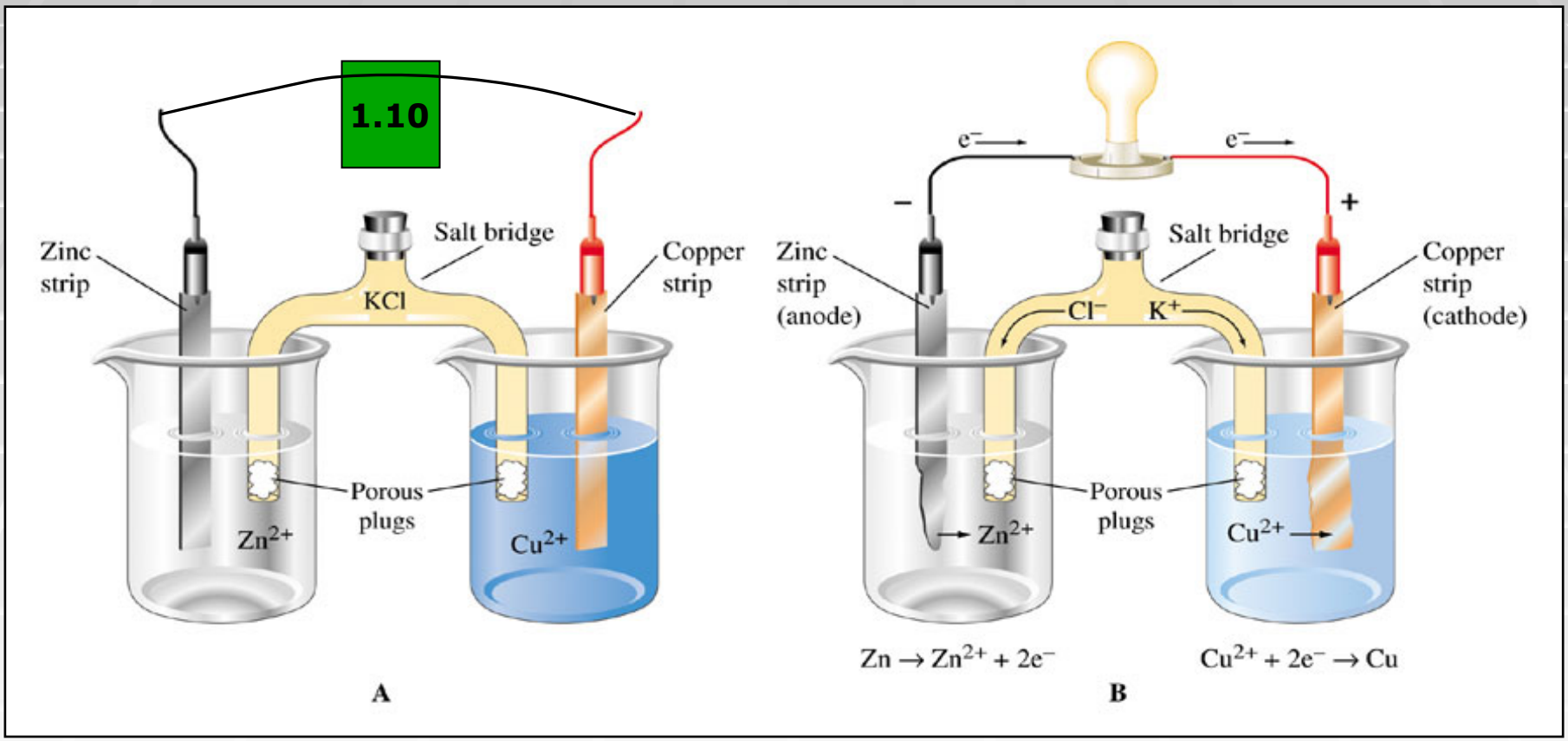
# Electrochemistry

# Capturing the Energy of Redox Reactions

- Many reactions provide useable energy directly in the form of heat.
- The transfer of electrons (movement of charge) involves a transfer of energy as well.
- If a redox reaction is controlled, the energy of the electron transfer can be converted to usable forms, typically heat or magnetism.
- In order to control a redox process, the oxidation and reduction half-reactions need to be separated.

# Voltaic / Galvanic Cell

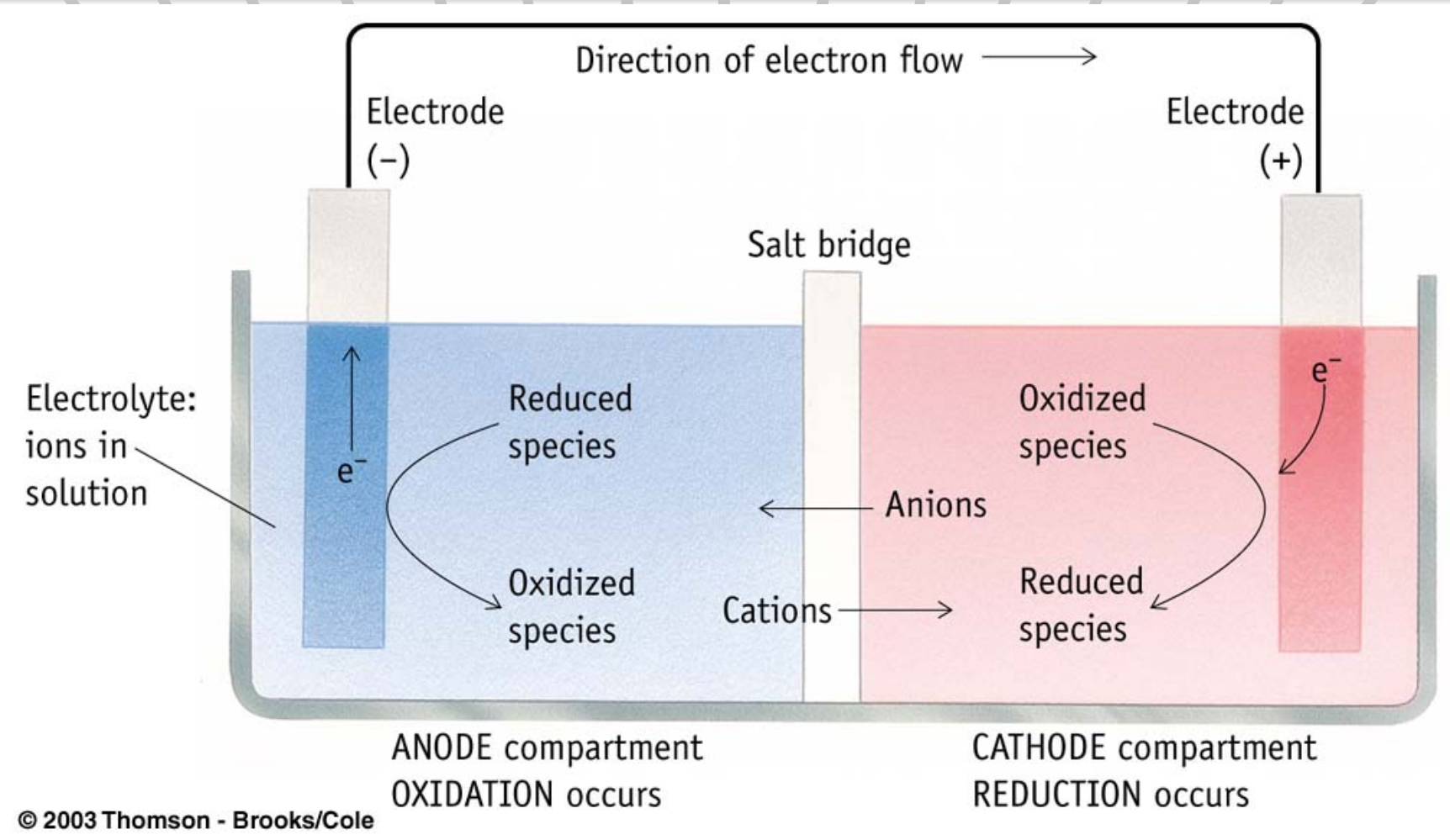
- The following electrochemical cell produces energy by the reaction of $Cu^{2+}$ ions with Zn metal.
- A cell that produces energy when a spontaneous reaction occurs is called a voltaic or galvanic cell.



