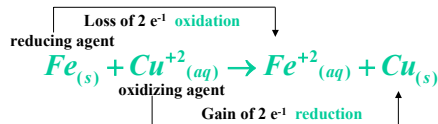


Chapter 17

Electrochemistry

Oxidation-Reduction Reactions

- Describing Oxidation-Reduction Reactions
 - An **oxidizing agent** is a species that oxidizes another species; **it is itself reduced.**
 - A **reducing agent** is a species that reduces another species; **it is itself oxidized.**

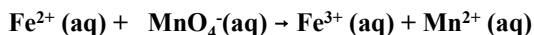


Electrochemistry

- The study of the interchange of chemical and electrical energy.

Skeleton Oxidation-Reduction Equations

- Identify what species is being oxidized (this will be the “reducing agent”)
- Identify what species is being reduced (this will be the “oxidizing agent”)
- What species result from the oxidation and reduction?
- Does the reaction occur in acidic or basic solution?



Review of Terms

- oxidation-reduction (redox) reaction: involves a transfer of electrons from the reducing agent to the oxidizing agent.
- oxidation: loss of electrons
- reduction: gain of electrons

Steps in Balancing Oxidation-Reduction Equations in Acidic solutions

1. Assign oxidation numbers to each atom so that you know what is oxidized and what is reduced
2. Split the skeleton equation into two half-reactions—one for the oxidation reaction (element increases in oxidation number) and one for the reduction (element decreases in oxidation number)

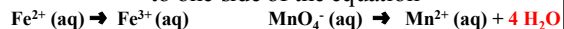


3. Complete and balance each half reaction

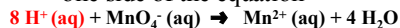
a. Balance all atoms except O and H



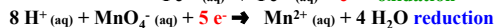
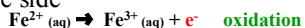
b. Balance O atoms by adding H_2O to one side of the equation



c. Balance H atoms by adding H^+ to one side of the equation



d. Balance the electric charge by adding electrons (e^-) to the more positive side

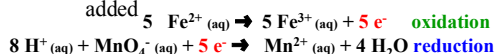


Galvanic Cell (Voltaic Cell)

•A device in which chemical energy is changed to electrical energy.

4. Combine the two half-reactions to obtain the balanced oxidation-reduction equation

a. Multiply each half reaction by a factor which will allow the e^- 's to cancel when the equations are added



b. Simplify the equation by canceling species which occur on both sides of the equation and reduce the coefficients to the smallest whole number. Check

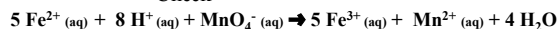
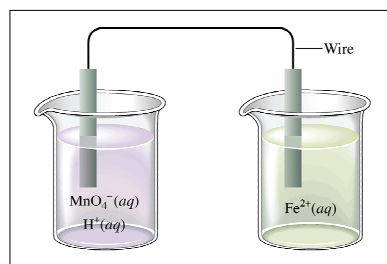


Figure 17.1: Schematic of a method to separate the oxidizing and reducing agents of a redox reaction. (The solutions also contain counterions to balance the charge.)



Additional Steps for Balancing Oxidation-Reduction Equations in Basic Solutions

5. Note the number of H^+ ions in the equation. Add this number of OH^- ions to both sides of the equation

6. Simplify the equation by noting that H^+ reacts with OH^- to give H_2O . Cancel any H_2O 's that occur on both sides of the equation and reduce the equation to simplest terms

Figure 17.2: Galvanic cells can contain a salt bridge as in (a) or a porous-disk connection as in (b).

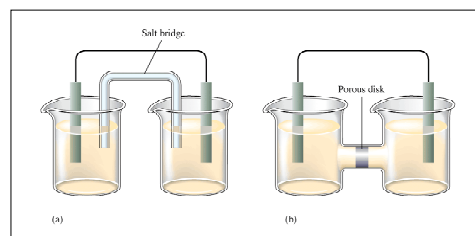
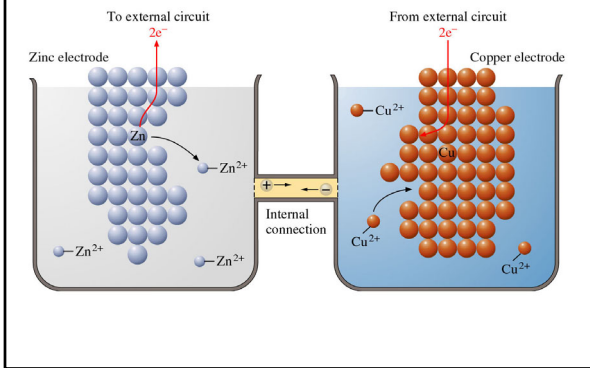
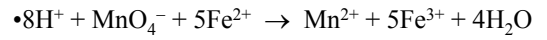


Figure 20.2: Atomic view of voltaic cell.



Half-Reactions

•The overall reaction is split into two half-reactions, one involving oxidation and one reduction.



