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Chapter 17
Electrochemistry

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Review

- Oxidation
  - Loss of electrons
  - Occurs at electrode called the ***anode***
- Reduction
  - Gain of electrons
  - Occurs at electrode called the ***cathode***
- Redox reactions
  - ***Oxidation and reduction occur together***

Outline

1. Voltaic cells
2. Standard voltages
3. Relations between E°, ΔG° and K
4. Electrolytic cells
5. Commercial cells

Voltaic Cells

- In principle, any spontaneous redox reaction can serve as the source of energy for a voltaic cell
- Cell design
  - Oxidation at one electrode (anode)
  - Reduction at the other electrode (cathode)
  - Electrons move through an external circuit from the anode to the cathode

Electrochemistry

- ***Electrochemistry*** is the study of the conversion of electrical and chemical energy
- The conversion takes place in an electrochemical cell, of which there are two main types
  - Voltaic cells
  - Electrolytic cells

Mnemonic

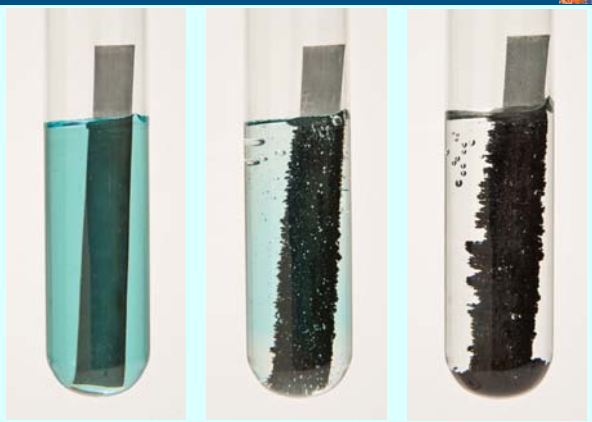
- Oxidation and anode both begin with vowels
  - *An ox*
- Reduction and cathode both begin with consonants
  - *Red cat*

$Zn\text{-}Cu^{2+}$ Reaction

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

Figure 17.2

Figure 17.1 – Zinc/Copper(II) Reaction



Tracing the Flow of Electrons,

1. At the zinc electrode, electrons are produced

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

   The sign of this electrode is (-); think of it as an electron pump

   Electrons flow from the red lead, through the voltmeter, to the black lead; the needle deflection indicates the cell voltage
2. The electrons enter the cathode, at which

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

   The sign of this electrode is (+)

$Zn\text{-}Cu^{2+}$ Cell

- To set up a voltaic cell for the same reaction, we separate the two half-reactions into half cells
  - Zn anode dips into a solution of Zn^{2+} ions
  - Cu cathode dips into a solution of Cu^{2+} ions
  - The external circuit consists of two wires connected to a voltmeter

Tracing the Flow of Electrons, (Cont'd)

3. As the half reactions occur

   A surplus of positive ions builds up at the anode

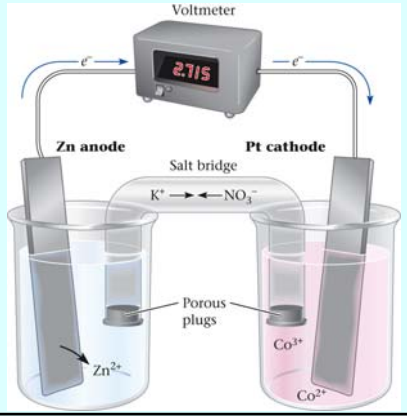
   A surplus of negative ions builds up at the cathode

   Anions and cations must flow to balance charge

Salt Bridges

- 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 is frequently used
  - Cations flow toward the cathode to neutralize the build-up of negative charge
  - Anions flow toward the anode to neutralize the build-up of positive charge

Figure 17.3



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

$$Zn\left|Zn^{2+}\right\|Cu^{2+}\left|Cu\right.$$

Example 17.1

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,

(a) Draw a sketch of the cell, labeling the anode, the cathode, and the direction of electron flow.

(b) Write the half-reaction that takes place at the anode and at the cathode.

(c) Write a balanced equation for the cell reaction.

(d) Write an abbreviated notation for the cell.

continued

Other Salt Bridge Cells

- Many spontaneous redox reactions can be set up as electrochemical cells
  - Ni (s) + Cu^{2+} (aq) → Ni^{2+} (aq) + Cu (s)

$$Ni\left|Ni^{2+}\right\|Cu^{2+}\left|Cu\right.$$

  - Zn (s) + $2Co^{3+}$ (aq) → Zn^{2+} (aq) + $2Co^{2+}$ (aq)

$$Zn\left|Zn^{2+}\right\|Co^{3+},Co^{2+}\left|Pt\right.$$

    - Note that because both species in the reduction are ions, an inert platinum electrode is required

Example 17.1, (Cont'd)

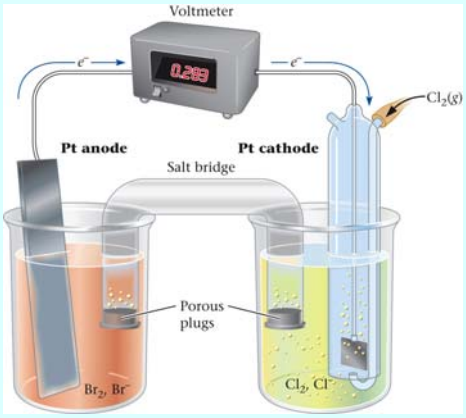
STRATEGY

1. Split the equation into two half-reactions.
2. Recall that the anode
   - is where oxidation takes place.
   - is the electrode toward which anions move.
   - is where electrons are produced.
3. 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: $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ (reduction) anode: $2Br^-(aq) \longrightarrow Br_2(l) + 2e^-$ (oxidation)
(c) Balanced equation	$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$
(d) Abbreviated cell notation	$Pt \mid Br_2, Br^- \parallel Cl^- \mid Cl_2 \mid Pt$