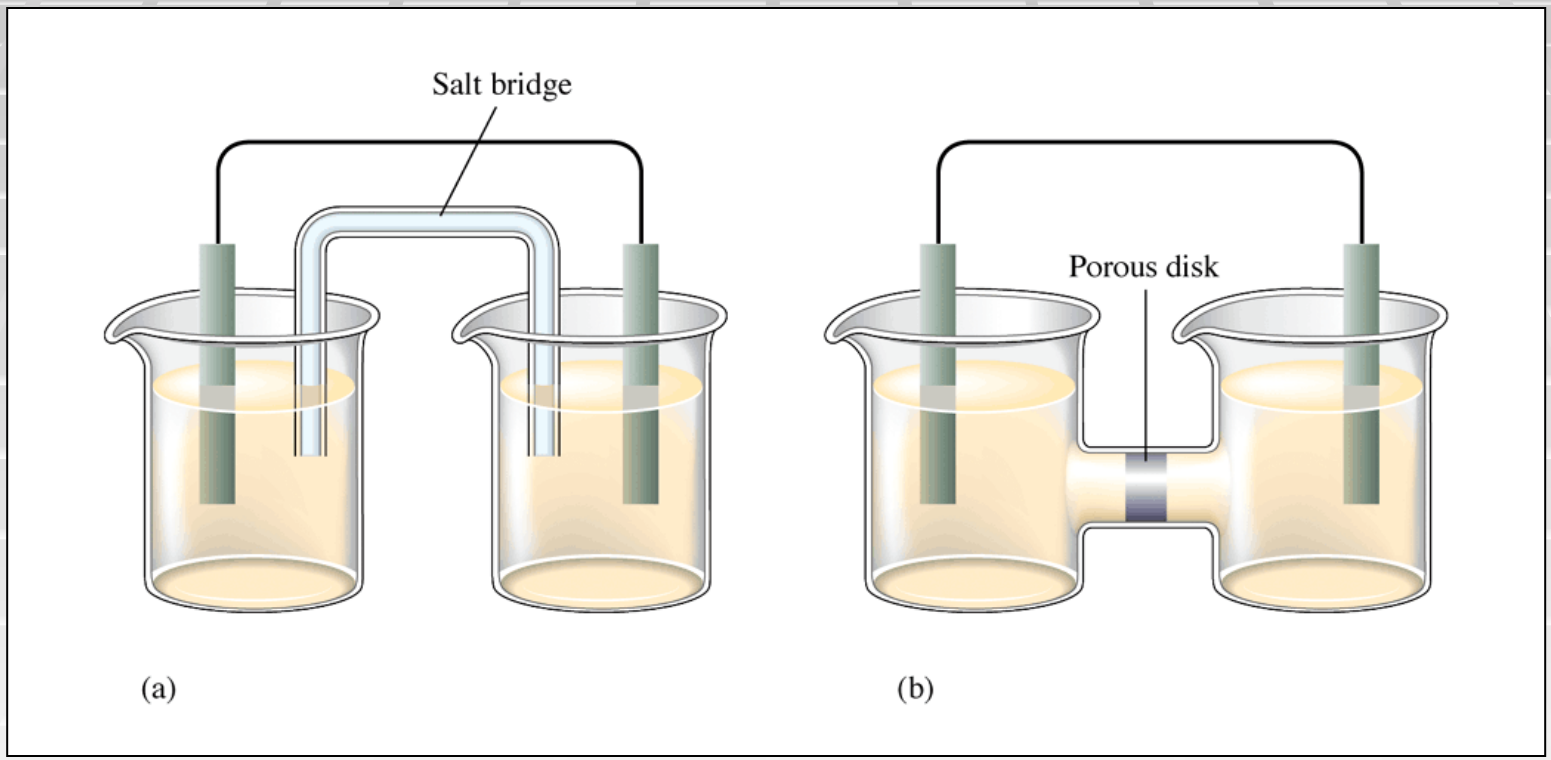
# Electrochemistry

- A redox reaction can be separated into its ½-reactions and allowed to react in separate chambers that are connected by a wire and a salt bridge.
- Electrons are "pushed" along the wire from the ½-cell where oxidation occurs to the reduction ½-cell.
- Charge balance is maintained for the ½-cells by a salt bridge.
- The oxidation ½-cell is called the ANODE.
- The reduction ½-cell is called the CATHODE.

