# Chapter 20. Electrochemistry

20.1 Oxidation-Reduction Reactions

- Chemical reactions in which the oxidation state of one or more substance changes are called oxidation-reduction reactions (redox reactions).
- Oxidation involves loss of electrons (OIL).
- Reduction involves gain of electrons (RIG).
- **Electrochemistry** is the branch of chemistry that deals with relationships between electricity and chemical reactions.
- Consider the spontaneous reaction that occurs when Zn is added to HCl.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$
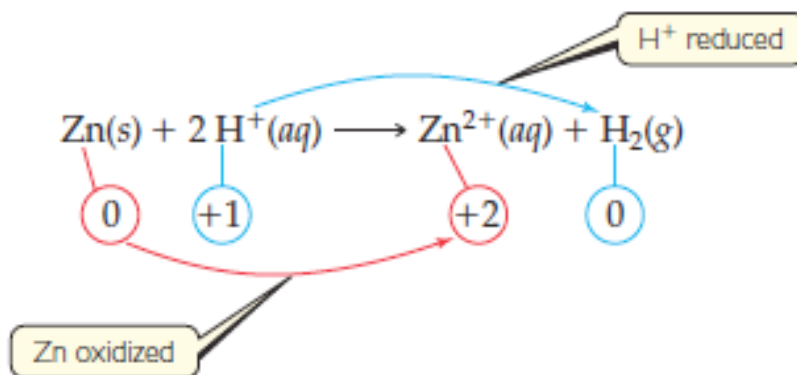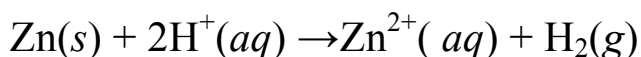
- The oxidation numbers of Zn and H^+ have changed.
  - o The oxidation number of Zn has increased from 0 to +2.
  - o The oxidation number of H has decreased from + 1 to 0.
    - ▪ Therefore, Zn is oxidized to Zn^{2+}, while H^+ is reduced to H_2.
- H^+ causes Zn to be oxidized.
  - o Thus, H^+ is the **oxidizing agent or oxidant**.
- Zn causes H^+ to be reduced.
  - o Thus, Zn is the **reducing agent or reductant**.

- Note that the reducing agent is oxidized and the oxidizing agent is reduced.

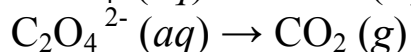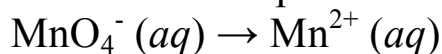## 20.2 Balancing Oxidation-Reduction Equations
- Recall the law of conservation of mass: The amount of each element present at the beginning of the reaction must be present at the end.
- Conservation of charge: Electrons are not lost in a chemical reaction.
- Some redox equations may be easily balanced by inspection.
    - However, for many redox reactions we need to look carefully at the transfer of electrons.

Half-Reactions
- **Half-reactions** are a convenient way of separating oxidation and reduction reactions.
- Consider the reaction:
$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$$
- The oxidation half-reaction is:
$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$$
- Note that electrons are a product here.
- The reduction half-reaction is:
$$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$$
- Note that electrons are a reactant here.

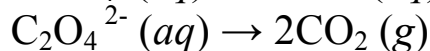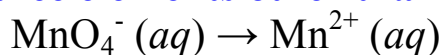# Balancing Equations by the Method of Half-Reactions

