide ions (OH^-) appear that react with the iron(II) and/or iron(III) ions:

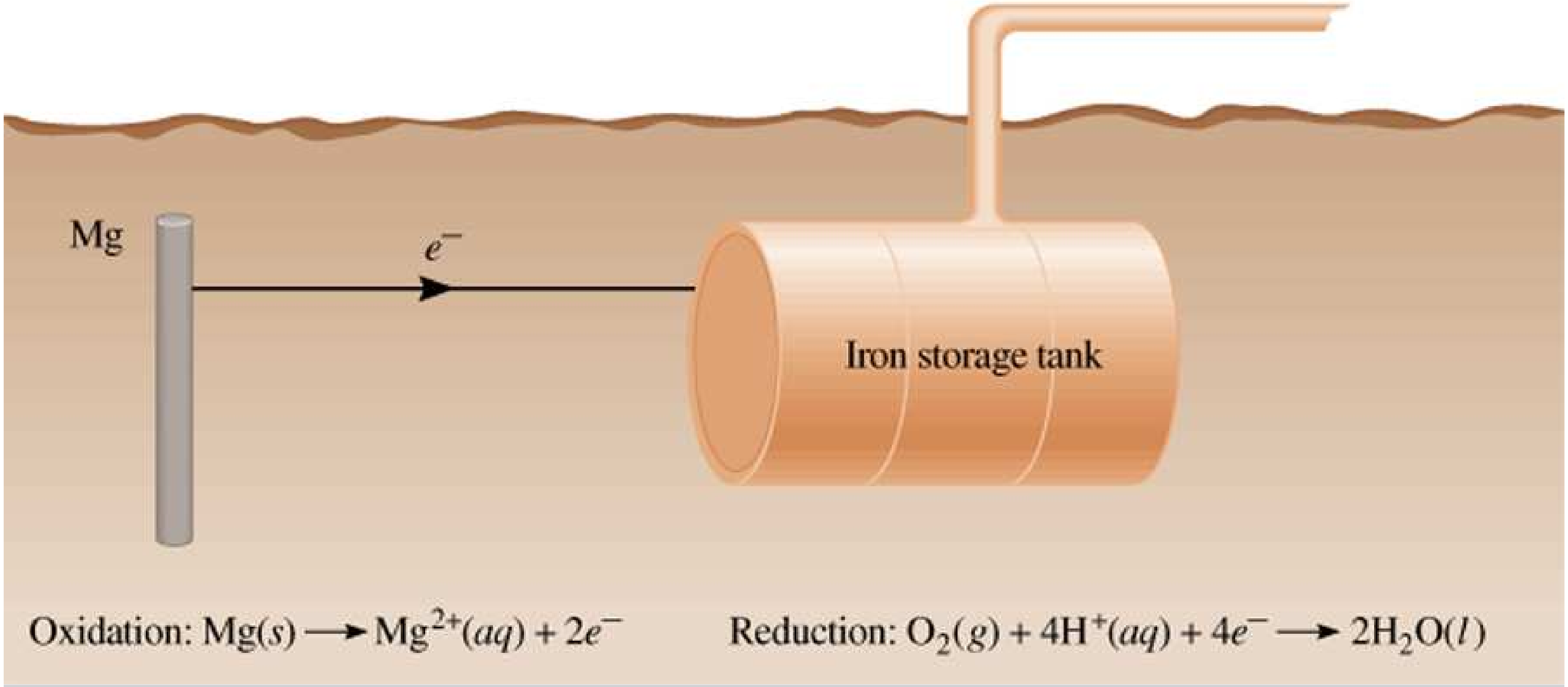
$$Fe^{2+}(aq) + 2\,OH^-(aq) \rightleftharpoons Fe(OH)_2(s)$$

$$Fe^{3+}(aq) + 3\,OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$$

These can dry to make plain iron(III) oxide, Fe_2O_3. This is the red, powdery stuff we call "rust".