# A generic voltaic cell

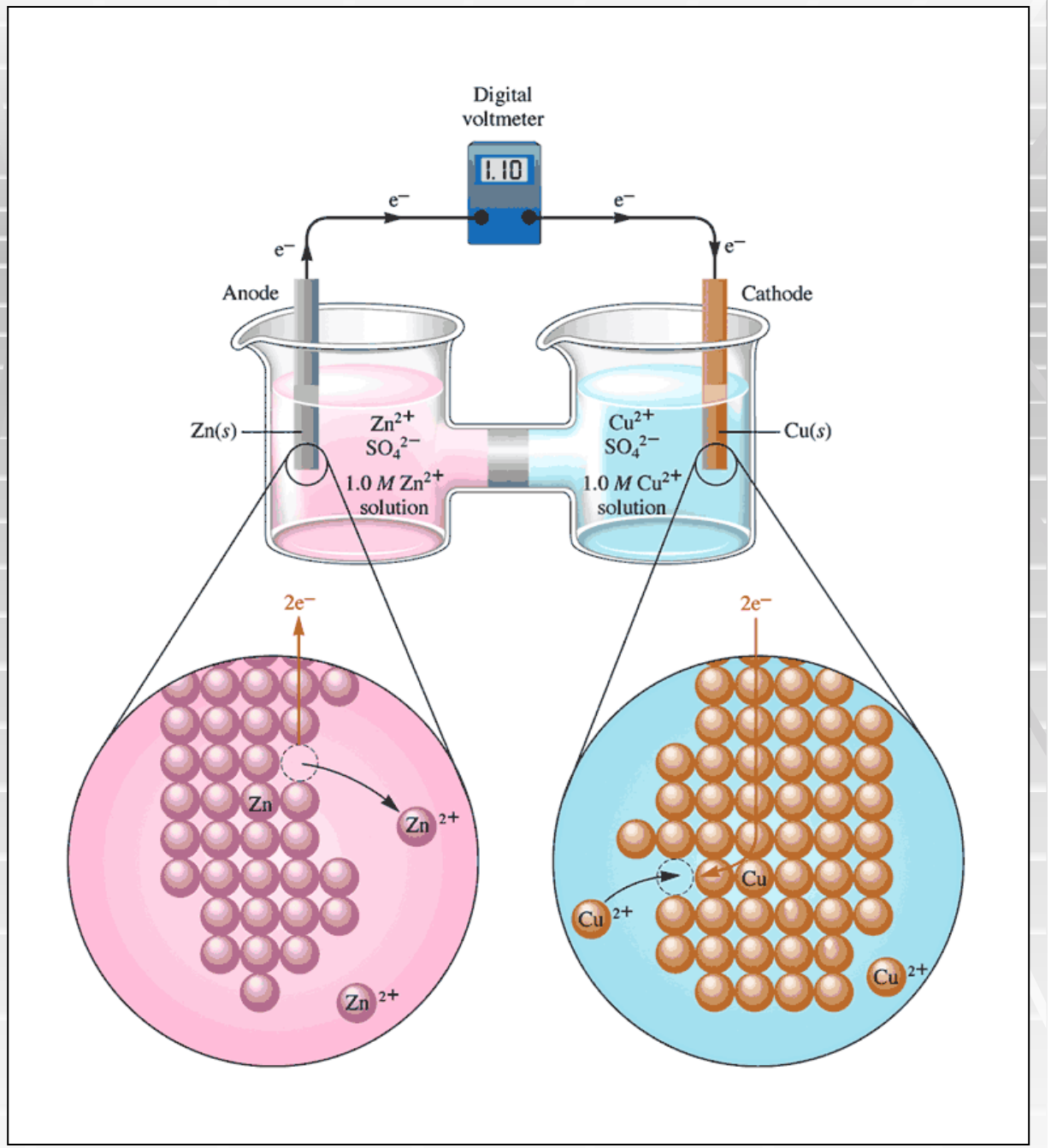


# Galvanic cells can contain a salt bridge as in (a) or a porous-disk connection as in (b).



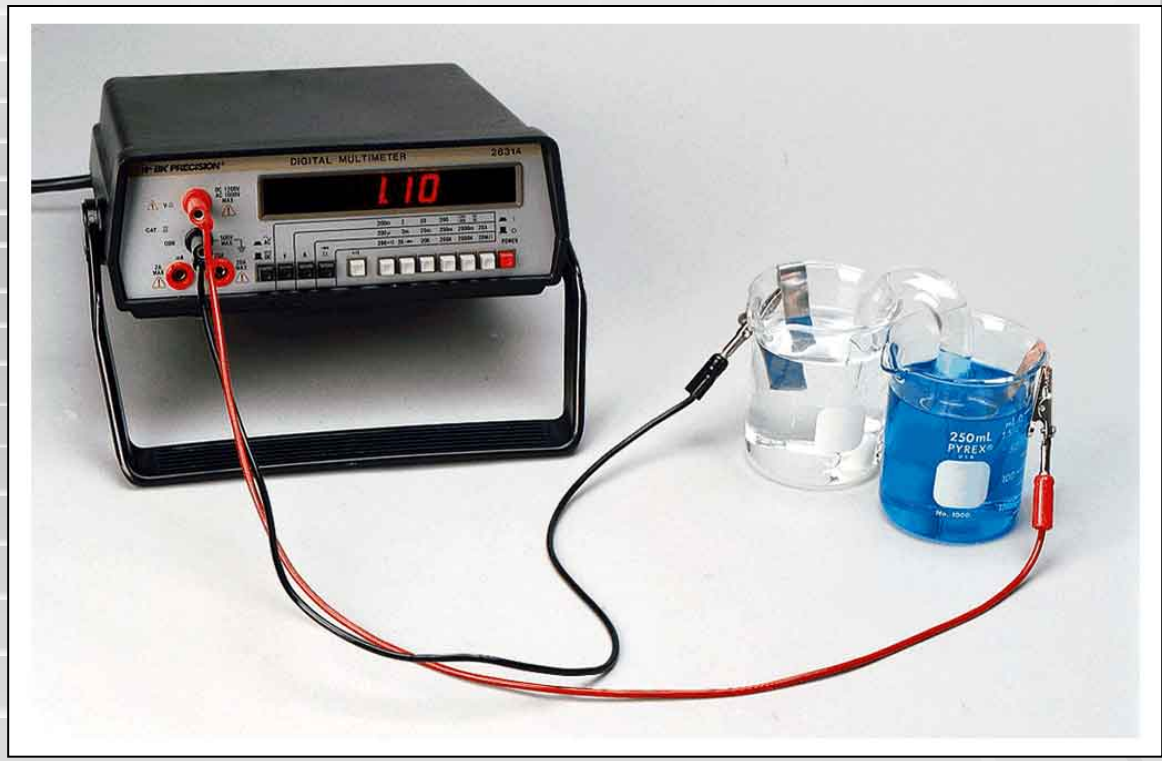
# Zn/Cu cell (cont.)

- Write the reaction for each ½-cell.
- Write the overall reaction.
- Write the cell notation.



# Zn/Cu cell (cont.)

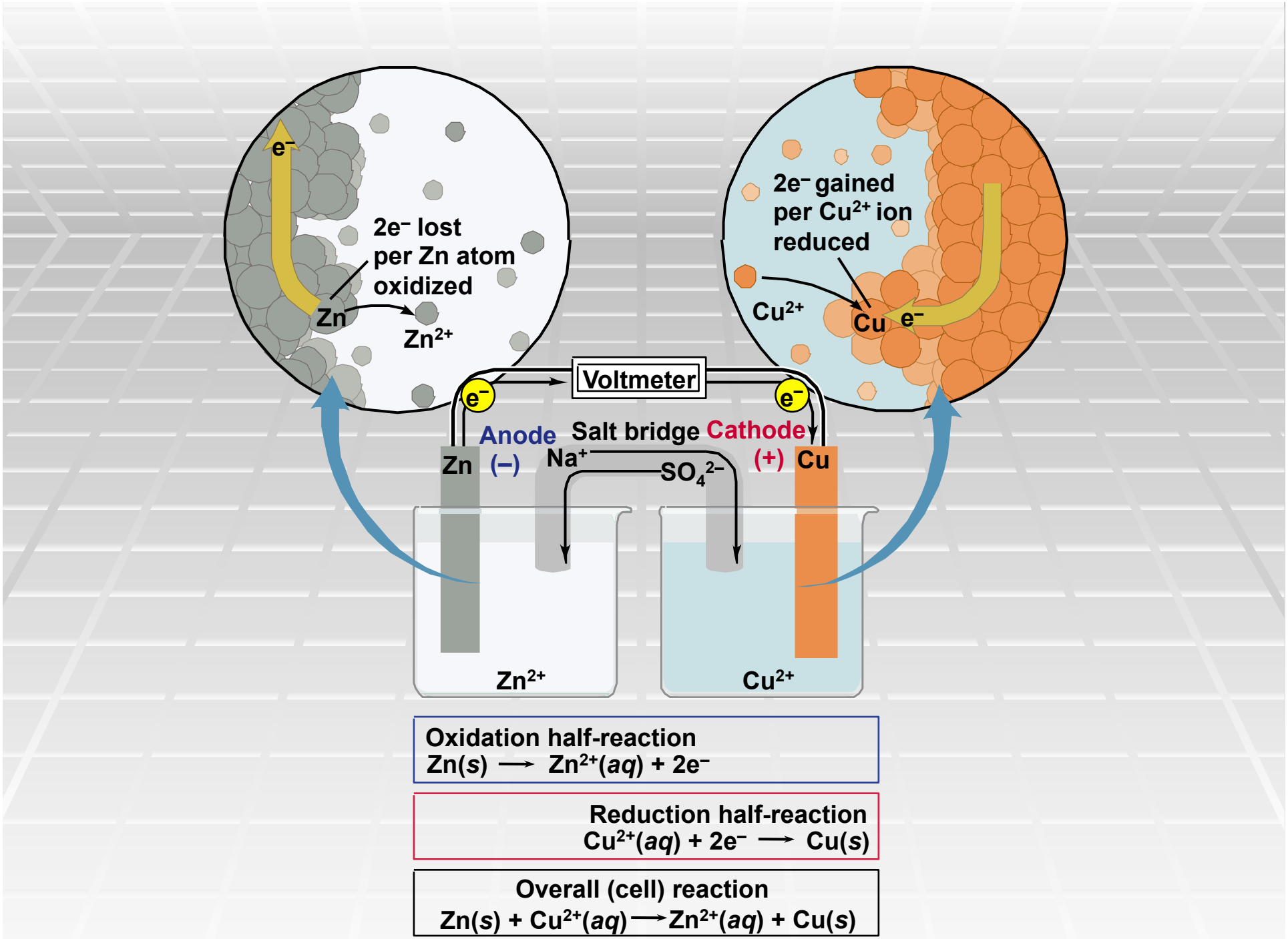
- Calculate the standard cell potential (E°) for the Zn/Cu cell.




$$E^{o}_{cell} = E^{o}_{red} + E^{o}_{oxid}$$

*Book Method :*

$$E^{\circ}_{cell} = E^{\circ}_{red,CATHODE(reduction)} - E^{\circ}_{red,ANODE(oxidation)}$$




**Oxidation half-reaction**

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

**Reduction half-reaction**

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

**Overall (cell) reaction**

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

# Electrical Potential

- Electromotive force (emf) is the driving or pushing of electrons from the anode to the cathode.
- Electrons always flow from the electrode with the lower reduction potential to the electrode with the higher reduction potential.
- Cell potential (E°) is related to electrical work (Joules) as charge (coulombs) flows in a circuit:

**Volt (V) = Joule (J) / coulomb (C)**

- A coulomb is the amount of charge that passes a single point in an electrical circuit when one ampere of current flows for 1 second.

**1 Coulomb = 1 Ampere • second**

**1 Coulomb = charge of $6.24 \times 10^{18}$ electrons**

**charge of 1 electron = $1.602 \times 10^{-19}$ C**

# Electrical Potential

- Galvanic cells must always have a positive cell potential.
- Which of the following redox pairs will function at the ANODE in each of the following pairs? Also calculate the cell potential.
  - **$Cd^{2+}$ / Cd and $Sn^{4+}$ / $Sn^{2+}$**
  - **$Zn^{2+}$ / Zn and $Al^{3+}$ / Al**
  - **$Br_2$ / $Br^-$ and $MnO_4^-$ / $Mn^{2+}$**

# Standard Potentials

- Standard potentials are measured for Standard Thermodynamic conditions:

  **T = 298 K**

  **[X] = 1 *M*  $P_X$ = 1 atm**

- All standard reduction potentials are measured relative to the Standard Hydrogen Electrode (**SHE**).
- SHE is composed of a solution that is 1.0 *M* $H^+$ and an enclosed atmosphere with $P_{H2}$ = 1.0 atm
- SHE is assigned a standard reduction potential of zero.