- Consider the titration of an acidic solution of $Na_2C_2O_4$ (sodium oxalate, colorless) with $KMnO_4$ (deep purple)
  - MnO_4^- is reduced to Mn^{2+} (pale pink) while the $C_2O_4^{2-}$ is oxidized to CO_2.
  - The equivalence point is indicated by the presence of a pale pink color
  - If more $KMnO_4$ is added, the solution turns purple due to the excess $KMnO_4$.
- What is the balanced chemical equation for this reaction?
- We can determine this using the method of half-reactions:
  - Write down the two incomplete half reactions
    $$MnO_4^- \, (aq) \rightarrow Mn^{2+} \, (aq)$$
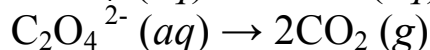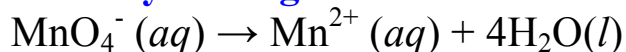 $$C_2O_4^{2-} \, (aq) \rightarrow CO_2 \, (g)$$
- Balance each half reaction:
  - **First, balance elements other than H and O.**
    $$MnO_4^- \, (aq) \rightarrow Mn^{2+} \, (aq)$$
    $$C_2O_4^{2-} \, (aq) \rightarrow 2CO_2 \, (g)$$
  - **Then balance O by adding water.**
    $$MnO_4^- \, (aq) \rightarrow Mn^{2+} \, (aq) + 4H_2O(l)$$
    $$C_2O_4^{2-} \, (aq) \rightarrow 2CO_2 \, (g)$$
  - **Then balance H by adding H^+.**
    $$8H^+(aq) + MnO_4^- \, (aq) \rightarrow Mn^{2+} \, (aq) + 4H_2O(l)$$
    $$C_2O_4^{2-} \, (aq) \rightarrow 2CO_2 \, (g)$$
- **Finish by balancing charge by adding electrons (to the more positive side)**
  - For the permanganate half-reaction, note that there is a charge of 7+ on the left and 2+ on the right.
  - Therefore, 5 electrons need to be added to the left:
    $$5e^- + 8H^+(aq) + MnO_4^- \, (aq) \rightarrow Mn^{2+} \, (aq) + 4H_2O(l)$$
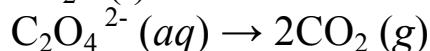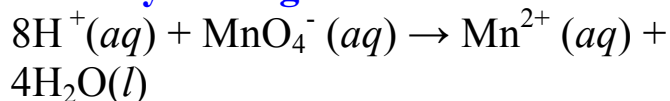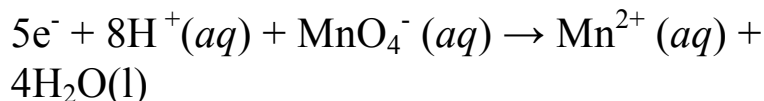
- In the oxalate half-reaction, there is a 2- charge on the left and a 0 charge on the right, so we need to add two electrons to the products:

$$C_2O_4{}^{2-} (aq) \rightarrow 2CO_2 (g) + 2e^-$$

- Multiply each half-reaction to make the number of electrons equal.
  - To balance the 5 electrons for permanganate and 2 electrons for oxalate, we need 10 electrons for both.
    - Multiplying gives:

$$10e^- + 16H^+(aq) + 2MnO_4{}^- (aq) \rightarrow 2Mn^{2+} (aq) + 8H_2O(l)$$

$$5\ C_2O_4{}^{2-} (aq) \rightarrow 10\ CO_2 (g) + 10e^-$$
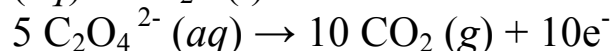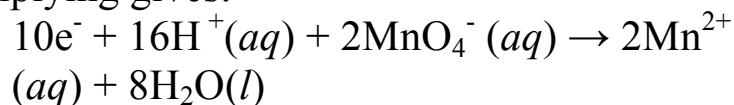
- Now add the reactions and simplify.

$$5C_2O_4{}^{2-} (aq) + 16H^+(aq) + 2MnO_4{}^- (aq) \rightarrow 2Mn^{2+} (aq) + 8H_2O(l) + 10\ CO_2 (g)$$
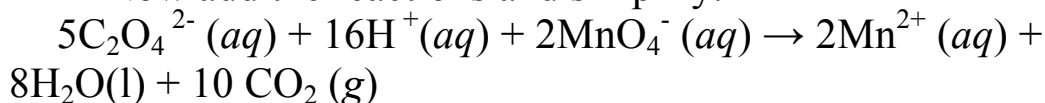
- The equation is now balanced!
- Note that all of the electrons have cancelled out!