•Reduction: $8\text{H}^+ + \text{MnO}_4^- + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

•Oxidation: $5\text{Fe}^{2+} \rightarrow 5\text{Fe}^{3+} + 5\text{e}^-$

Anode and Cathode

- **OXIDATION** occurs at the **ANODE**.
- **REDUCTION** occurs at the **CATHODE**.

Figure 17.7: The schematic of a galvanic cell based on the half-reactions

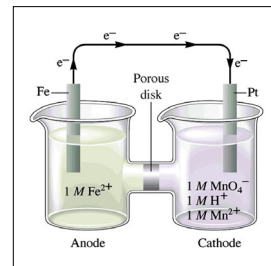
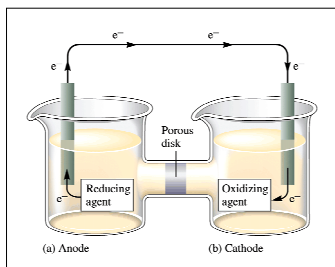


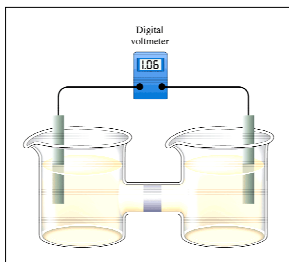
Figure 17.3: An electrochemical process involves electron transfer at the interface between the electrode and the solution. (a) The species in the solution acting as the reducing agent supplies electrons to the anode. (b) The species in the solution acting as the oxidizing agent receives electrons from the cathode.



Cell Potential

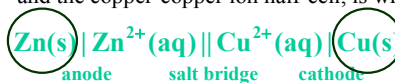
•Cell Potential or Electromotive Force (emf): The “pull” or driving force on the electrons.

Figure 17.4: Digital voltmeters draw only a negligible current and are convenient to use.



Notation for Galvanic Cells

- It is convenient to have a **shorthand** way of designating particular Galvanic cells.
- The cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written



- The cell **terminals** are at the extreme ends in the cell notation.

Notation for Galvanic Cells

- It is convenient to have a **shorthand** way of designating particular Galvanic cells.
- The cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written



- The anode (oxidation half-cell) is written on the left. The cathode (reduction half-cell) is written on the right.

Notation for Galvanic Cells

- It is convenient to have a **shorthand** way of designating particular Galvanic cells.
- The cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written



- A single vertical bar indicates a phase boundary, such as between a solid terminal and the electrode solution.

Notation for Galvanic Cells

- It is convenient to have a **shorthand** way of designating particular Galvanic cells.
- The cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written



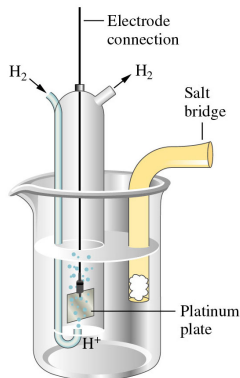
- The two electrodes are connected by a salt bridge, denoted by two vertical bars.

Notation for Galvanic Cells

- When the **half-reaction involves a gas**, an inert material such as platinum serves as a terminal and an electrode surface on which the reaction occurs.
- Figure 20.5 shows a **hydrogen electrode**: hydrogen bubbles over a platinum plate immersed in an acidic solution.
- The cathode half-reaction is



Figure 20.5: A hydrogen electrode.



[Return to slide 50](#)

Notation for Galvanic Cells

- To fully specify a voltaic cell, it is necessary to give the **concentrations of solutions** and the **pressure of gases**.
 - In the cell notation, these are written in parentheses. For example,



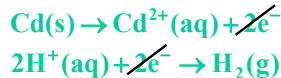
Notation for Galvanic Cells

- When the **half-reaction involves a gas**, an inert material such as platinum serves as a terminal and an electrode surface on which the reaction occurs.
- The notation for the hydrogen electrode, written as a cathode, is



A Problem To Consider

- Give the overall cell reaction for the Galvanic cell $\text{Cd(s)} | \text{Cd}^{2+}(\text{1.0 M}) || \text{H}^+(\text{aq}) | \text{H}_2(\text{1.0 atm}) | \text{Pt}$
- The half-cell reactions are



Notation for Galvanic Cells

- When the **half-reaction involves a gas**, an inert material such as platinum serves as a terminal and an electrode surface on which the reaction occurs.
 - To write such an electrode as an anode, you simply reverse the notation.



Standard Cell emf's and Standard Electrode Potentials

- A **cell emf** is a measure of the driving force of the cell reaction.
 - A **reduction potential** is a measure of the tendency to gain electrons in the reduction half-reaction. The oxidation state of the reactant becomes less positive.
 - The **oxidation potential** for an oxidation half-reaction is the negative of the reduction potential for the reverse reaction.

Standard Cell emf's and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (Table 17.1) are tabulated as **reduction** potentials.
- Consider the zinc-copper cell described earlier.