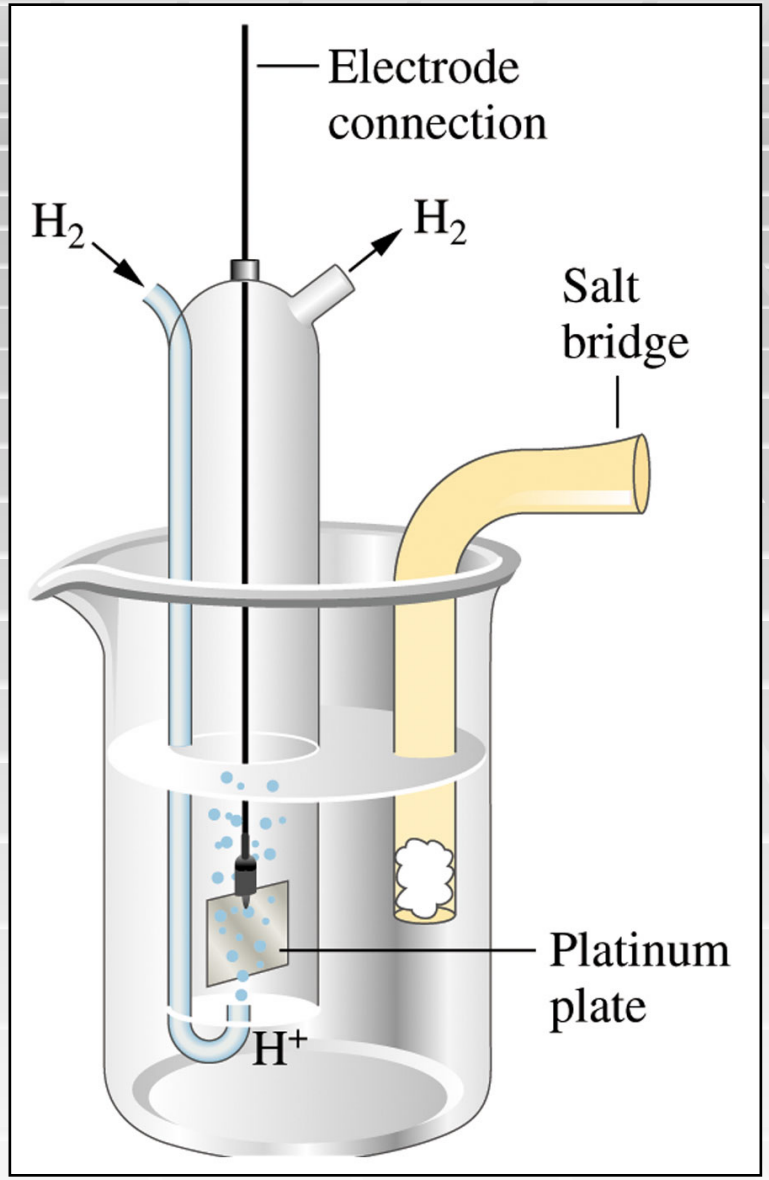
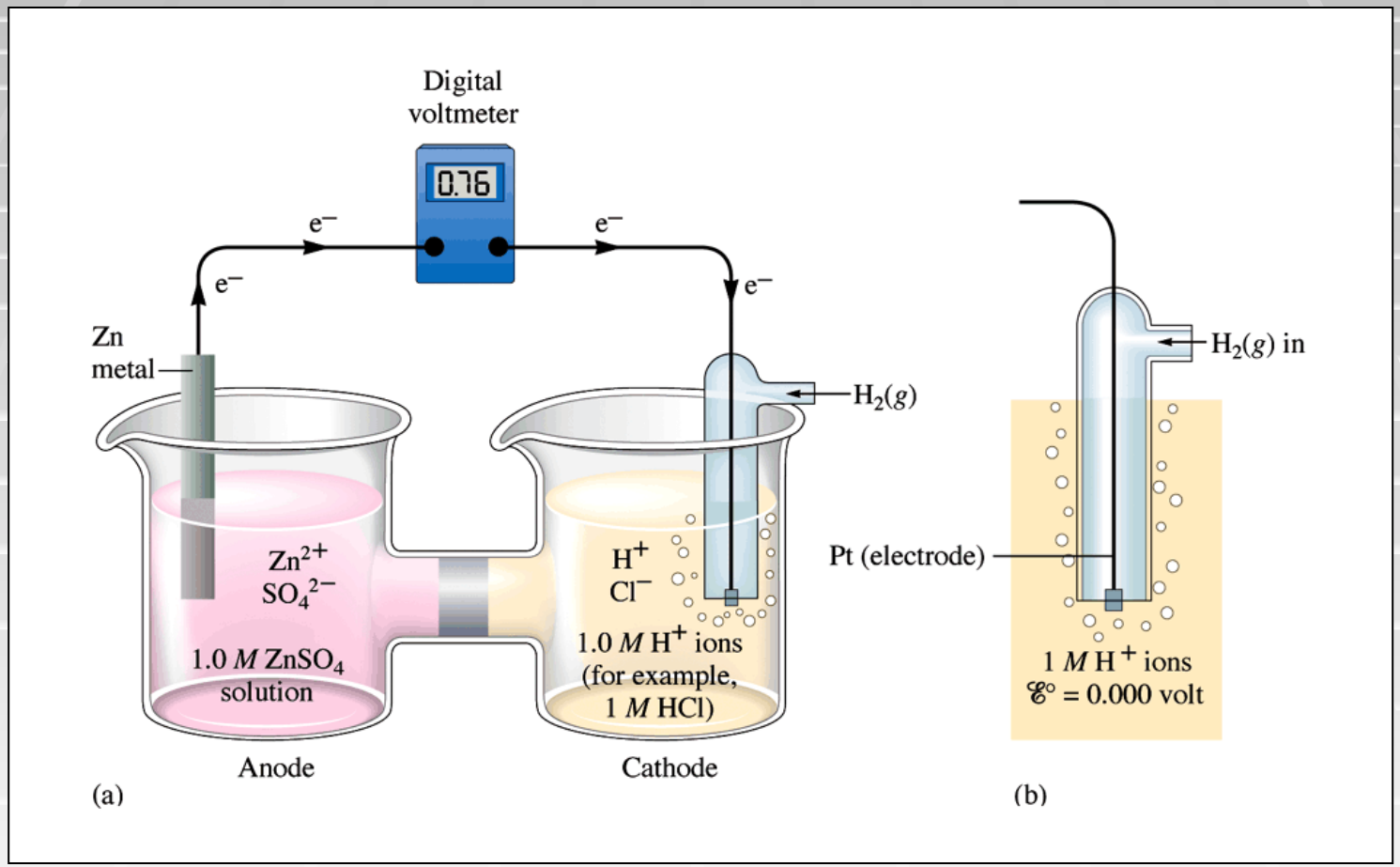


Figure a: A galvanic cell involving the reactions:

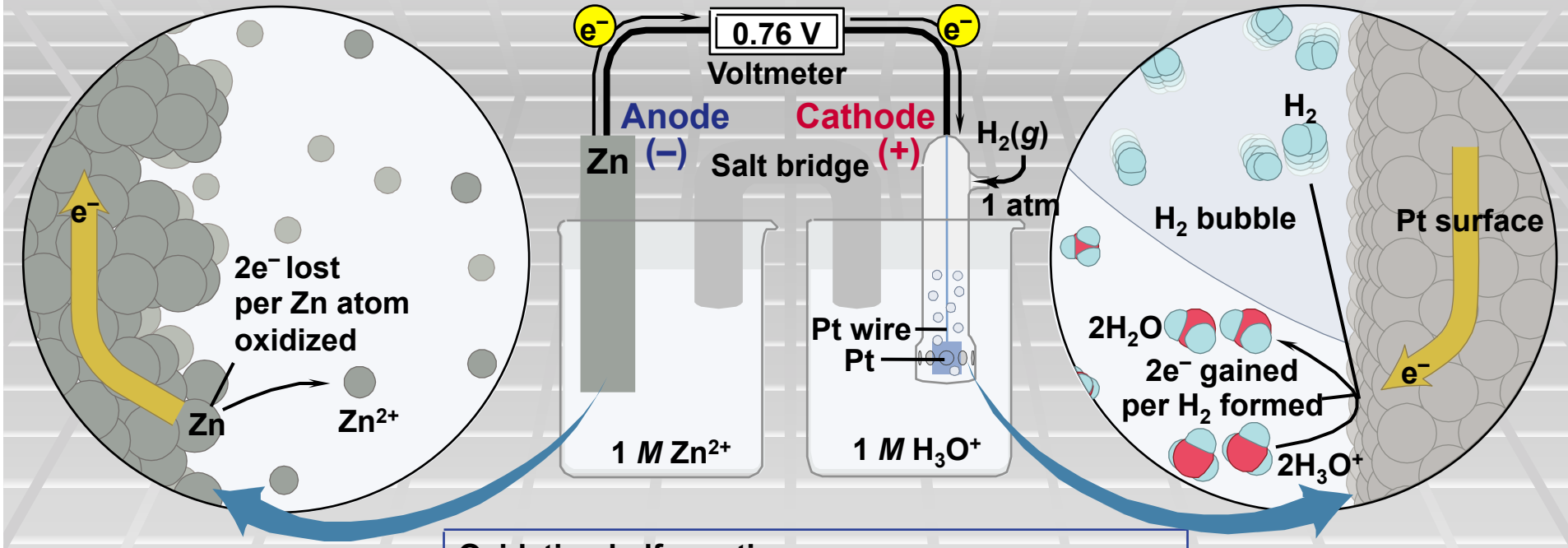
$Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation - at the anode)

$2\ H^+ + 2\ e^- \rightarrow H_2$ (reduction - at the cathode)

has a potential of 0.76 V.




*What is the reduction potential for Zinc?*




**Oxidation half-reaction**

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

**Reduction half-reaction**

$$2H_3O^+(aq) + 2e^- \longrightarrow H_2(g) + 2H_2O(l)$$

**Overall (cell) reaction**

$$Zn(s) + 2H_3O^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) + 2H_2O(l)$$

The potential of the standard reference electrode is defined as 0.00 V, so the cell potential equals the negative of the anode potential; that is, 0.76 V = 0.00 V – $E^0_{zinc}$, so $E^0_{zinc} = -0.76$ V.

# Electrochemical Cell with Cu and SHE

- Cu has a standard reduction potential of + 0.34 V.
- Will copper be oxidized or reduced in a cell with SHE?
- Diagram a standard cell that could be used to find the standard reduction potential of copper. Use SHE as one electrode in the cell.

# Relative Oxidizing and Reducing Power

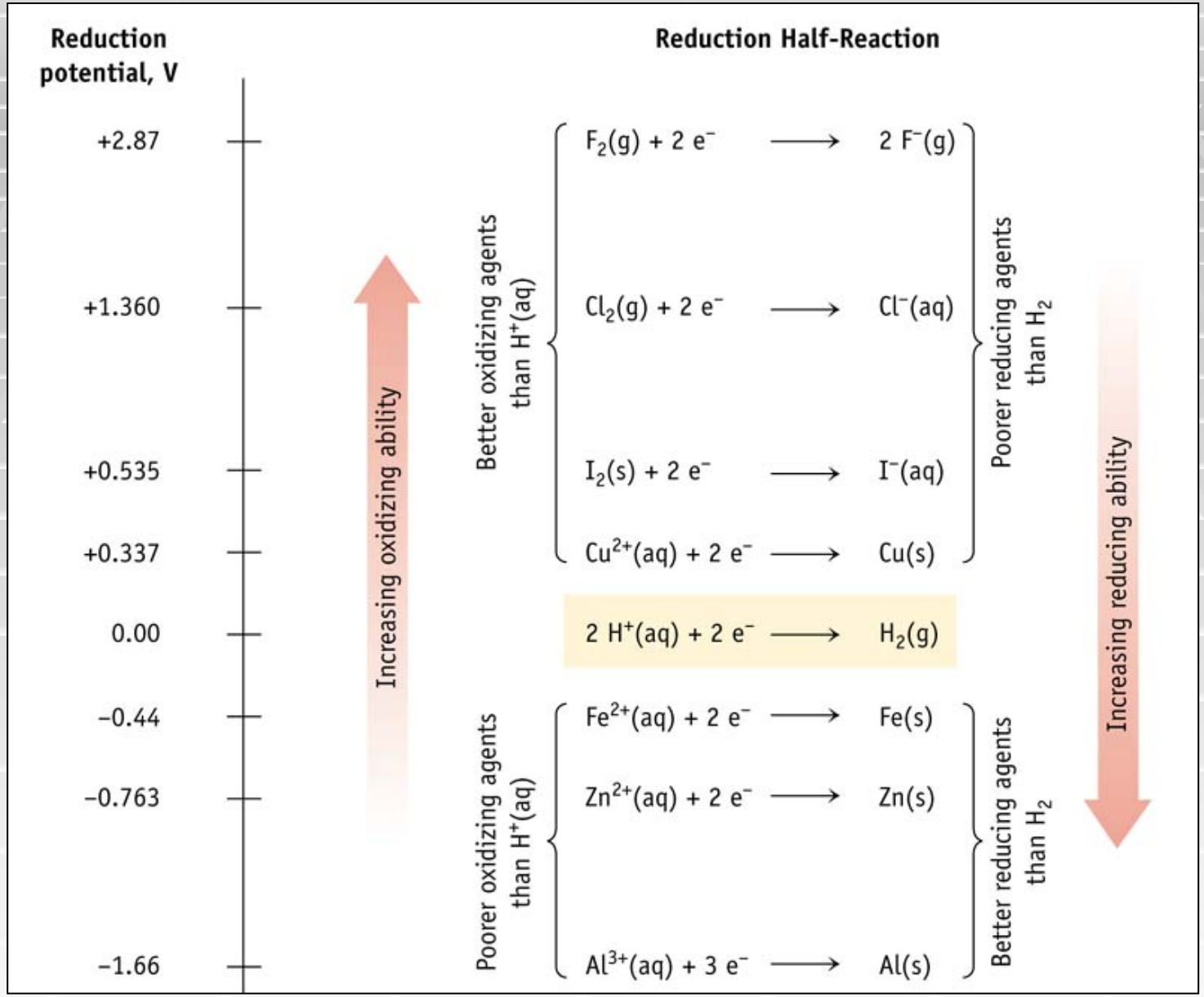
**Table 21.2 Selected Standard Electrode Potentials (298 K)**

| Half-Reaction | $E^0_{\text{half-cell}}$ (V) |
|---|---|
| $F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$ | +2.87 |
| $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ | +1.36 |
| $MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$ | +1.23 |
| $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$ | +0.96 |
| $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ | +0.80 |
| $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ | +0.77 |
| $O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$ | +0.40 |
| $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ | +0.34 |
| $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ | 0.00 |
| $N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$ | −0.23 |
| $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ | −0.44 |
| $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ | −0.76 |
| $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ | −0.83 |
| $Na^+(aq) + e^- \rightleftharpoons Na(s)$ | −2.71 |
| $Li^+(aq) + e^- \rightleftharpoons Li(s)$ | −3.05 |

Strength of oxidizing agent ↑

Strength of reducing agent ↓

# Relative Oxidizing and Reducing Power



# Relative Oxidizing and Reducing Power

- Which of the following is most easily oxidized?

  **Al** **Sn** **Cd**

- Which of the following is most easily reduced?

  **$Mg^{2+}$** **$Na^{+}$** **$Fe^{3+}$**

- Which of the following is the best reducing agent?

  **Zn** **$Zn^{2+}$** **$Fe^{2+}$**

- Which of the following is the best oxidizing agent?

  **$H^{+}$** **$Ni^{2+}$** **$Fe^{2+}$**

# Relative Oxidizing and Reducing Power

- Which of the following can reduce $Al^{3+}$?

  **K** *or* **Fe**

- Which of the following can oxidize Al?

  **$Mg^{2+}$** *or* **$Zn^{2+}$**

- Which of the following can reduce $H^{+}$?

  **$F^{-}$** *or* **Ni**

- Which of the following can oxidize $H_2$?