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                    Write separate half-reactions

         Oxidation                                    Reduction
         half-reaction          Balancing order       half-reaction
                                a. elements (except H,O)
                                b. oxygen (use $H_2O$)
            Balance             c. hydrogen (use $H^+$)    Balance
                                d. charge (use electrons)
      Balanced oxidation                            Balanced reduction
      half-reaction                                 half-reaction

   Equalize electrons                                        Equalize electrons
   transferred              Add half-reactions               transferred

                              Cancel identical species

                         Check that elements and
                         charges are balanced
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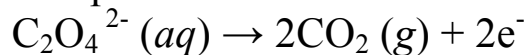
Balancing Equations for Reactions Occurring in Basic Solution

- The same method as above is used, but OH^- is added to "neutralize" the H^+ used.
- The equation must again be simplified by canceling like terms on both sides of the equation.
-

Write separate half-reactions

Oxidation half-reaction

Balance

Balanced oxidation half-reaction

Equalize electrons transferred

Balancing order
a. elements (except H,O)
b. oxygen (use H_2O)
c. hydrogen (use H^+)
d. charge (use electrons)

Reduction half-reaction

Balance

Balanced reduction half-reaction

Equalize electrons transferred

Add half-reactions

Cancel identical species

Check that elements and charges are balanced

Add OH^- to both sides of equation (equal to H^+)

Form H_2O on the side containing H^+ and OH^- ions

Eliminate number of H_2O appearing on both sides

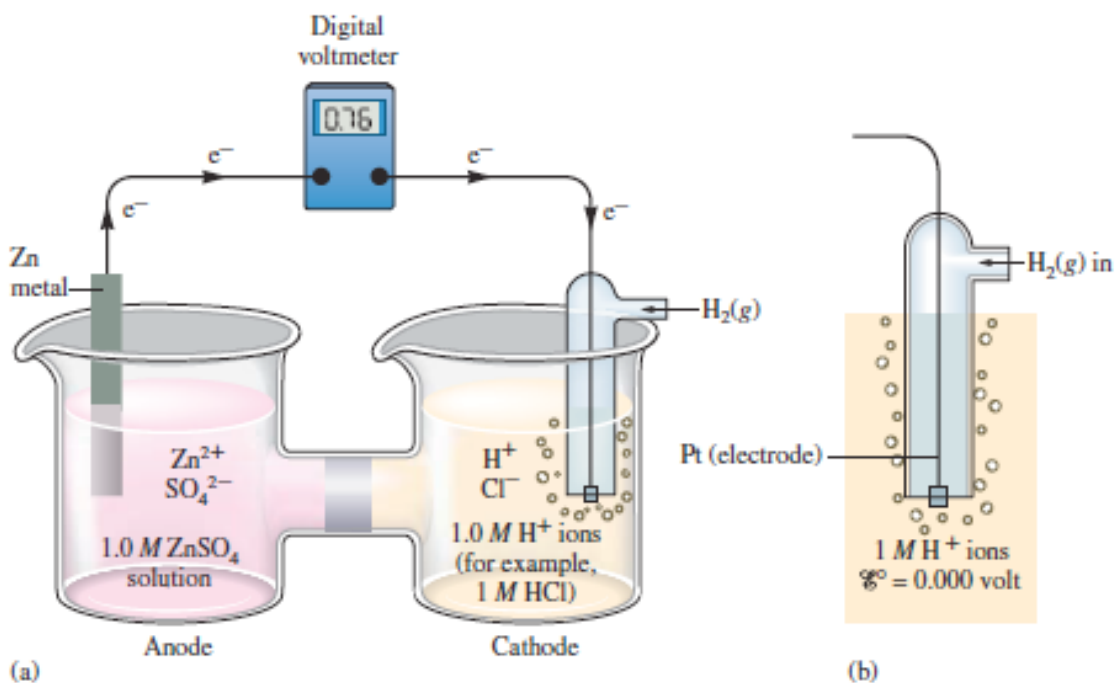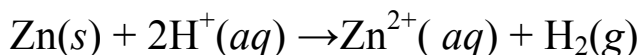Check that elements and charges are balanced

Electrical current is the flow of electric charge. Electrons flowing through a wire or ions flowing through a solution both constitute electrical current. Since redox reactions involve the transfer of electrons from one substance to another, these reactions have the potential to generate electrical current.