Figure 17.4



E° for a Standard Cell

- Zn (s) + $2H^+$ (aq, 1M) → Zn^{2+} (aq, 1M) + H_2 (g, 1 atm)
- Temperature is held constant (usually at 25 ° C)
- E° = +0.762V

Voltaic Cell Summary

- A voltaic cell contains two half-cells
- Each half cell consists of an electrode dipping into an aqueous solution
- In one half cell, the anode, oxidation occurs
- In the other half cell, the cathode, reduction occurs

E° Oxidation and Reduction

$$E^\circ = E^\circ_{red} + E^\circ_{ox}$$

- Zn (s) + $2H^+$ (aq, 1M) → Zn^{2+} (aq, 1M) + H_2 (g, 1 atm)

$$+0.762V = E^\circ_{red}(H^+ \rightarrow H_2) + E^\circ_{ox}(Zn \rightarrow Zn^{2+})$$

- The value of E° cannot be measured for a half-cell
- The value of E° for the hydrogen reduction is assigned to be 0.000 V
- Therefore, the E° for the oxidation of zinc is +0.762

Standard Voltages

- The cell voltage is the driving force for an electrochemical reaction
  - Intensive property; independent of the number of electrons flowing through the cell
  - Depends on the nature of the redox reaction and on the concentration of species involved
- Standard voltages are measured with
  - All aqueous concentrations at 1M
  - The pressure of all gases at 1 atm

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:
  - Zn^{2+} (aq) + $2e^-$ → Zn (s) E°_{red} = -0.762V
  - Zn (s) → Zn^{2+} (aq) + $2e^-$ E°_{ox} = +0.762V
- Standard voltages for oxidation and reduction are ***equal in magnitude and opposite in sign***

Strengths of Oxidizing and Reducing Agents

- In a table of reduction potentials
- Oxidizing agents are located on the left side
  - The more positive E°_{red} is, the stronger the oxidizing agent
    - The strong oxidizing agents are on the bottom left of the table
- Reducing agents are located on the right side
  - The more negative E°_{red} is, the stronger the reducing agent
    - The strong reducing agents are on the top right of the table

Table 17.1, (Cont'd)

TABLE 17.1 Standard Potentials in Water Solution at 25°C

Basic Solution, $[OH^-] = 1\ M$

		E°_{red} (V)
$Fe(OH)_2(s) + 2e^-$	$\longrightarrow Fe(s) + 2OH^-(aq)$	−0.891
$2H_2O + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.828
$Fe(OH)_3(s) + e^-$	$\longrightarrow Fe(OH)_2(s) + OH^-(aq)$	−0.547
$S(s) + 2e^-$	$\longrightarrow S^{2-}(aq)$	−0.445
$NO_3^-(aq) + 2H_2O + 3e^-$	$\longrightarrow NO(g) + 4OH^-(aq)$	−0.140
$NO_3^-(aq) + H_2O + 2e^-$	$\longrightarrow NO_2^-(aq) + 2OH^-(aq)$	0.004
$ClO_4^-(aq) + H_2O + 2e^-$	$\longrightarrow ClO_3^-(aq) + 2OH^-(aq)$	0.398
$O_2(g) + 2H_2O + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.401
$ClO_3^-(aq) + 3H_2O + 6e^-$	$\longrightarrow Cl^-(aq) + 6OH^-(aq)$	0.614
$ClO^-(aq) + H_2O + 2e^-$	$\longrightarrow Cl^-(aq) + 2OH^-(aq)$	0.890

Table 17.1

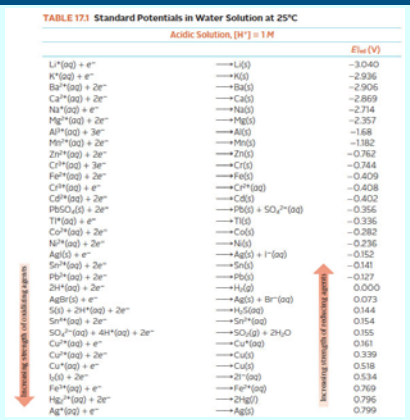


TABLE 17.1 Standard Potentials in Water Solution at 25°C

Acidic Solution, $[H^+] = 1\ M$

		E°_{red} (V)
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.040
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.936
$Ba^{2+}(aq) + 2e^-$	$\longrightarrow Ba(s)$	−2.906
$Ca^{2+}(aq) + 2e^-$	$\longrightarrow Ca(s)$	−2.869
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.357
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.68
$Mn^{2+}(aq) + 2e^-$	$\longrightarrow Mn(s)$	−1.182
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.762
$Cr^{3+}(aq) + 3e^-$	$\longrightarrow Cr(s)$	−0.744
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.409
$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.408
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.402
$PbSO_4(s) + 2e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Tl^+(aq) + e^-$	$\longrightarrow Tl(s)$	−0.336
$Co^{2+}(aq) + 2e^-$	$\longrightarrow Co(s)$	−0.282
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.236
$AgI(s) + e^-$	$\longrightarrow Ag(s) + I^-(aq)$	−0.152
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.141
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.127
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0.000
$AgBr(s) + e^-$	$\longrightarrow Ag(s) + Br^-(aq)$	0.073
$S(s) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2S(aq)$	0.144
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.154
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow SO_2(g) + 2H_2O$	0.155
$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.161
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.339
$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.518
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.534
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.769
$Hg_2^{2+}(aq) + 2e^-$	$\longrightarrow 2Hg(l)$	0.796
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.799