  **$Sn^{4+}$** *or* **$Zn^{2+}$**

# Relationship of Free Energy and Cell Potential

- The free energy change for a reaction relates to the maximum amount of work that can be done by a chemical system:

$$\Delta G = w_{max}$$

- Electrical work is related to cell potential and the number of electrons transferred in a chemical process:

$$w_{max} = -nFE$$

- Combining these two equations, we can relate free energy change and cell potential:

$$\Delta G = -nFE$$

Where n = # electrons transferred (as determined from the balanced reaction), and F = Faraday constant:

$$F = 96{,}485 \frac{J}{V \cdot mol(electron)} = 96{,}485 \frac{C}{mol(electron)}$$

# Standard Free energy and Cell Potential

- Under standard thermodynamic conditions:

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

## Standard Cell Potentials & K

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

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

# Standard and Non-Standard Cell Potentials

$$E^{o}_{cell} = E^{o}_{red} + E^{o}_{oxid}$$

$$E_{cell} = E_{red} + E_{oxid}$$

Book Method :

$$E_{cell} = E_{red,CATHODE} - E_{red,ANODE}$$

# Nernst Equation

- Under non-standard conditions of pressure or concentration (at 298 K):

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

- Because R,T, and F are all constant (T=298 K), we often use the following form of the Nernst equation:

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

# Electrochemical Cell Diagrams

Diagram a functional voltaic cell with the following couple under standard conditions:

{$Fe^{+2}$ / Fe}  {$OCl^-_{(aq)}$ / $Cl^-_{(aq)}$ (in basic solution)}

***Be sure to include all of the following in the diagram:***

- Label cathode and anode
- Appropriate metal electrodes
- Concentrations of important SPECIES in each cell.
- BALANCED half reaction occurring in each cell.
- All components required to have an operating circuit.

# $Fe^{2+}$ / $OCl^-$ Cell diagram (cont.)

- Write the balanced overall reaction for the cell.
- Calculate E° for the cell.
- Calculate $\Delta G°$ for the reaction.
- Calculate K for the reaction.
- Calculate $E_{cell}$ (at 298 K) if:

**$[Fe^{2+}] = 0.10\ M$**

**$[OCl^-] = 0.25\ M$**

**$[Cl^-] = 0.50\ M$**

**pH = 12.00**

# Electrochemical Cell Diagram

Diagram a functional voltaic cell with the following couple under standard conditions:

{$Cu^{+2}$ / Cu}  {$MnO_{4\,(aq)}^{-}$ / $Mn^{2+}_{(aq)}$ (in acidic solution)}

***Be sure to include all of the following in the diagram:***

- Label cathode and anode
- Appropriate metal electrodes
- Concentrations of important SPECIES in each cell.
- BALANCED half reaction occurring in each cell.
- All components required to have an operating circuit.

# $Cu^{2+}$ / $MnO_4^-$ Cell diagram (continued)

- Write the balanced overall reaction for the cell.
- Calculate E° for the cell.
- Calculate $\Delta G°$ for the reaction.
- Calculate K for the reaction.
- Calculate $E_{cell}$ (at 298 K) if:

$[Cu^{2+}] = 2.0\ M$

$[MnO_4^-] = 0.10\ M$

$[Mn^{2+}] = 0.50\ M$

$[H^+] = 1.0 \times 10^{-4}\ M$

# The Nernst Equation and non-standard half-cells

- Calculate the $E_{red}$ for a $Ni^{2+}/Ni_{(s)}$ ½-cell when $[Ni^{2+}] = 0.001\ M$.

- Calculate the $E_{red}$ for a $Ni^{2+}/Ni_{(s)}$ ½-cell when $[Ni^{2+}] = 5.0\ M$.

- Calculate the $E_{oxid}$ for a $Sn^{4+}/\ Sn^{2+}$ ½-cell when $[Sn^{4+}] = 0.50\ M$ & $[Sn^{2+}] = 0.00025\ M$.

# Concentration Cells

- A cell prepared with the same ½ - reaction in both compartments with dissolved species at varying concentrations.
- Electrochemical equivalent of dilution.
- The compartment with the more concentrated solution acts as the _____.
- The compartment with the more dilute solution acts as the _____.

# Concentration Cells

- **Consider a cell made with a $Zn^{2+}$ (1.0 *M*) / $Zn_{(s)}$ electrode and a $Zn^{2+}$ (0.0001 *M*) / $Zn_{(s)}$ electrode.**
  - *Calculate the individual ½ - cell potentials.*
  - *Find the overall cell potential.*

# Concentration Cells

- Consider a general concentration cell.

# Equilibrium Constant & Cell potentials

- Based on cell potentials, calculate K for the following reactions at 25˚C:

# Equilibrium Constant & Cell potentials

- Based on cell potentials for the appropriate ½-reactions, calculate the $K_{sp}$ value for AgCl at 25˚C.

- Compare this to the listed value in the book.

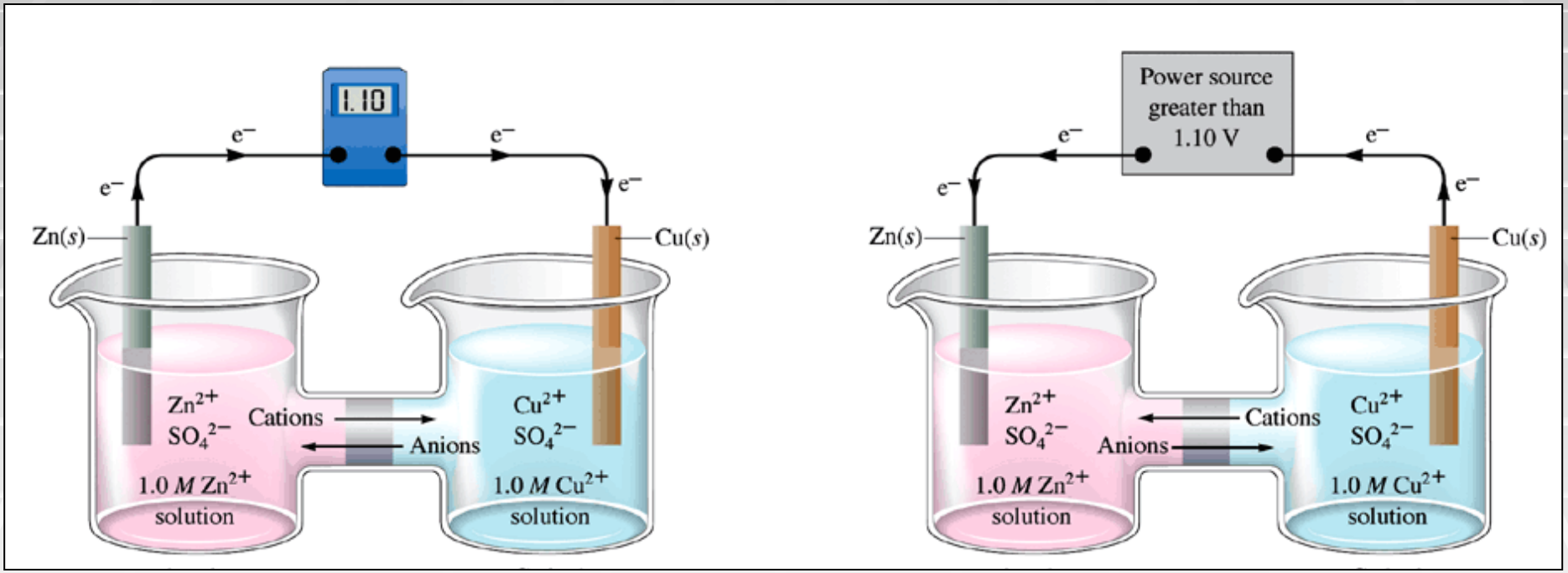
# Electrolysis

- Electrolysis is the use of an applied electrical current to bring about chemical change.
- A voltaic (or galvanic) cell produces electrical energy as a spontaneous reaction occurs.
- An electrolytic cell uses electrical energy to drive the non-spontaneous chemical process.

# Galvanic and Electrolytic Cell Comparison

Figure (A): A standard galvanic cell based on the spontaneous reaction

Figure (B): A standard electrolytic cell. A power source forces the opposite reaction




Anode Cathode Cathode Anode

# Formation of $CuBr_2$

- Elemental bromine reacts with metal copper in a highly product favored reaction:

- Based on the ½-cell potentials, estimate a value of K for this reaction.