20.3 Voltaic Cells, Galvanic Cells, Electrochemical Cells,
The generation of electricity through redox reactions is carried out in a device called an electrochemical cell. A voltaic (or galvanic) cell is an electrochemical cell that produces electrical current from a spontaneous chemical reaction.
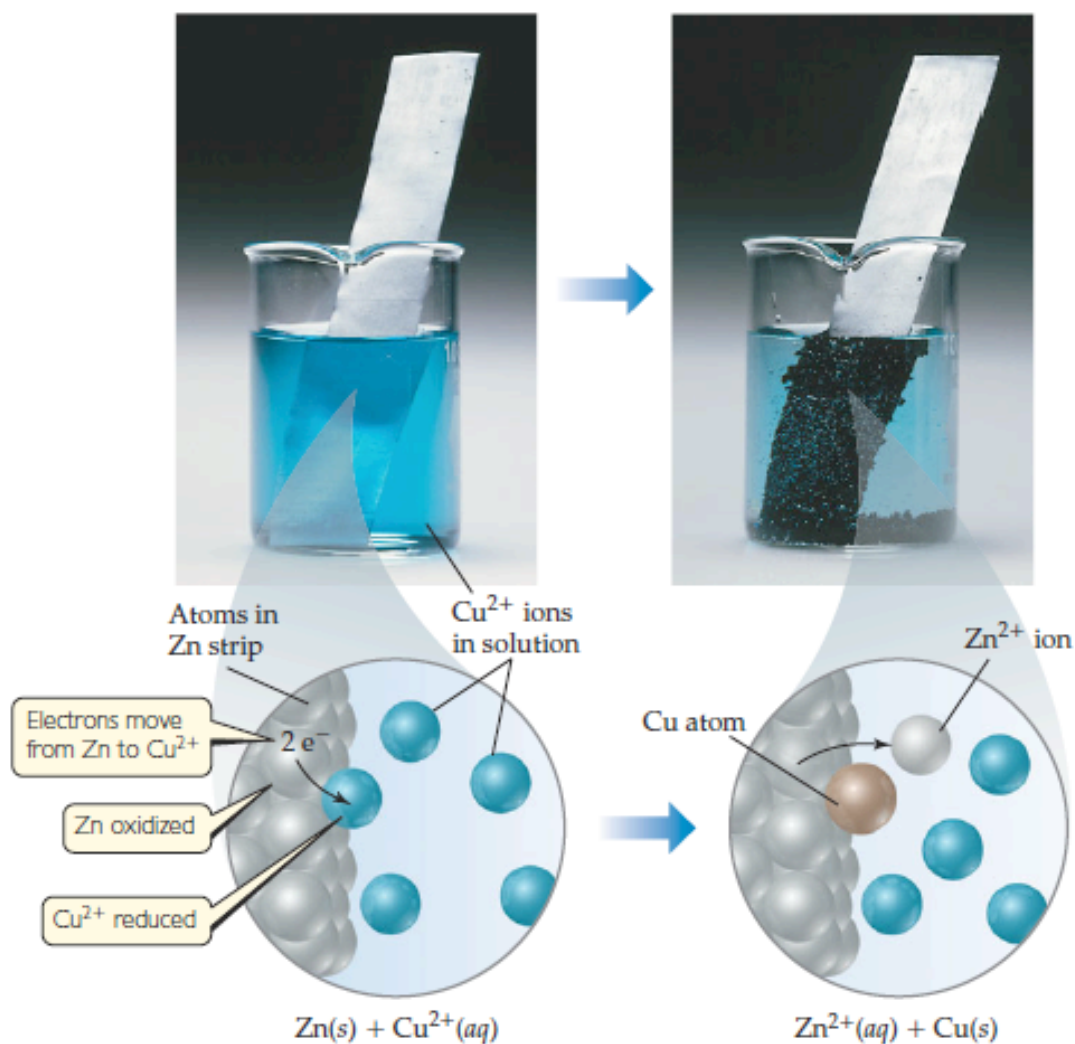A second type of electrochemical cell, called an electrolytic cell, consumes electrical current to drive an nonspontaneous chemical reaction.