Table 17.1, (Cont'd)

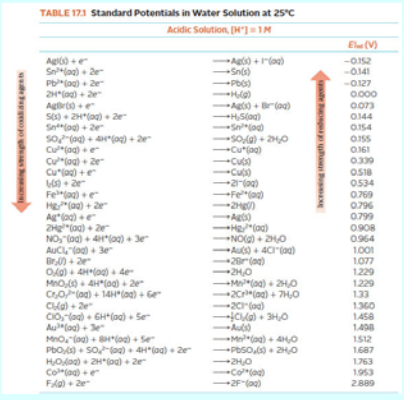


TABLE 17.1 Standard Potentials in Water Solution at 25°C

Acidic Solution, $[H^+] = 1\ M$

		E°_{red} (V)
$AgI(s) + e^-$	$\longrightarrow Ag(s) + I^-(aq)$	−0.152
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.141
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.127
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0.000
$AgBr(s) + e^-$	$\longrightarrow Ag(s) + Br^-(aq)$	0.073
$S(s) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2S(aq)$	0.144
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.154
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow SO_2(g) + 2H_2O$	0.155
$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.161
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.339
$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.518
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.534
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.769
$Hg_2^{2+}(aq) + 2e^-$	$\longrightarrow 2Hg(l)$	0.796
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.799
$2Hg^{2+}(aq) + 2e^-$	$\longrightarrow Hg_2^{2+}(aq)$	0.908
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow NO(g) + 2H_2O$	0.964
$AuCl_4^-(aq) + 3e^-$	$\longrightarrow Au(s) + 4Cl^-(aq)$	1.001
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.077
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O$	1.229
$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Mn^{2+}(aq) + 2H_2O$	1.229
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O$	1.33
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.360
$ClO_3^-(aq) + 6H^+(aq) + 5e^-$	$\longrightarrow \frac{1}{2}Cl_2(g) + 3H_2O$	1.458
$Au^{3+}(aq) + 3e^-$	$\longrightarrow Au(s)$	1.498
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O$	1.512
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow PbSO_4(s) + 2H_2O$	1.687
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O$	1.763
$Co^{3+}(aq) + e^-$	$\longrightarrow Co^{2+}(aq)$	1.953
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.889

Trends in the Table

- Reducing agent strength decreases down the table
  - Look on the right-hand side of the arrow for the reducing agent
- Oxidizing agent strength increases down the table
  - Look at the left-hand side of the arrow for the oxidizing agent

Lithium as a Reducing Agent

Example 17.2

EXAMPLE 17.2 CONCEPTUAL

Consider the following species in acidic solution: MnO_4^-, I^-, NO_3^-, H_2S, and Fe^{2+}. Using Table 17.1,

a. classify each of these as an oxidizing and/or reducing agent.
b. arrange the oxidizing agents in order of increasing strength.
c. do the same with the reducing agents.

STRATEGY

Recall that the oxidizing agents are located in the left column of Table 17.1 and the reducing agents are in the right column of the same table.

SOLUTION

MnO_4^-	found in the left column, oxidizing agent
I^-	found in the right column, reducing agent
NO_3^-	found in the left column, oxidizing agent
H_2S	found in the right column, reducing agent
Fe^{2+}	found in both the left column and right column, oxidizing and reducing agent

b and c

STRATEGY AND SOLUTION

b. Going down the left column, the oxidizing agents increase in strength.
$Fe^{2+} < NO_3^- < MnO_4^-$

c. Going *up* the right column, the reducing agents increase in strength.
$Fe^{2+} < I^- < H_2S$

Example 17.3, (Cont'd)

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

Calculation of E°

$$E^\circ = E^\circ_{red} + E^\circ_{ox}$$

- Look up the reduction potentials for both half cells
- Change the sign of the oxidation half reaction
- Add the two numbers together
- The resulting E° is always positive for a voltaic cell
- Never multiply E° by any coefficient

Example 17.3, (Cont'd)

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

$E^\circ_{red} + E^\circ_{ox} = 1.201\ V$

$0 + E^\circ_{ox} = 1.201\ V$; E°_{ox} for the half-reaction $Cd(s) \longrightarrow Cd^{2+}(aq) + 2e^- = 1.201\ V$

Since E°_{red} for Cd^{2+} is asked for, then $E^\circ_{red} = -(E^\circ_{ox}) = -1.201\ V$

Example 17.3

EXAMPLE 17.3 GRADED

Consider the voltaic cell in which the reaction is

$$2Ag^+(aq) + Cd(s) \longrightarrow 2Ag(s) + Cd^{2+}(aq)$$

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

Figure 17.5: Reaction of Ni with Cu^{2+}

Figure 17.6: Oxidation of Iron by Acid

Example 17.4, (Cont'd)

SOLUTION

1. oxidation numbers	Fe: $+3 \longrightarrow +2$ reduction I: $-1 \longrightarrow 0$ oxidation
2. half-reactions	$2Fe^{3+}(aq) + 2e^- \longrightarrow 2Fe^{2+}(aq)$ $\quad E^\circ_{red} = +0.769$ V $2I^-(aq) \longrightarrow I_2(s) + 2e^-$ $\quad E^\circ_{ox} = -0.534$ V
E°	$E^\circ = 0.769\text{ V} + (-0.534\text{ V}) = +0.235$ V $E^\circ > 0$, the reaction will occur at standard conditions.

(b)

ANALYSIS

Information given:	oxidation half-reaction ($Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$)
Information implied:	Table 17.1 (standard reduction potentials)
Asked for:	Will HCl oxidize Fe?