# Electrolysis of $CuBr_2$

- $CuBr_2$ does not spontaneously decompose to $Cu_{(s)}$ and $Br_{2(l)}$. Consider the reaction:

- If we wish to drive this reaction, we must change the conditions to make this process favorable.
- We can apply an external voltage from a power source.
- The voltage we apply must be greater in magnitude than the cell potential for the spontaneous reaction, and applied in the reverse polarity.

# Electrolysis of $CuBr_2$ (continued)

- What minimum voltage must be applied to electrolyze copper (II) bromide?
- Consider a diagram of the electrolytic cell:
- Note that the electrolytic cell need not be separated into individual compartments.

# Electrolysis of $H_2O$

- Consider the electrolysis of water under neutral conditions with a strong electrolyte like KCl in solution (to increase the conductivity of the water). View quicktime movie.

- Diagram the electrolytic cell.
- Write both ½-reactions.
- Determine the minimum potential needed to electrolyze the water.

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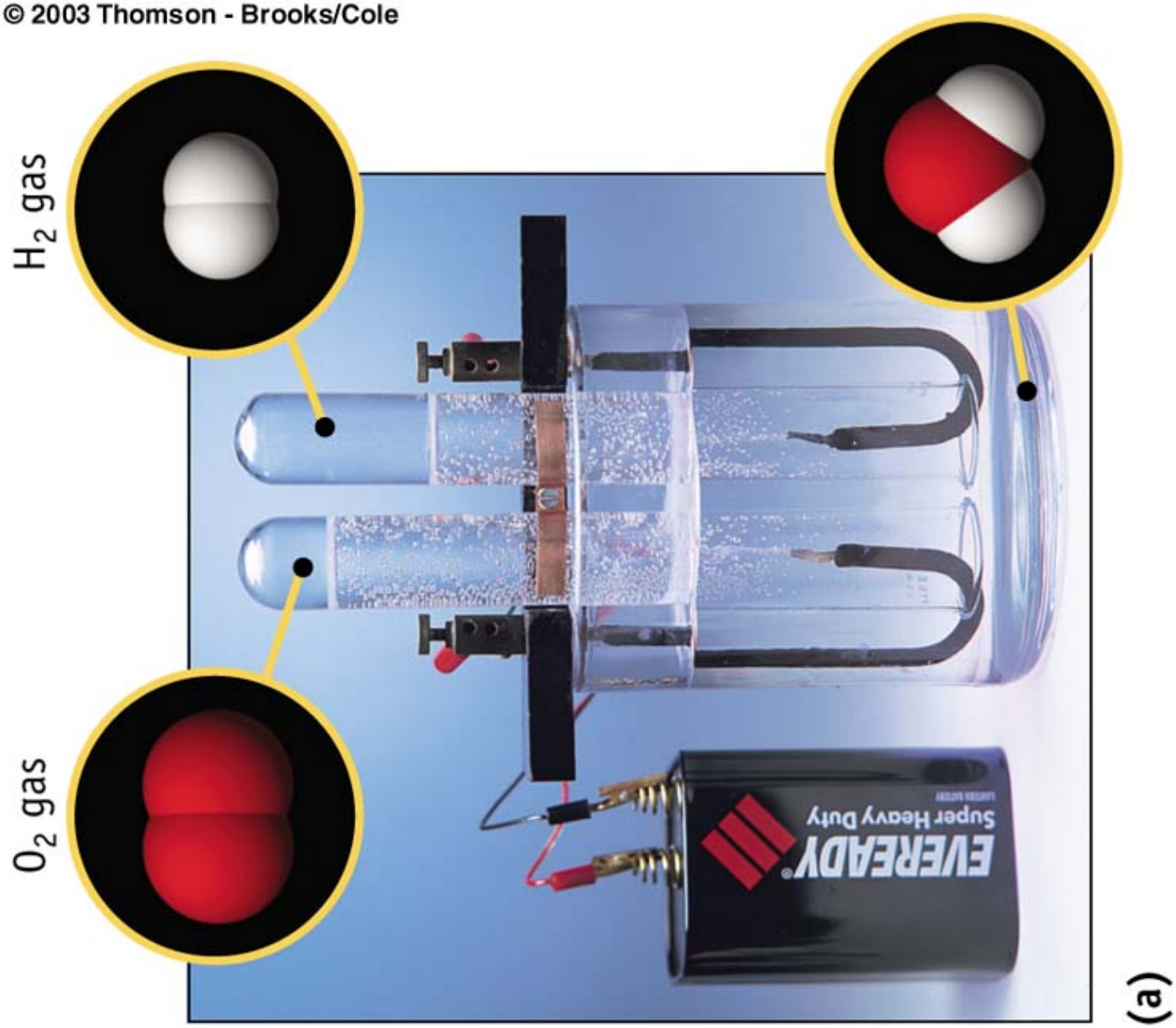


# Electrolysis of $H_2O$ (continued)

- If we try to electrolyze other compounds in water, we must consider whether the electrolysis of water or of the ion in solution is more favorable at that electrode.

# Electrolysis of KBr

- To determine if KBr can be electrolyzed to $K_{(s)}$ and $Br_{2(l)}$ in aqueous solution, we must consider all potential reactions at the cathode and anode.

- CATHODE:

- ANODE:

# Electrolysis of KBr (continued)

- Based on the cathode and anode reactions that are most favorable, write the overall reactions for the electrolysis of a KBr solution.

- Calculate the minimum applied voltage to drive this reaction.

# Electrolysis of KBr (continued)

- In order to separate KBr into its elements, molten KBr must be electrolyzed. Because of the high temperature required, special equipment is needed.
- Consider a diagram of the electrolysis of molten KBr:
- Estimate the minimum applied voltage to drive the reaction.

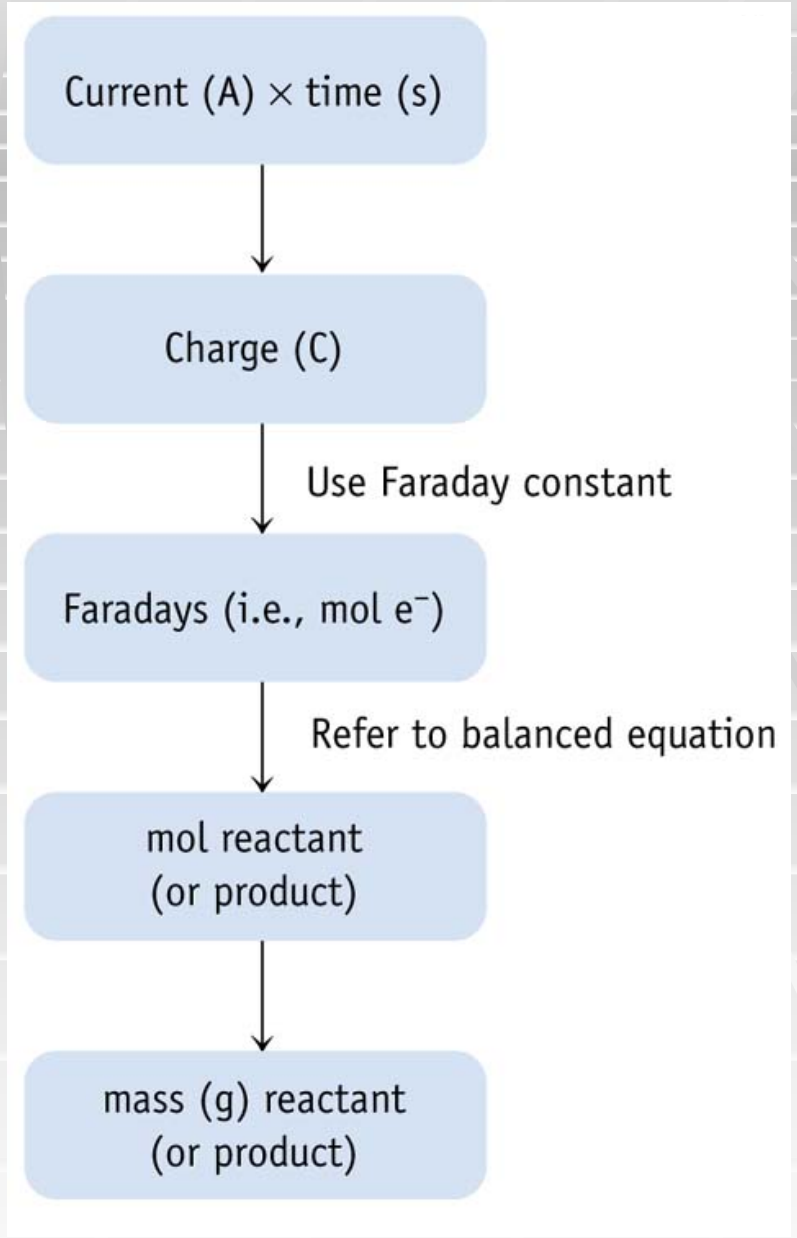
# Electrolysis & Current

- Electrolytic processes are important in the production of a number of important industrial chemicals:  aluminum metal, copper metal, chlorine gas, sodium hydroxide, and many others.
- To determine the mass that is formed when an electrolytic process takes place, we must know the current applied and the time it is applied.
- Current (ampere) is the flow of charge.