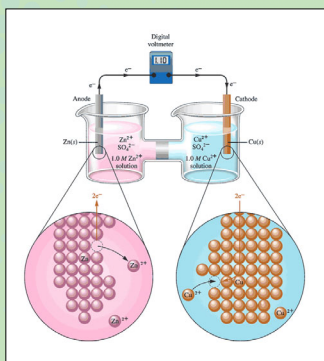
- The two half-reactions are



TABLE 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	E° (V)	Half-Reaction	E° (V)
F ₂ + 2e ⁻ → 2F ⁻	2.87	O ₂ + 2H ₂ O + 4e ⁻ → 4OH ⁻	0.40
Ag ⁺ + e ⁻ → Ag(s)	1.99	Cu ²⁺ + 2e ⁻ → Cu	0.34
Co ³⁺ + e ⁻ → Co ²⁺	1.82	Hg ₂ Cl ₂ + 2e ⁻ → 2Hg + 2Cl ⁻	0.27
H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O	1.78	AgCl + e ⁻ → Ag + Cl ⁻	0.22
Ce ⁴⁺ + e ⁻ → Ce ³⁺	1.70	SO ₄ ²⁻ + 4H ⁺ + 2e ⁻ → H ₂ SO ₃ + H ₂ O	0.20
PSO ₄ + 4H ⁺ + SO ₄ ²⁻ + 2e ⁻ → P(SO ₃) ₂ + 2H ₂ O	1.69	Cu ²⁺ + e ⁻ → Cu ⁺	0.16
MnO ₂ + 4H ⁺ + 3e ⁻ → MnO + 2H ₂ O	1.68	2H ⁺ + 2e ⁻ → H ₂	0.00
2e ⁻ + 2H ⁺ + IO ₃ ⁻ → IO ₂ ⁻ + H ₂ O	1.60	Fe ³⁺ + 3e ⁻ → Fe	-0.036
MnO ₂ + 8H ⁺ + 5e ⁻ → Mn ²⁺ + 4H ₂ O	1.51	Pb ²⁺ + 2e ⁻ → Pb	-0.13
Au ³⁺ + 3e ⁻ → Au	1.50	Sr ²⁺ + 2e ⁻ → Sr	-0.14
PbO ₂ + 4H ⁺ + 2e ⁻ → Pb ²⁺ + 2H ₂ O	1.46	Ni ²⁺ + 2e ⁻ → Ni	-0.23
Cl ₂ + 2e ⁻ → 2Cl ⁻	1.36	PbSO ₄ + 2e ⁻ → Pb + SO ₄ ²⁻	-0.35
CrO ₇ ²⁻ + 14H ⁺ + 6e ⁻ → 2Cr ³⁺ + 7H ₂ O	1.33	Cd ²⁺ + 2e ⁻ → Cd	-0.40
O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	1.23	Fe ²⁺ + 2e ⁻ → Fe	-0.44
MnO ₄ ⁻ + 4H ⁺ + 2e ⁻ → MnO ₂ + 2H ₂ O	1.21	Cr ³⁺ + e ⁻ → Cr ²⁺	-0.50
IO ₃ ⁻ + 6H ⁺ + 5e ⁻ → I ₂ + 3H ₂ O	1.20	Cr ³⁺ + 3e ⁻ → Cr	-0.73
Br ₂ + 2e ⁻ → 2Br ⁻	1.09	Zn ²⁺ + 2e ⁻ → Zn	-0.76
VO ₂ ⁺ + 2H ⁺ + e ⁻ → VO ²⁺ + H ₂ O	1.00	2H ₂ O + 2e ⁻ → H ₂ + 2OH ⁻	-0.83
AuCl ₄ ⁻ + 3e ⁻ → Au + 4Cl ⁻	0.99	Mn ²⁺ + 2e ⁻ → Mn	-1.18
NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO + 2H ₂ O	0.96	Al ³⁺ + 3e ⁻ → Al	-1.66
ClO ₃ ⁻ + e ⁻ → ClO ₂ ⁻	0.954	H ₂ + 2e ⁻ → 2H ⁻	-2.23
2Hg ²⁺ + 2e ⁻ → Hg ₂ ²⁺	0.91	Mg ²⁺ + 2e ⁻ → Mg	-2.37
Ag ⁺ + e ⁻ → Ag	0.80	La ³⁺ + 3e ⁻ → La	-2.37
Hg ₂ ²⁺ + 2e ⁻ → 2Hg	0.80	Na ⁺ + e ⁻ → Na	-2.71
Fe ³⁺ + e ⁻ → Fe ²⁺	0.77	Cd ²⁺ + 2e ⁻ → Cd	-2.76
O ₂ + 2H ⁺ + 2e ⁻ → H ₂ O ₂	0.68	Ba ²⁺ + 2e ⁻ → Ba	-2.90
MnO ₄ ⁻ + e ⁻ → MnO ₄ ²⁻	0.56	K ⁺ + e ⁻ → K	-2.92
I ₂ + 2e ⁻ → 2I ⁻	0.54	Li ⁺ + e ⁻ → Li	-3.05
Cu ⁺ + e ⁻ → Cu	0.52		

Figure 17.6: A galvanic cell involving the half-reactions
 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$ (anode)
 and
 $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$ (cathode),
 with $\xi_{\text{cell}}^{\circ} = 1.10\text{V}$



Standard Cell emf's and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (Table 17.1) are tabulated as **reduction** potentials.
- The copper half-reaction is a reduction.
- Write E_{Cu} for the electrode potential.