STRATEGY

1. $HCl(aq)$ is made up of two ions, H^+ and Cl^-. Since an oxidizing agent is needed (to oxidize Fe to Fe^{2+}), find either H^+ or Cl^- (or both) in the left column of Table 17.1.
2. Write the possible half-reactions.
3. Write the redox reaction and find E°.

Spontaneity of Redox Reactions

- If the calculated voltage of a redox reaction is positive, the reaction is spontaneous
- If the calculated voltage of a redox reaction is negative, the reaction is nonspontaneous

Example 17.4, (Cont'd)

SOLUTION

1. Oxidizing agent	Only H^+ appears in the left column.
2. Half-reactions	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ $\quad E^\circ_{red} = 0.000$ V $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ $\quad E^\circ_{ox} = 0.409$ V
3. Redox reaction	$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$ $\quad E^\circ = 0.409$ V $E^\circ > 0$, HCl will oxidize Fe at standard conditions (Figure 17.6, page 536).

(c)

ANALYSIS

Information given:	ions in acidic solution (Cl^-, Fe^{2+}, Cr^{2+}, I_2)
Information implied:	Table 17.1
Asked for:	Will a redox reaction occur when the ions are mixed?

STRATEGY

1. Check the left column of Table 17.1 to determine which of the ions are oxidizing agents (i.e., they are reduced). Write the reduction half-reactions of the oxidizing agents.
2. Check the right column of Table 17.1 to determine which of the ions are reducing agents (i.e., they are oxidized). Write the reduction half-reactions of the reducing agents.
3. Write all possible combinations of oxidation and reduction half-reactions. The combination(s) that give positive E° values are possible.
4. Write the redox equation(s) for the reaction(s) that occur.

continued

Example 17.4

EXAMPLE 17.4

Using standard potentials from Table 17.1, decide whether at standard concentrations

(a) the reaction
$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$
will occur.

(b) $Fe(s)$ will be oxidized to Fe^{2+} by treatment with hydrochloric acid.

(c) a redox reaction will occur when the following species are mixed in acidic solution: Cl^-, Fe^{2+}, Cr^{2+}, I_2.

(a)

ANALYSIS

Information given:	equation for the reaction ($2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$)
Information implied:	Table 17.1 (standard reduction potentials)
Asked for:	Will the reaction occur?

STRATEGY

1. Assign oxidation numbers.
2. Write oxidation and reduction half-reactions. Include E°_{ox} and E°_{red}.
3. Find E°. The reaction will occur if $E^\circ > 0$.

continued

Example 17.4, (Cont'd)

SOLUTION

1. Oxidizing agents	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	$E^\circ_{red} = -0.409$ V
	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	$E^\circ_{red} = +0.534$ V
2. Reducing agents	$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$	$E^\circ_{ox} = -1.360$ V
	$Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + e^-$	$E^\circ_{ox} = +0.408$ V
	$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$	$E^\circ_{ox} = -0.769$ V
3. Possible combinations	$Fe^{2+} + Cl^-$: $E^\circ < 0$	$I_2 + Cl^-$: $E^\circ < 0$
	$Fe^{2+} + Cr^{2+}$: $E^\circ < 0$	$I_2 + Cr^{2+}$: $E^\circ > 0$ ✔
	$Fe^{2+} + Fe^{2+}$: $E^\circ < 0$	$I_2 + Fe^{2+}$: $E^\circ < 0$
4. Redox reaction	$I_2(s) + 2Cr^{2+}(aq) \longrightarrow 2I^-(aq) + 2Cr^{3+}(aq)$	$E^\circ = 0.942$ V

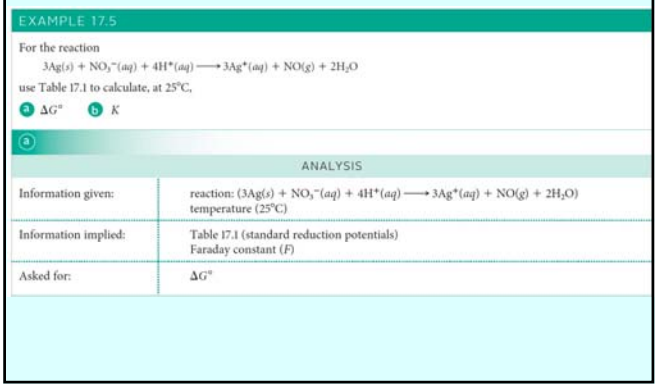
Relations Between E, ΔG° and K

- There is a relationship between the spontaneity of the reaction in a voltaic cell, the free energy change, and therefore the equilibrium constant
- E° and ΔG°

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

  - ΔG° is the standard free energy change (gases, 1 atm; solutions, 1 M)
  - E° is the standard cell voltage
  - n is the number of moles of electrons transferred in the reaction
  - F is called the Faraday constant, the charge on a mole of electrons

Example 17.5



EXAMPLE 17.5

For the reaction

$3Ag(s) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Ag^+(aq) + NO(g) + 2H_2O$

use Table 17.1 to calculate, at 25°C,

(a) ΔG° (b) K

(a)

ANALYSIS

Information given:	reaction: $(3Ag(s) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Ag^+(aq) + NO(g) + 2H_2O)$ temperature (25°C)
Information implied:	Table 17.1 (standard reduction potentials) Faraday constant (F)
Asked for:	ΔG°