**1 ampere (A) = 1 coulomb (C) / second (s)**

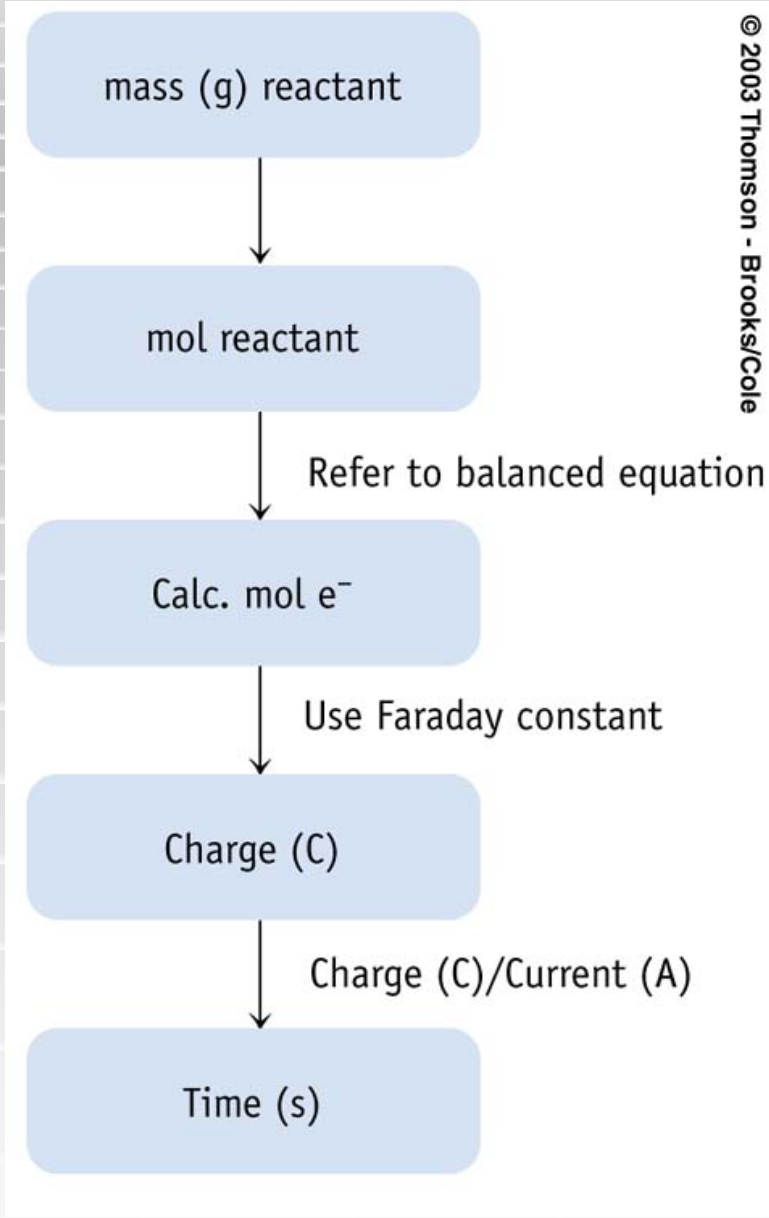
# Electrolysis and counting electrons

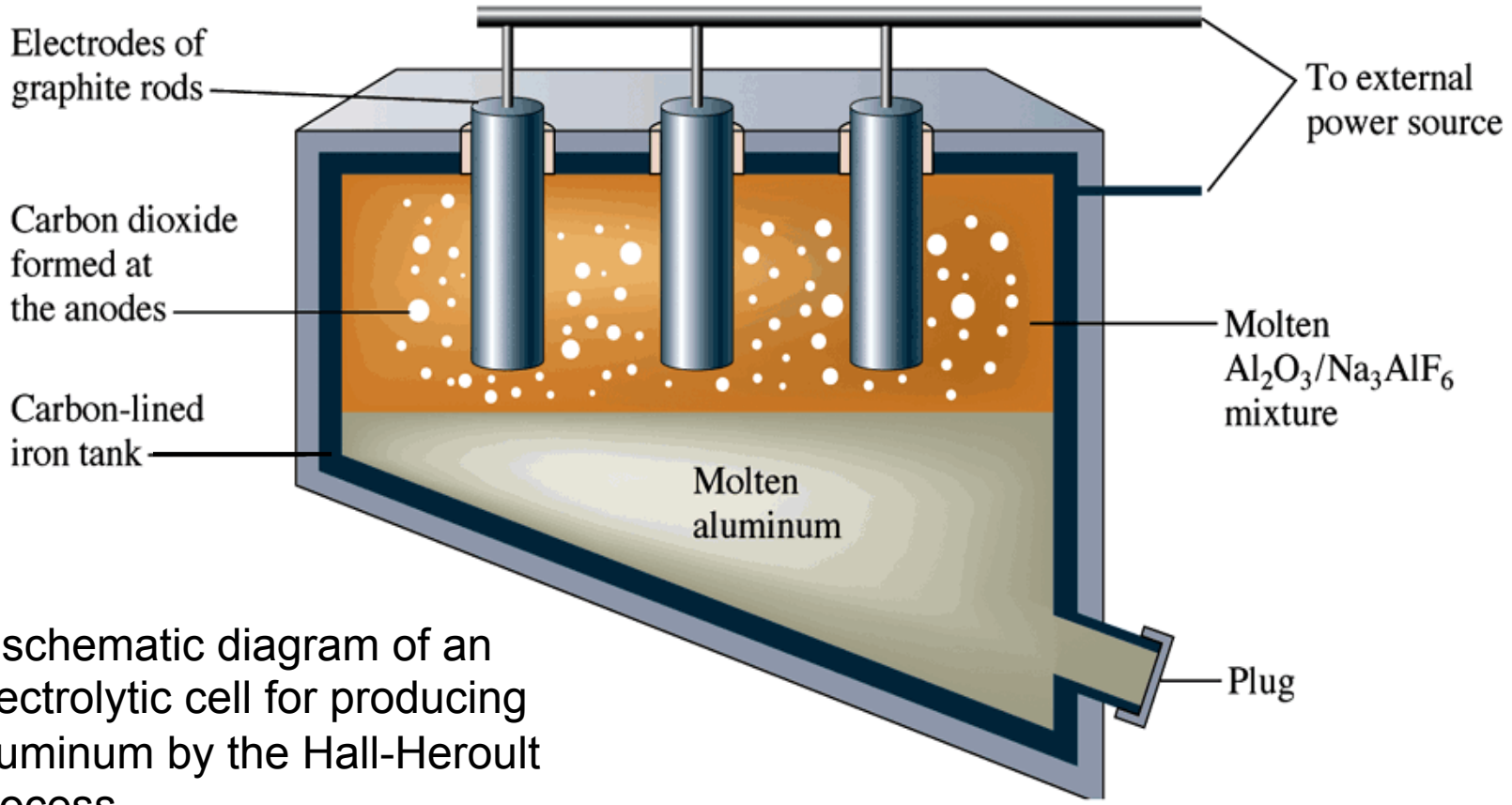
- What mass of zinc can be plated by the application of 10.0 A for 30.0 minutes?



# Electrolysis and counting electrons

- What time is required to plate 500. mg of gold onto a ring by applying a current of 5.0 A to a solution of $AuCl_3$?






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

Aluminum is produced commercially by the process illustrated above. What current must be applied to produce 1000. kg of aluminum in 2.0 hours?