Standard Cell emf's and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (Table 17.1) are tabulated as **reduction** potentials.
- The zinc half-reaction is an oxidation.
- If you write E_{Zn} for the reduction potential of zinc, then $-E_{\text{Zn}}$ is the oxidation potential of zinc.



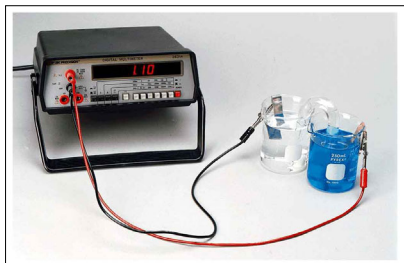
Standard Cell emf's and Standard Electrode Potentials

- By convention, the **Table of Standard Electrode Potentials** (Table 17.1) are tabulated as **reduction** potentials.
- For this cell, the cell emf is the sum of the **reduction potential for the copper** half-cell and the **oxidation potential for the zinc** half-cell.

$$E_{\text{cell}} = E_{\text{Cu}} + (-E_{\text{Zn}})$$

$$E_{\text{cell}} = E_{\text{Cu}} - E_{\text{Zn}} = (+.34\text{V}) - (-.76\text{V}) = 1.10\text{V}$$

An electrochemical cell with a measured potential of 1.10 V.



A Problem To Consider

- Calculate the standard emf for the following Galvanic cell at 25 °C using standard electrode potentials. What is the overall reaction?



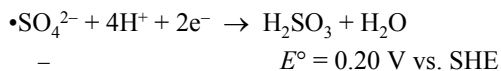
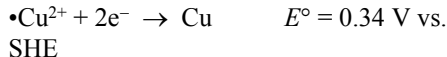
- The reduction half-reactions and standard potentials are



The most positive E° value will proceed as written

Standard Reduction Potentials

The E° values corresponding to reduction half-reactions with all solutes at 1M and all gases at 1 atm.



A Problem To Consider

- Calculate the standard emf for the following Galvanic cell at 25 °C using standard electrode potentials. What is the overall reaction?

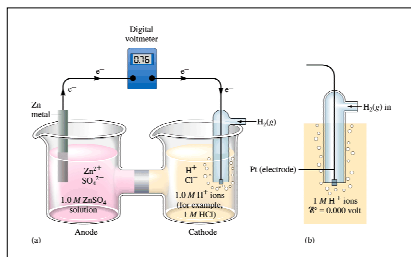


- You reverse the first half-reaction and its half-cell potential to obtain



Select the least common denominator which give equal numbers of electrons in anode & cathode reactions

Figure 17.5: (a) A galvanic cell involving the reactions $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (at the anode) and $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (at the cathode) has a potential of 0.76 V. (b) The standard hydrogen electrode where $\text{H}_2(\text{g})$ at 1 atm is passed over a platinum electrode in contact with 1 M H^+ ions. This electrode process (assuming ideal behavior) is arbitrarily assigned a value of exactly zero volts.

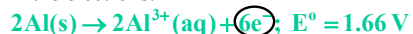


A Problem To Consider

- Calculate the standard emf for the following Galvanic cell at 25 °C using standard electrode potentials. What is the overall reaction?

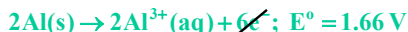


- To obtain the overall reaction we must balance the electrons.



A Problem To Consider

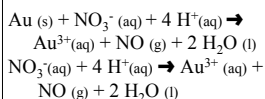
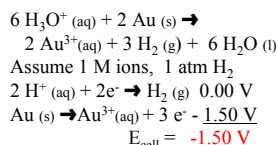
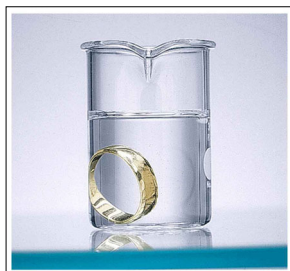
- Calculate the standard emf for the following Galvanic cell at 25 °C using standard electrode potentials. What is the overall reaction?
 $\text{Al(s)} | \text{Al}^{3+}(\text{aq}) || \text{Fe}^{2+}(\text{aq}) | \text{Fe(s)}$
- Now we add the reactions to get the overall cell reaction and cell emf.



emf and Work

$$\text{emf} = \text{potential difference (V)} = \frac{\text{work (J)}}{\text{charge (C)}}$$

A gold ring does not dissolve in nitric acid.



$$E_{\text{cathode}} + E_{\text{anode}} = 0.96 \text{ V} - 1.50 \text{ V} = -0.54 \text{ V}$$

Electromotive Force

- We can now write an expression for the **maximum work attainable** by a voltaic cell.
- Let n be the number of (mol) electrons transferred in the overall cell reaction.
- The **maximum work** for molar amounts of reactants is

$$w_{\text{max}} = -nFE_{\text{cell}}$$

Recall that $w_{\text{max}} = \Delta G$

Electromotive Force

- The **movement of electrons** is analogous to the pumping of water from one point to another.
- An electric charge moves from a point of high electrical potential (**high electrical pressure**) to one of lower electrical potential.
- The **work** expended in moving the electrical charge through a conductor depends on the amount of charge and the potential difference.