17.6 Corrosion

Cathodic Protection of an Iron Storage Tank



Oxidation: $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

QUESTION

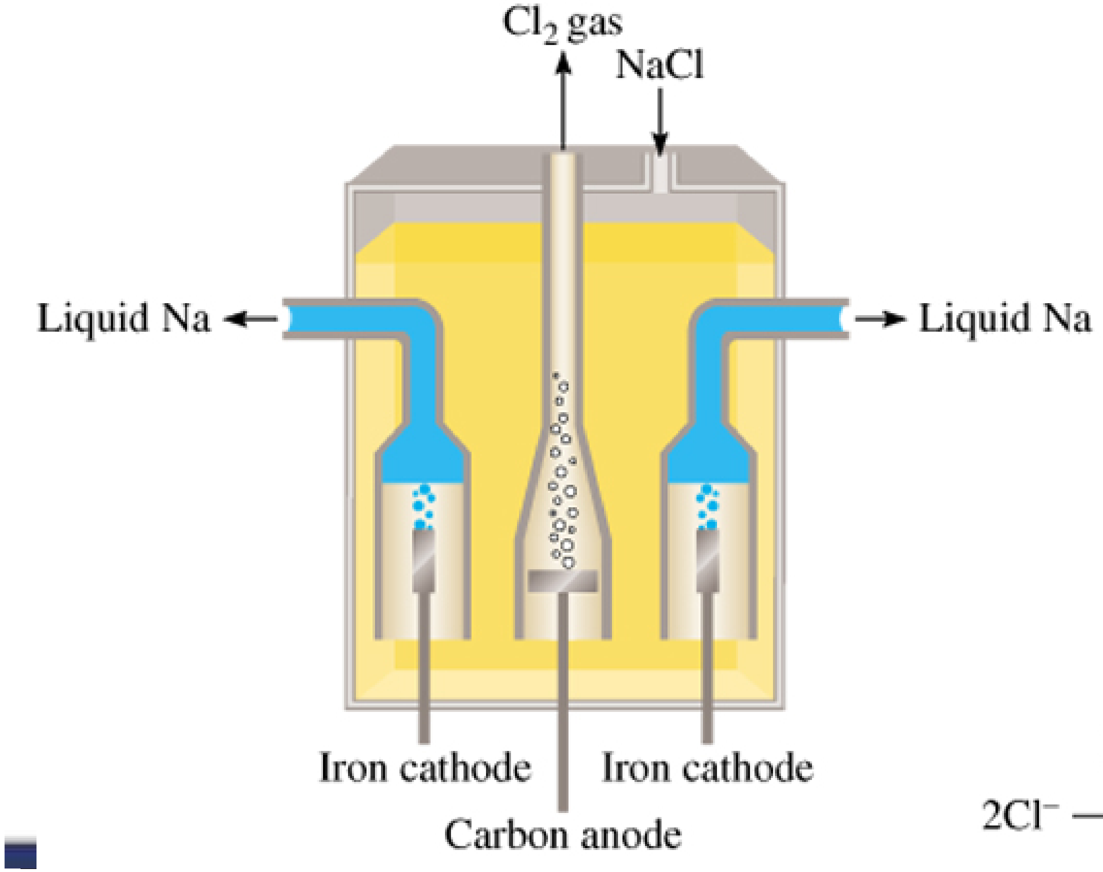
For cathodic protection used to prevent corrosion of iron to be effective which of the following must be true?

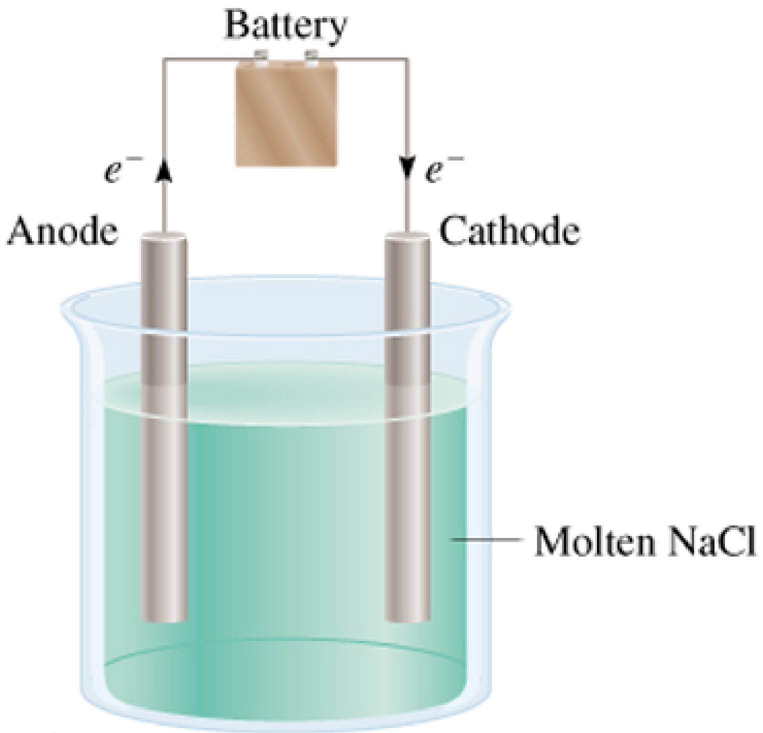
1. The anode used must be a better oxidizing agent than iron.
2. The sacrificial anode used must react with oxygen to protect the iron from reacting with oxygen.
3. Iron must have a reduction potential than the metal used as the anode.
4. In cathodic protection systems a metal is attached or connected to iron in such a way that electrons flow away from the iron.

Choice 3 correctly explains the set up for cathodic protection of iron. To cathodically protect iron from corrosion means to allow another metal, in contact with the iron sample, to oxidize in place of iron. Thus the other metal sacrifices itself or oxidizes in place of the iron. Only a metal that is a better reducing agent than iron can do this.

17.7 Electrolysis

Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.