E° and K

- Recall that

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

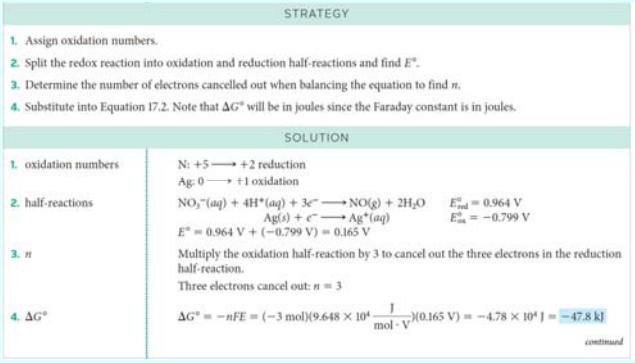
- So

$$-RT\ln K = -nFE^\circ$$

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

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

Example 17.5, (Cont'd)



STRATEGY

1. Assign oxidation numbers.
2. Split the redox reaction into oxidation and reduction half-reactions and find E°.
3. Determine the number of electrons cancelled out when balancing the equation to find n.
4. Substitute into Equation 17.2. Note that ΔG° will be in joules since the Faraday constant is in joules.

SOLUTION

1. oxidation numbers	N: +5 ⟶ +2 reduction Ag: 0 ⟶ +1 oxidation
2. half-reactions	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$ $\quad E^\circ_{red} = 0.964$ V $Ag(s) + e^- \longrightarrow Ag^+(aq)$ $\quad E^\circ_{ox} = -0.799$ V $E^\circ = 0.964\text{ V} + (-0.799\text{ V}) = 0.165$ V
3. n	Multiply the oxidation half-reaction by 3 to cancel out the three electrons in the reduction half-reaction. Three electrons cancel out: $n = 3$
4. ΔG°	$\Delta G^\circ = -nFE = (-3\text{ mol})(9.648 \times 10^4 \frac{\text{J}}{\text{mol} \cdot \text{V}})(0.165\text{ V}) = -4.78 \times 10^4\text{ J} = -47.8\text{ kJ}$

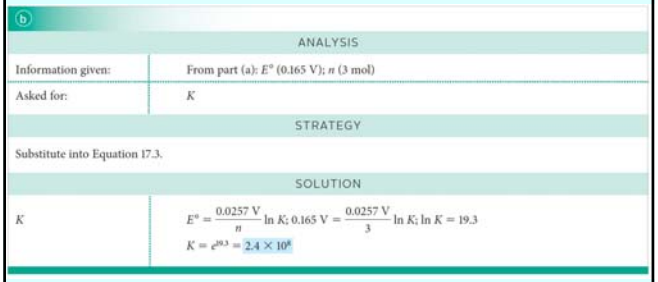
continued

E° and K, (Cont'd)

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

- The equation applies at 25 ° C
- Note that
  - If E° is positive, K is greater than 1
  - If E° is negative, K is less than 1

Example 17.5, (Cont'd)



(b)

ANALYSIS

Information given:	From part (a): E° (0.165 V); n (3 mol)
Asked for:	K

STRATEGY

Substitute into Equation 17.3.

SOLUTION

K	$E^\circ = \frac{0.0257\text{ V}}{n}\ln K$; $0.165\text{ V} = \frac{0.0257\text{ V}}{3}\ln K$; $\ln K = 19.3$ $K = e^{19.3} = 2.4 \times 10^8$

Table 17.2

TABLE 17.2 Relation Between $E°$, K, and $\Delta G°$ ($n = 2$)

$E°$ (V)	K	$\Delta G°$ (kJ)	$E°$ (V)	K	$\Delta G°$ (kJ)
+2.00	4×10^{67}	−400	−2.00	3×10^{-68}	+400
+1.00	6×10^{33}	−200	−1.00	2×10^{-34}	+200
+0.50	8×10^{16}	−100	−0.50	1×10^{-17}	+100
+0.25	3×10^{8}	−50	−0.25	4×10^{-9}	+50
+0.10	2×10^{3}	−20	−0.10	0.0004	+20
+0.05	50	−10	−0.05	0.02	+10
0.00	1	0			

Voltaic Cell and Equilibrium

- As a voltaic cell operates, the concentration of reactant decreases and the concentration of product increases
  - Eventually the forward and reverse reactions come to equilibrium
  - Once equilibrium is reached, there is no net driving force

E° and Extent of Reaction

- As there is with ΔG°, there is clearly a connection between E° and the position of equilibrium
  - If E° is greater than 0.10 V, the reaction goes largely to completion (K is large)
  - If E° is less than -0.10 V, the reaction does not proceed to any appreciable extent (K is small)

The Nernst Equation

- Recall that

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

- We can substitute for E° and obtain

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

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

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

Effect of Concentration on Voltage

- Since there is clearly an effect of concentration on ΔG°, there is a concentration effect on E° as well
- Voltage will increase if
  - The concentration of reactant is increased
  - The concentration of product is reduced
- Voltage will decrease if
  - The concentration of reactant is decreased
  - The concentration of product is increased

Interpreting Q in the Nernst Equation

- If Q > 1, product concentrations are higher than those of reactants
  - E is less than E°
- If Q < 1, reactant concentrations are higher than those of products
  - E is greater than E°
- If Q = 1, standard conditions prevail
  - E = E°

Example 17.6

EXAMPLE 17.6 GRADED

Consider a voltaic cell in which the following reaction occurs:

$$O_2(g, 0.98\ \text{atm}) + 4H^+(aq, \text{pH} = 1.24) + 4Br^-(aq, 0.15\ M) \longrightarrow 2H_2O + 2Br_2(l)$$

(a) Calculate E for the cell at 25°C.