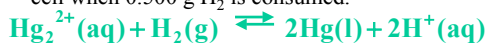
Free Energy and Cell Potential

$$\square \Delta G^{\circ} = -nFE^{\circ}$$

- n = number of moles of electrons
- F = Faraday = 96,485 coulombs per mole of electrons

A Problem To Consider

- The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H₂ is consumed.

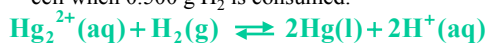


- The half-reactions are



A Problem To Consider

- The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H₂ is consumed.



- For 0.500 g H₂, the maximum work is

$$0.500 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.02 \text{ g H}_2} \times \frac{-1.25 \times 10^5 \text{ J}}{1 \text{ mol H}_2} = -3.09 \times 10^4 \text{ J}$$

A Problem To Consider

- The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H₂ is consumed.

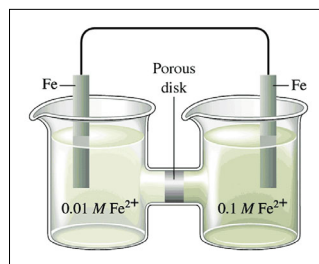


- n = 2, and the maximum work for the reaction is written as

$$w_{\text{max}} = -nFE_{\text{cell}}$$

$$w_{\text{max}} = -2 \times (9.65 \times 10^4 \text{ C}) \times (0.650 \text{ V})$$

Figure 17.10: A concentration cell containing iron electrodes and different concentrations of Fe²⁺ ion in the two compartments.



A Problem To Consider

- The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H₂ is consumed.



- n = 2, and the maximum work for the reaction is written as

$$w_{\text{max}} = -nFE_{\text{cell}}$$

$$w_{\text{max}} = -1.25 \times 10^5 \text{ J}$$

TABLE 17.2

Some Ions Whose Concentrations Can Be Detected by Ion-Selective Electrodes

Cations	Anions
H ⁺	Br ⁻
Cd ²⁺	Cl ⁻
Ca ²⁺	CN ⁻
Cu ²⁺	F ⁻
K ⁺	NO ₃ ⁻
Ag ⁺	S ²⁻
Na ⁺	

The Nernst Equation

- We can calculate the potential of a cell in which some or all of the components are not in their standard states.

$$E = E^\circ - \frac{0.0592}{n} \log(Q)$$

Dependence of emf on Concentration

- The result rearranges to give the **Nernst equation**, an equation relating the cell emf to its **standard emf** and the **reaction quotient**.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log Q$$

Dependence of emf on Concentration

- Recall that the free energy change, ΔG , is related to the standard free energy change, ΔG° , by the following equation.

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

- Here Q is the thermodynamic reaction quotient.

Dependence of emf on Concentration

- The result rearranges to give the **Nernst equation**, an equation relating the cell emf to its **standard emf** and the **reaction quotient**.
 - Substituting values for R and F at 25 °C, we get

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q$$

(values in volts at 25 °C)

Dependence of emf on Concentration

- Recall that the free energy change, ΔG , is related to the standard free energy change, ΔG° , by the following equation.

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

- If we substitute $\Delta G = -nFE_{\text{cell}}$ and $\Delta G = -nFE_{\text{cell}}^\circ$ into this equation, we get

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q$$

Dependence of emf on Concentration

- The result rearranges to give the **Nernst equation**, an equation relating the cell emf to its **standard emf** and the **reaction quotient**.
 - The Nernst equation illustrates why cell emf decreases as the cell reaction proceeds.
 - As reactant concentrations decrease and product concentrations increase, **Q increases**, thus increasing log Q which **in turn decreases the cell emf**.

A Problem To Consider

- What is the emf of the following Galvanic cell at 25 °C?



The standard emf of the cell is 1.10 V.

- The cell reaction is



- The number of electrons transferred is 2; hence $n = 2$. The reaction quotient is

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1.00 \times 10^{-5}}{0.100} = 1.00 \times 10^{-4}$$

A Problem To Consider

- What is the emf of the following Galvanic cell at 25 °C?



The standard emf of the cell is 1.10 V.

- The standard emf is 1.10 V, so the Nernst equation becomes

$$E_{\text{cell}} = 1.10 \text{ V} - (-0.12) = 1.22 \text{ V}$$

- The cell emf is 1.22 V.