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

Digital voltmeter

Zn metal

Zn²⁺
SO₄²⁻

1.0 M ZnSO₄ solution

Anode

(a)

H⁺
Cl⁻

1.0 M H⁺ ions
(for example, 1 M HCl)

Cathode

—H₂(g)

Pt (electrode)

—H₂(g) in

1 M H⁺ ions
$\mathscr{E}° = 0.000$ volt

(b)

- The energy released in a spontaneous redox reaction may be used to perform electrical work.
- **Voltaic or galvanic cells** are devices in which electron transfer occurs via an external circuit.
- Voltaic cells utilize spontaneous reactions,
- If a strip of Zn is placed in a solution of $CuSO_4$, Cu is deposited on the Zn and the Zn dissolves by forming Zn^{2+}.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
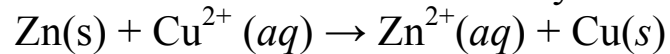
   o Zn is spontaneously oxidized to Zn^{2+} by Cu^{2+}
   o The Cu^{2+} is spontaneously reduced to Cu^o by Zn.
   o The entire process is spontaneous.

Atoms in Zn strip Cu^{2+} ions in solution Zn^{2+} ion

Electrons move from Zn to Cu^{2+} — $2e^-$ Cu atom

Zn oxidized

Cu^{2+} reduced

$Zn(s) + Cu^{2+}(aq)$ $Zn^{2+}(aq) + Cu(s)$
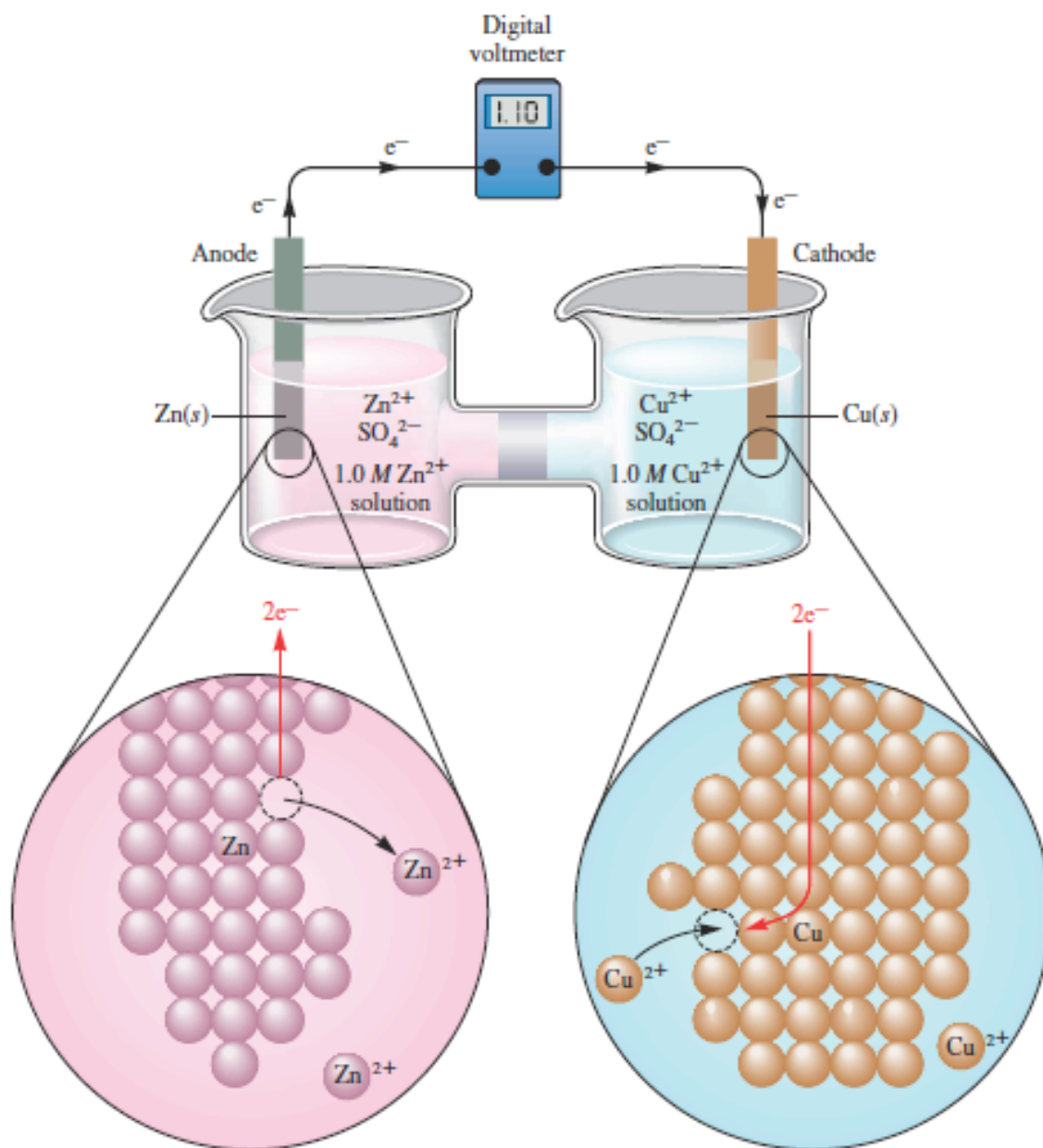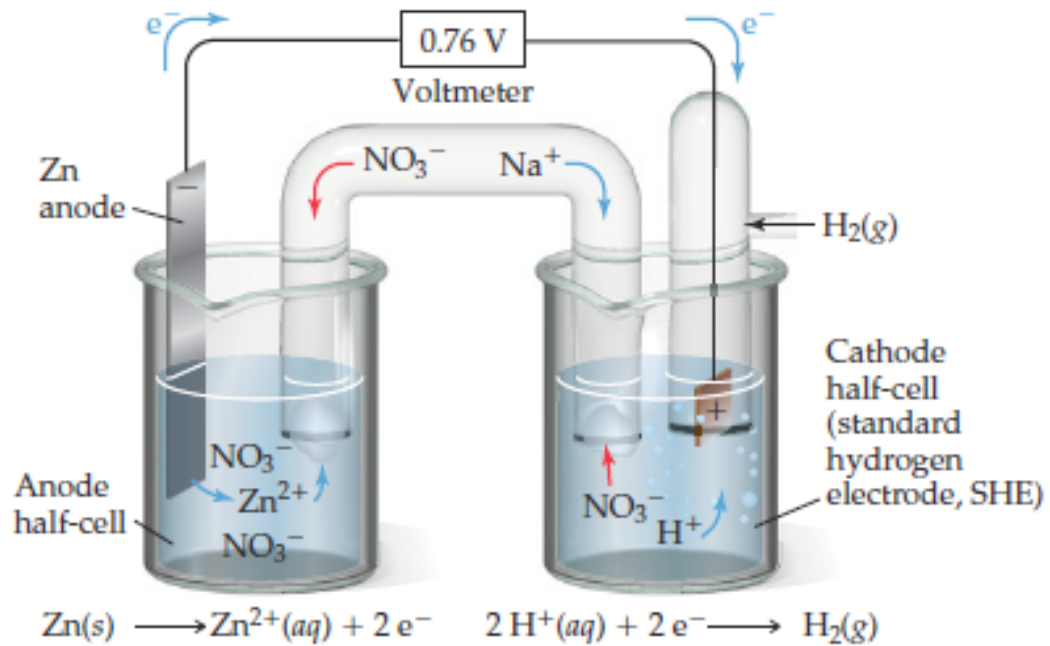
- This voltaic cells consists of electrodes:
    - An oxidation half-reaction:
        $$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
    - Oxidation takes place at the **anode**.
- A reduction half-reaction:
        $$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
    - Reduction takes place at the **cathode**.
- A salt bridge (used to complete the electrical circuit).
    - Cations move from anode to cathode.
    - Anions move from cathode to anode.
- The two solid metals are the **electrodes** (cathode and anode).
- As oxidation occurs, Zn is converted to Zn^{2+} and $2e^-$.
    - The electrons flow towards the cathode where they are used in the reduction reaction.
- We expect the Zn electrode to lose mass and the Cu electrode to gain mass.
- Electrons flow from the anode to the cathode.
    - Therefore, the anode is negative and the cathode is positive.
    - Electrons cannot flow through the solution; they have to be transported through an external wire.
    - Anions and cations move through a porous barrier or salt bridge.
    - Cations move into the cathodic compartment to neutralize the excess negatively charged ions (Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ so the counter ion of Cu is in excess).
    - Anions move into the anodic compartment to neutralize the excess Zn^{2+} ions formed by oxidation