Oxidation

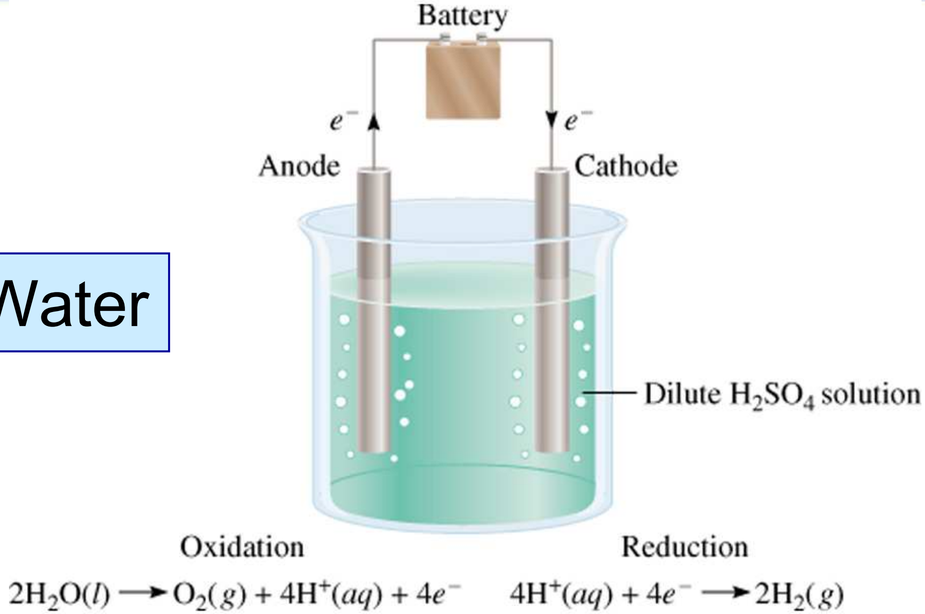
$2Cl^- \longrightarrow Cl_2(g) + 2e^-$

Reduction

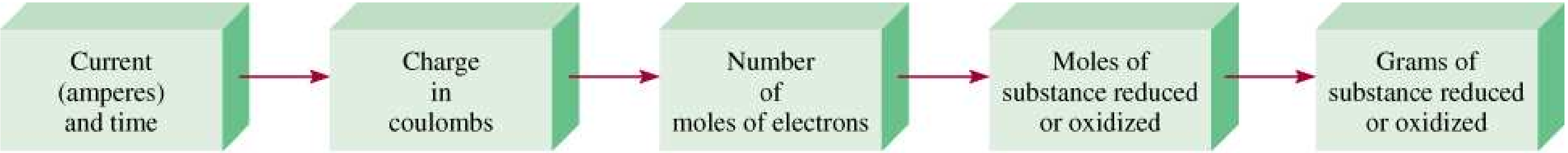
$2Na^+ + 2e^- \longrightarrow 2Na(l)$

17.7 Electrolysis

Electrolysis of Water



Electrolysis and Mass Changes

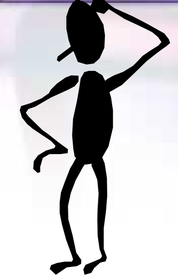


Current (amperes) and time → Charge in coulombs → Number of moles of electrons → Moles of substance reduced or oxidized → Grams of substance reduced or oxidized

charge (C) = current (A) x time (s)

$\boxed{1 \text{ mole } e^- = 96{,}500 \text{ C}}$

Review Exercise



How much Ca will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

Anode: $2Cl^- (l) \longrightarrow Cl_2 (g) + 2e^-$

Cathode: $Ca^{2+} (l) + \boxed{2e^-} \longrightarrow Ca (s)$

$$Ca^{2+} (l) + 2Cl^- (l) \longrightarrow Ca (s) + Cl_2 (g)$$

2 mole e^- = 1 mole Ca

$$\text{mol Ca} = 0.452 \frac{\cancel{C}}{\cancel{s}} \times 1.5\ \cancel{hr} \times 3600 \frac{\cancel{s}}{\cancel{hr}} \times \frac{1\ \cancel{mol}\ e^-}{96{,}500\ \cancel{C}} \times \frac{1\ \text{mol Ca}}{2\ \cancel{mol}\ e^-}$$

= 0.0126 mol Ca

= 0.50 g Ca

QUESTION

If you decided to chrome plate your spatula in chemistry lab, how long would it take to plate out 0.850 grams of Cr (from a solution of Cr^{3+}) if you used a current of 10.0 amps?

1. 473 seconds
2. 158 seconds
3. 1.47 seconds
4. 1 580 seconds

Choice 1 correctly reports the time needed for this plating method. The seconds can be calculated accurately when the +3 charge for the Chromium ion is correctly used.

$$((\text{Grams} \times \text{charge}/\text{grams per mole}) \times 96485)/\text{amps} = \text{seconds}$$

Chemistry In Action: Dental Filling Discomfort

Hg_2^{2+}/Ag_2Hg_3 0.85 V

Sn^{2+}/Ag_3Sn -0.05 V

Sn^{2+}/Ag_3Sn -0.05 V

Corrosion of a Dental Filling