A Problem To Consider

- What is the emf of the following galvanic cell at 25 °C?



The standard emf of the cell is 1.10 V.

- The standard emf is 1.10 V, so the Nernst equation becomes

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q$$

Concentration Cell

- ... a cell in which both compartments have the same components but at different concentrations.

A Problem To Consider

- What is the emf of the following Galvanic cell at 25 °C?

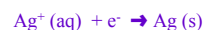
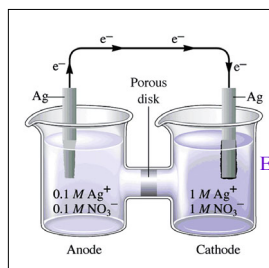


The standard emf of the cell is 1.10 V.

- The standard emf is 1.10 V, so the Nernst equation becomes

$$E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0592}{2} \log(1.00 \times 10^{-4})$$

Figure 17.9: A concentration cell that contains a silver electrode and aqueous silver nitrate in both compartments.



$$E_{\text{cell}} = 0.80 \text{ V}, [\text{Ag}^+] = 1.0 \text{ M}$$

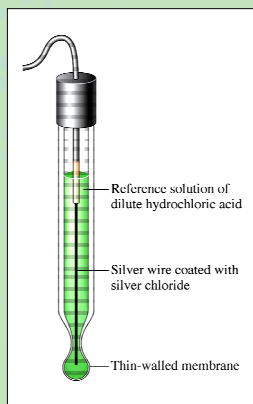
$$\text{Since } K = 1/[\text{Ag}^+]$$

$$E_{\text{cell}} = E^{\circ} - (0.0591/n) \log \{1/[\text{Ag}^+]\}$$

$$E_{\text{cell}} = 0.80 \text{ V} - (0.0591/1) \log (1/0.01) \\ = 0.80 \text{ V} - 0.12 \text{ V} \\ = 0.68 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cath}} + E_{\text{anode}} = 0.80 \text{ V} + (-0.68) \\ = +0.12 \text{ V}$$

Figure 17.12: A glass electrode contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane in which a silver wire coated with silver chloride has been embedded.



Equilibrium Constants from emf's

- Some of the most important results from electrochemistry are the relationships among E°_{cell} , free energy, and equilibrium constant.
 - The measurement of cell emf's gives you yet another way of calculating equilibrium constants.

Calculation of Equilibrium Constants for Redox Reactions

- At equilibrium, $E_{\text{cell}} = 0$ and $Q = K$.

$$\log(K) = \frac{nE^{\circ}}{0.0592} \text{ at } 25^{\circ}\text{C}$$

Equilibrium Constants from emf's

- Some of the most important results from electrochemistry are the relationships among E°_{cell} , free energy, and equilibrium constant.
 - Combining the previous equation, $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$, with the equation $\Delta G^{\circ} = -RT \ln K$, we get

$$nFE^{\circ}_{\text{cell}} = RT \ln K$$

Equilibrium Constants from emf's

- Some of the most important results from electrochemistry are the relationships among E°_{cell} , free energy, and equilibrium constant.
 - In Chapter 16 we saw that ΔG equals the maximum useful work of a reaction.
 - For a Galvanic cell, $\text{work} = -nFE^{\circ}$, so when reactants are in their standard states

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

Equilibrium Constants from emf's

- Some of the most important results from electrochemistry are the relationships among E°_{cell} , free energy, and equilibrium constant.
 - Or, rearranging, we get

$$E^{\circ}_{\text{cell}} = \frac{2.303RT}{nF} \log K$$

Equilibrium Constants from emf's

- Some of the most important results from electrochemistry are the relationships among E°_{cell} , free energy, and equilibrium constant.
- Substituting values for the constants R and F at 25 °C gives the equation

$$E^\circ_{\text{cell}} = \frac{0.0592}{n} \log K$$

(values in volts at 25 °C)

A Problem To Consider

- The standard emf for the following cell is 1.10 V.
 $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$
 Calculate the equilibrium constant K_c for the reaction
 $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
- Note that $n=2$. Substituting into the equation relating E°_{cell} and K gives

$$1.10 \text{ V} = \frac{0.0592}{2} \log K$$

Equilibrium Constants from emf's

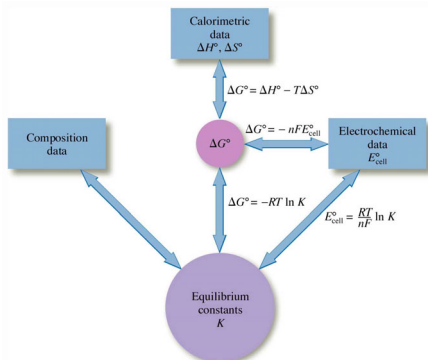
- Some of the most important results from electrochemistry are the relationships among E°_{cell} , free energy, and equilibrium constant.
- Figure 20.7 summarizes the various relationships among K, ΔG° , and E°_{cell} .