(b) When the voltaic cell is at 35°C, E is measured to be 0.039 V. What is $E°$ at 35°C?

continued

Example 17.6, (Cont'd)

SOLUTION

$E°$	$0.039\ \text{V} = E° - \frac{(8.31\ \text{J/mol}\cdot\text{K})(308\text{K})}{4\,(9.648 \times 10^4\ \text{J/mol}\cdot\text{V})} \ln (1.8 \times 10^6)$
	$E° = 0.039\ \text{V} + 0.126\ \text{V} = 0.165\ \text{V}$

Example 17.6, (Cont'd)

(a)

ANALYSIS

Information given:	reaction: $(O_2(g) + 4H^+(aq) + 4Br^-(aq) \longrightarrow 2Br_2(l) + 2H_2O)$ P_{O_2} (0.98 atm); $[H^+]$ (pH = 1.24); $[Br^-]$ (0.15 M) temperature (25°C)
Information implied:	Table 17.1 (standard reduction potentials)
Asked for:	E

STRATEGY

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

$$E = E° - \frac{0.0257}{n} \ln Q$$

Example 17.7

EXAMPLE 17.7

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

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

It is found that the voltage is +0.560 V when $[Zn^{2+}] = 0.85\ M$ and $P_{H_2} = 0.988$ atm. What is the pH in the H_2-H half-cell?

ANALYSIS

Information given:	reaction: $(Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g))$ E (0.560 V); T (25°C) P_{H_2} (0.988 atm); $[Zn^{2+}]$(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 $E°$. $(E°_{red} + E°_{ox})$
3. Substitute into the Nernst equation (Equation 17.4) for $T = 25°C$ and find Q.
4. Write the Q expression and substitute given concentrations and pressures to find $[H^+]$. Change $[H^+]$ to pH.

continued

Example 17.6, (Cont'd)

SOLUTION

1. $[H^+]$	$1.24 = -\log_{10}[H^+]$; $[H^+] = 0.058\ M$
Q	$Q = \frac{1}{(P_{O_2})[H^+]^4[Br^-]^2} = \frac{1}{(0.98)(0.058)^4(0.15)^2} = 1.8 \times 10^6$
2. Oxidation numbers	O: 0 ⟶ −2 (reduction); Br: −1 ⟶ 0 (oxidation)
Half-reactions	$O_2(g) + 4H^+(aq) + 4e^-(aq) \longrightarrow 2H_2O$ $2Br^-(aq) \longrightarrow Br_2(l) + 2e^-$
n	The oxidation half-reaction must be multiplied by 2 to cancel out the four electrons in the reduction half-reaction. $n = 4$
3. $E°$	$E°_{red}$ for $O_2 = 1.299$ V; $E°_{red}$ for $Br^- = -1.077$ V $E° = 1.229\ \text{V} + (-1.077\ \text{V}) = 0.152\ \text{V}$
4. E	$E = 0.152\ \text{V} - \frac{0.0257}{4} \ln (1.8 \times 10^6) = 0.030\ \text{V}$

(b)

ANALYSIS

Information given:	E (0.039 V) at T (35°C) From part (a): Q (1.8×10^6); n (4 moles)
Information implied:	R and F values in joules
Asked for:	$E°$ at 35°C

STRATEGY

Substitute into the Nernst equation for any T.

$$E = E° - \frac{RT}{nF} \ln Q$$

continued

Example 17.7, (Cont'd)

SOLUTION

1. Oxidation numbers	Zn: 0 ⟶ +2 oxidation; H^+: +1 ⟶ 0 reduction
Half-reactions	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ $\quad Zn(s) \longrightarrow 2e^- + Zn^{2+}(aq)$
n	2 electrons cancel out so $n = 2$.
2. $E°$	$E° = E°_{ox}\,Zn + E°_{red}\,H^+ = 0.762\ \text{V} + 0\ \text{V} = 0.762\ \text{V}$
3. Q	$E = E° - \frac{0.0257}{n} \ln Q$; $0.560\ \text{V} = 0.762\ \text{V} - \frac{0.0257}{2} \ln Q$
	$\frac{0.0257}{2} \ln Q = 0.762\ \text{V} - 0.560\ \text{V}$; $\ln Q = 15.7$; $Q = 6.7 \times 10^6$
4. $[H^+]$	$Q = \frac{[Zn^{2+}](P_{H_2})}{[H^+]^2}$; $[H^+] = \left[\frac{(0.85)(0.988)}{6.7 \times 10^6}\right]^{\frac{1}{2}} = 3.5 \times 10^{-4}$
pH	$\text{pH} = -\log_{10}(3.5 \times 10^{-4}) = 3.45$

pH and Specific Ion Electrodes

- Glass electrodes can be constructed such that the difference in concentration of ion inside and outside the electrode may be measured
  - pH meter electrodes
  - Specific ion electrodes

Quantitative Relationships

- $Ag^+ (aq) + e^- \rightarrow Ag (s)$
  - 1 mol e^- → 1 mol Ag
- $Cu^{2+} (aq) + 2e^- \rightarrow Cu (s)$
  - 2 mol e^- → 1 mol Cu
- $Au^{3+} (aq) + 3e^- \rightarrow Au (s)$
  - 3 mol e^- → 1 mol Au

Figure 17.7: A pH Electrode

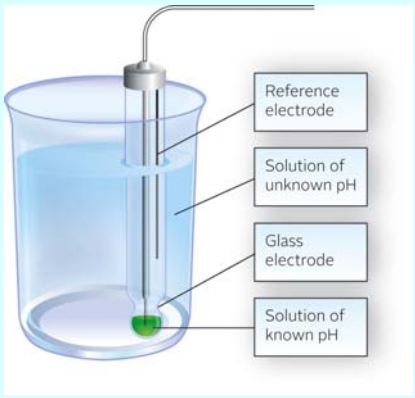
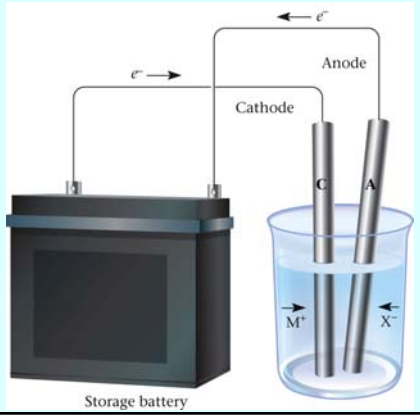


Figure 17.8



Electrolytic Cells

- In an ***electrolytic cell***, a nonspontaneous reaction may be caused to occur by the application of an external voltage
  - In essence, this means pumping electrons into the reaction
  - The process is called ***electrolysis***

Table 17.3

TABLE 17.3 Electrical Units

Quantity	Unit	Defining Relation	Conversion Factors
Charge	**coulomb (C)**	1 C = 1 A·s = 1 J/V	1 mol e^- = 9.648 × 10^4 C
Current	**ampere (A)**	1 A = 1 C/s	
Potential	**volt (V)**	1 V = 1 J/C	
Power	**watt (W)**	1 W = 1 J/s	
Energy	**joule (J)**	1 J = 1 V·C	1 kWh = 3.600 × 10^6 J

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 X 10^6 J = 3.600 X 10^3 kJ

Example 17.8, (Cont'd)

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 A = 1 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	$\text{time} = \frac{3.11 \times 10^5 \text{ C}}{6.00 \text{ C/s}} = 5.16 \times 10^4 \text{ s} = 14.4 \text{ h}$

Example 17.8

EXAMPLE 17.8

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

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O$$

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

(a) How many grams of chromium can be plated if the current is run for 48 minutes?

(b) How long will it take to completely convert 215 mL of 1.25 M $K_2Cr_2O_7$ to elemental chromium?

(c) How many kilowatt-hours of electrical energy are required to plate 1.00 g of chromium?

(a)

ANALYSIS

Information given:	reduction half-reaction: $(Cr_2O_7^{2-}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O)$ current (6.00 A); voltage (4.5 V); time in s (48 × 60)
Information implied:	1 C = 1 A · s; MM Cr
Asked for:	mass Cr plated

STRATEGY

1. 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:

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

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

$$\text{mol } e^- \xrightarrow{12 \text{ mol } e^-/2 \text{ mol Cr}} \text{mol Cr} \xrightarrow{\text{MM}} \text{mass Cr}$$

Example 17.8, (Cont'd)

(c)

ANALYSIS

Information given:	reduction half-reaction: $(Cr_2O_7^{2-}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O)$ 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 × V) and then convert to kWh (3.600×10^6 J = 1 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	$0.115 \text{ mol } e^- \times \frac{9.468 \times 10^4 \text{ C}}{1 \text{ mol } e^-} \times 4.5 \text{ V} \times \frac{1 \text{ J}}{1 \text{ C} \cdot \text{V}} \times \frac{1 \text{ kWh}}{3.600 \times 10^6 \text{ J}} = 0.014 \text{ kWh}$

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.

Example 17.8, (Cont'd)

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

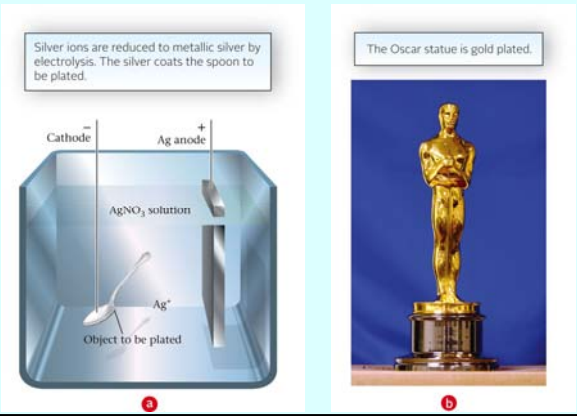
(b)

ANALYSIS

Information given:	reduction half-reaction: $(Cr_2O_7^{2-}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O)$ current (6.00 A); voltage (4.5 V) $K_2Cr_2O_7$: V (0.215 L); M (1.25)
Information implied:	1 C = 1A · s
Asked for:	time

continued

Figure 17.9: Application of Electrolysis – Metal Plating



Cell Reactions in Water Solution

- Reactions at the cathode
  - Reduction of a cation to its metal
    - $Ag^+ (aq) + e^- \rightarrow Ag (s)$ +0.799V
  - Reduction of water to hydrogen gas
    - $2H_2O + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$ -0.828V
- Anode reactions
  - Oxidation of an anion to a nonmetal
    - $2I^- (aq) \rightarrow I_2 (s) + 2e^-$ -0.534V
  - Oxidation of water to oxygen gas
    - $2H_2O \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$ -1.299V

Electrolysis of Aqueous KI

- Hydrogen gas (color from phenolphthalein, indicating the presence of OH^-) is produced at the cathode
- Iodine is produced at the anode

Which Reaction

- Water will be reduced when a cation is very difficult to reduce
  - K^+, Na^+, etc.
- Water will be oxidized when an anion is very difficult to oxidize
  - NO_3^-, SO_4^{2-}, etc.