A Problem To Consider

- The standard emf for the following cell is 1.10 V.
 $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$
 Calculate the equilibrium constant K_c for the reaction
 $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
- Solving for $\log K_c$, you find

$$\log K = 37.2$$

Figure 20.7: Relationships among composition, calorimetric, and electrochemical data.



A Problem To Consider

- The standard emf for the following cell is 1.10 V.
 $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$
 Calculate the equilibrium constant K_c for the reaction
 $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
- Now take the antilog of both sides:

$$K_c = \text{anti log}(37.2) = 1.6 \times 10^{37}$$

A Problem To Consider

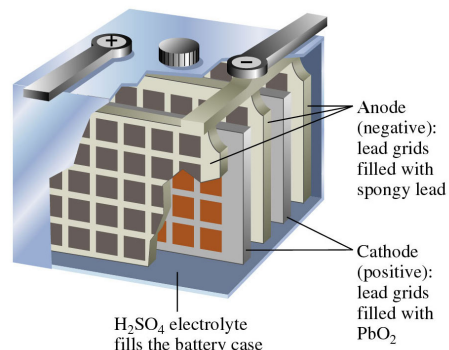
- The standard emf for the following cell is 1.10 V.

$$\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$$
 Calculate the equilibrium constant K_c for the reaction

$$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$$
- The number of significant figures in the answer equals the number of decimal places in 37.2 (one). Thus

$$K_c = 2 \times 10^{37}$$

Figure 20.12: A lead storage battery.



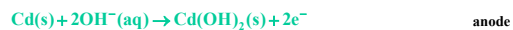
[Return to slide 92](#)

Batteries

- A battery is a galvanic cell or, more commonly, a group of galvanic cells connected in series.

Some Commercial Voltaic Cells

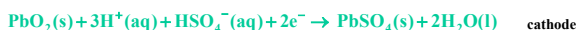
- The **nickel-cadmium cell (nicad cell)** consists of an anode of cadmium and a cathode of hydrated nickel oxide on nickel; the electrolyte is potassium hydroxide.
 - The electrode reactions are



[\(see Figure 20.14\)](#)

Some Commercial Voltaic Cells

- The **lead storage cell** (a rechargeable cell) consists of electrodes of lead alloy grids; one electrode is packed with a spongy lead to form the anode, and the other electrode is packed with lead dioxide to form the cathode.
 - The electrode reactions are



[\(see Figure 20.12\)](#)

Figure 20.14: Nicad storage batteries. Photo courtesy of American Color.



[Return to slide 93](#)

Figure 17.15: A mercury battery of the type used in calculators.

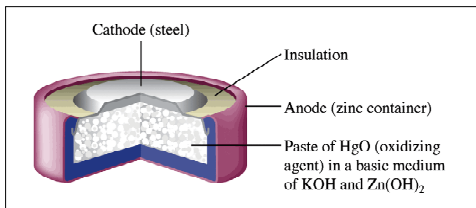
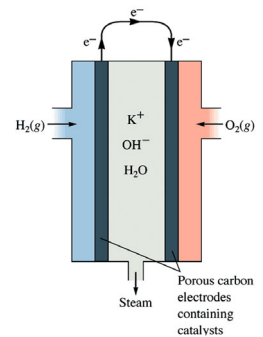


Figure 17.16: Schematic of the hydrogen-oxygen fuel cell.



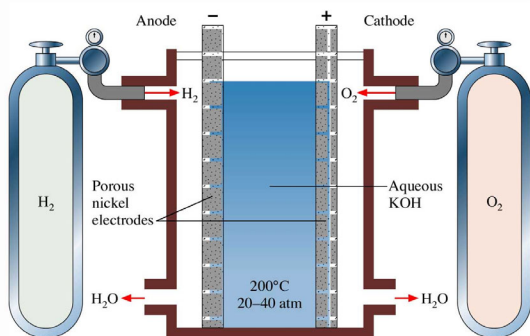
Fuel Cells

- ... galvanic cells for which the reactants are continuously supplied.
 - $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$
- anode: $2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$
- cathode: $4\text{e}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$

Corrosion

- Some metals, such as copper, gold, silver and platinum, are relatively difficult to oxidize. These are often called noble metals.

Figure 20.15: A hydrogen-oxygen fuel cell.



[Return to slide 94](#)

Figure 17.17: The electrochemical corrosion of iron.

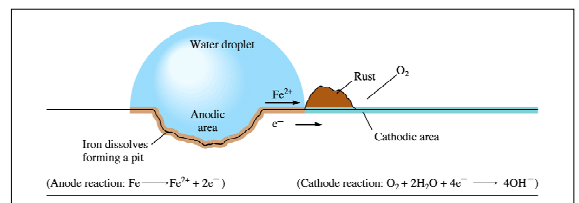
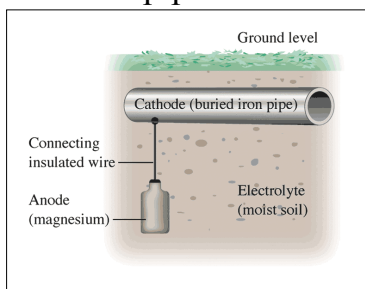


Figure 17.18: Cathodic protection of an underground pipe.