Commercial Cells

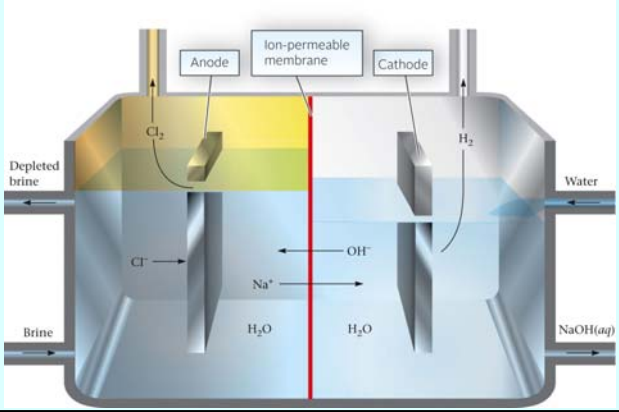
- Electrolysis of aqueous NaCl
  - Anode: $2Cl^- \rightarrow Cl_2 (g) + 2e^-$
  - Cathode: $2H_2O + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$
- Products
  - Chlorine: bleaching agent; used in manufacture of plastics such as PVC
  - Hydrogen: used to produce ammonia
  - NaOH: used to process paper, purify aluminum, manufacture glass

Table 17.4

TABLE 17.4 Electrolysis of Water Solutions

Solution	Cathode Product	Anode Product
$CuBr_2(aq)$	$Cu(s)$	$Br_2(l)$
$AgNO_3(aq)$	$Ag(s)$	$O_2(g)$
$KI(aq)$	$H_2(g)$	$I_2(s)$
$Na_2SO_4(aq)$	$H_2(g)$	$O_2(g)$

Chlor-Alkali Process



Primary Cells

- Primary cells (batteries) are non-rechargeable
- LeClanché cells
  - $Zn\ (s) + 2MnO_2\ (s) + 2NH_4^+\ (aq) \rightarrow Zn^{2+}\ (aq) + 2NH_3\ (aq) + H_2O$
  - Gas is produced (insulator)
- Alkaline batteries
  - Use KOH rather than NH_4Cl electrolyte
  - $Zn(s) + 2MnO_2\ (s) \rightarrow ZnO\ (s) + Mn_2O_3\ (s)$
  - No gas is produced

Figure 17.12 – Lead-Acid Auto Battery

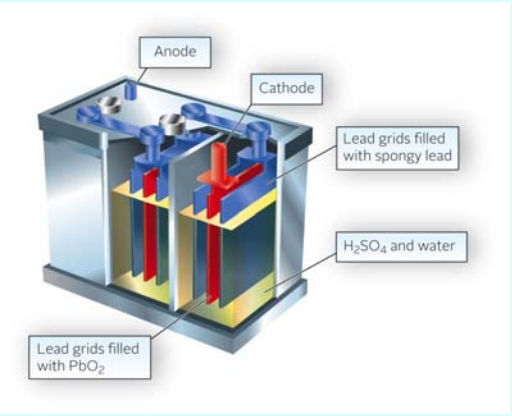
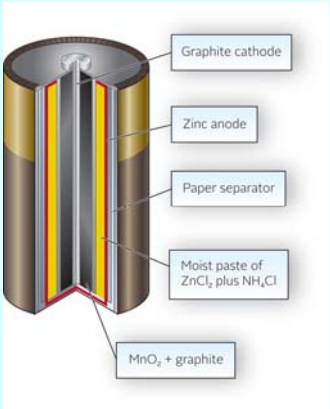


Figure 17.11 – Dry Cell Battery



Lead Storage Battery

- Disadvantages
  - Relatively low energy density (heavy!)
  - Capacity is about 2.5 W-hr/kg
  - When the battery is recharged, some water may be electrolyzed, producing a safety hazard
    - $2H_2O \rightarrow H_2\ (g) + O_2\ (g)\ \Delta G^\circ = +474.4$ kJ at 25 ° C

Storage (Rechargeable) Cells

- Secondary battery
- Can be recharged repeatedly
  - Cell is run in reverse (polarity is reversed)
- Examples
  - Lead-acid cell: six, 2.0 V lead cells
  - $Pb\ (s) + PbO_2\ (s) + 2H^+\ (aq) + 2HSO_4^-\ (aq) \rightarrow 2PbSO_4\ (s) + 2H_2O$
  - $\Delta G^\circ = -371.4$ kJ at 25 ° C

Nickel-based Batteries

- NiCad batteries
  - Anode is Cd
  - Cathode is nickeloxy hydroxide
- Nickel-metal hydride batteries
  - Anode is an alloy of several metals
  - Cathode is nickeloxy hydroxide
- Capacity is 80 W-hr/kg

Lithium-based Batteries

- Lithium batteries provide high voltages with light weight
  - Anode is made up of carbon layers with lithium ions embedded in them
  - Cathode is a lithium metal oxide like $LiCoO_2$
- Capacity is 150 W-hr/kg

Fuel Cells in Practice

- Clean, non-polluting
- Cost per kJ is high: chemistry is simple but the engineering is complex
- Storage of hydrogen as a fuel is difficult and potentially dangerous

Fuel Cells

- A fuel cell is essentially a battery with continuously supplied reactants
- Anode: $2H_2\,(g) + 4OH^-\,(aq) \rightarrow 4H_2O + 4e^-$
- Cathode: $O_2\,(g) + 2H_2O + 4e^- \rightarrow 4OH^-\,(aq)$
- Net: $2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O$ ΔG° = -474.4 kJ at 25 ° C

Key Concepts

1. Draw a diagram for a voltaic cell, labeling the electrodes and diagramming current flow
2. Use standard potentials to
   Compare relative strengths of oxidizing and reducing agents
   Calculate E and/or reaction spontaneity
3. Relate E° to ΔG° and K
4. Use the Nernst equation to relate voltage to concentration
5. Relate mass of product to charge, energy or current in electrolysis reactions

Hydrogen-Oxygen Fuel Cell Car: Honda Clarity