Electrolytic Cells

- An **electrolytic cell** is an electrochemical cell in which an electric current drives an otherwise nonspontaneous reaction.
- The process of producing a chemical change in an electrolytic cell is called **electrolysis**.
- Many important substances, such as aluminum metal and chlorine gas are produced commercially by electrolysis.

Electrolysis

- ... **forcing** a current through a cell to produce a chemical change for which the cell potential is negative.

Figure 17.19: (a) A standard galvanic cell based on the spontaneous reaction (b) A standard electrolytic cell. A power source forces the opposite reaction

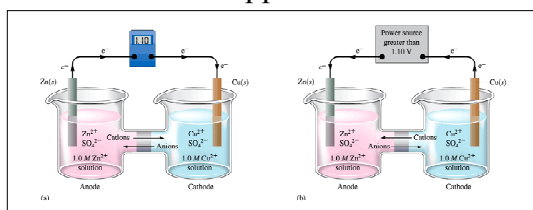


Figure 17.20: The electrolysis of water produces hydrogen gas at the cathode (on the right) and oxygen gas at the anode (on the left).



Figure 17.22: A schematic diagram of an electrolytic cell for producing aluminum by the Hall-Heroult process.

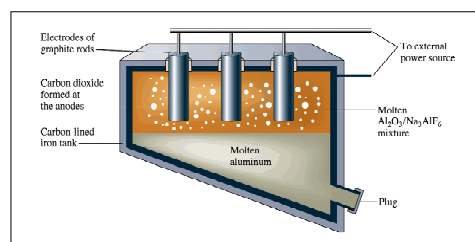


Figure 17.24: (a) A silver-plated teapot. (b) Schematic of the electroplating of a spoon.

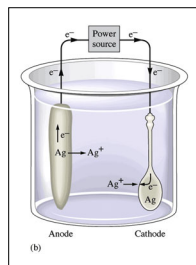
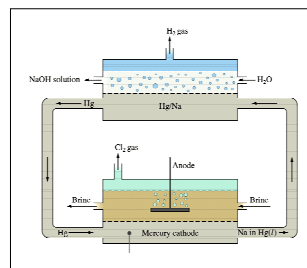


Figure 17.26: The mercury cell for production of chlorine and sodium hydroxide.



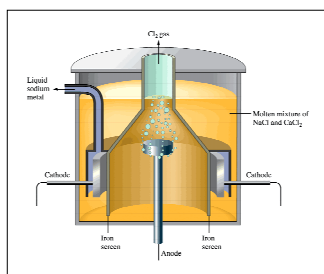
Electrolysis of Molten Salts

- A **Downs cell** is a commercial electrochemical cell used to obtain sodium metal by electrolysis of molten NaCl.
 - A number of other reactive metals are obtained by the electrolysis of a molten salt.
 - Lithium, magnesium, and calcium metals are all obtained by the electrolysis of the chlorides.

Stoichiometry of Electrolysis

- How much chemical change occurs with the flow of a given current for a specified time?
 - current and time \rightarrow quantity of charge \rightarrow moles of electrons \rightarrow moles of analyte \rightarrow grams of analyte

Figure 17.25: The Downs cell for the electrolysis of molten sodium chloride.



Stoichiometry of Electrolysis

- What is new in this type of stoichiometric problem is the measurement of numbers of electrons.
 - Electric current is measured in amperes.
 - An **ampere (A)** is the base SI unit of current equivalent to **1 coulomb/second**.

Stoichiometry of Electrolysis

- What is new in this type of stoichiometric problem is the measurement of numbers of electrons.
 - The quantity of electric charge passing through a circuit in a given amount of time is given by

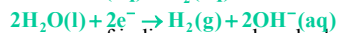
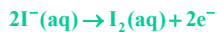
Electric charge(coul) = electric current (coul/sec) × time lapse(sec)

Coulombs x (mole e/96,500 coul) x (mole product/n mole e) x M_m =
grams product

Where n mole e are needed to produce 1 mole product

A Problem To Consider

- When an aqueous solution of potassium iodide is electrolyzed using platinum electrodes, the half-reactions are



How many grams of iodine are produced when a current of 8.52 mA flows through the cell for 10.0 min?

- When the current flows for 6.00×10^2 s (10.0 min), the amount of charge is

$$(8.52 \times 10^{-3} \text{ A}) \times (6.00 \times 10^2 \text{ s}) = 5.11 \text{ C}$$

$$5.11 \text{ C} \times (1 \text{ mole e}/96,500 \text{ C}) \times (1 \text{ mole I}_2/2 \text{ mole e}) \times (253.8 \text{ g I}_2/\text{mole}) = 0.00672 \text{ g}$$