**Molecular View of the Electrode Process**
- "Rules" of voltaic cells:

- At the anode electrons are products.
  - Oxidation occurs at the anode.
- At the cathode electrons are reagents.
  - Reduction occurs at the cathode.
- The flow of electrons from anode to cathode requires an external wire.
    - The transfer of ions through a salt bridge maintains overall charge balance for the two compartments.

Digital voltmeter

1.10

e^- e^-

e^- e^-

Anode   Cathode

$Zn(s)$ $Cu(s)$

Zn^{2+} Cu^{2+}
SO_4^{2-} SO_4^{2-}
$1.0\ M\ Zn^{2+}$ solution $1.0\ M\ Cu^{2+}$ solution

$2e^-$ $2e^-$

Zn   Cu

Zn^{2+} Cu^{2+}

Zn^{2+} Cu^{2+}

Cu^{2+}

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

The negative ions within the salt bridge flow to neutralize the accumulation of positive charge at the anode, and the positive ions flow to neutralize the accumulation of negative charge at the cathode.
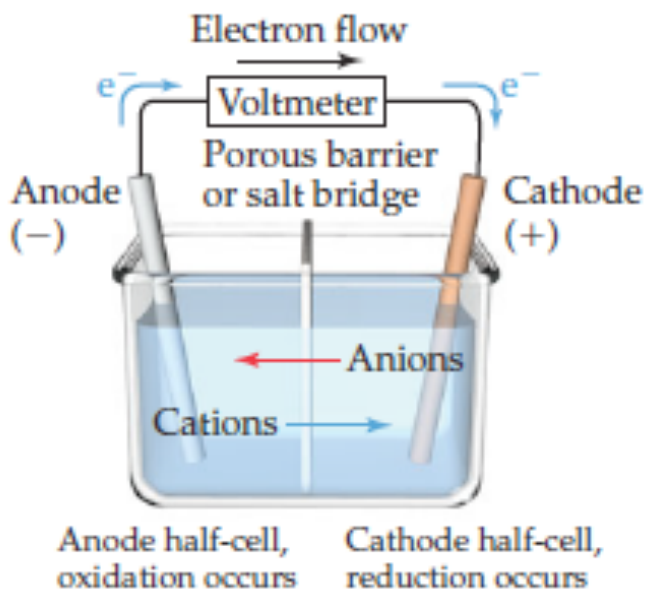
20.4 Cell EMF

- The flow of electrons from anode to cathode is spontaneous.
    - What is the "driving force"?
    - In a simple sense, we can compare the electron flow to the flow of water in a waterfall.

When the cells are connected, electrons flow from the electrode with more negative charge (greater potential energy) to the electrode with more positive charge (less potential energy)
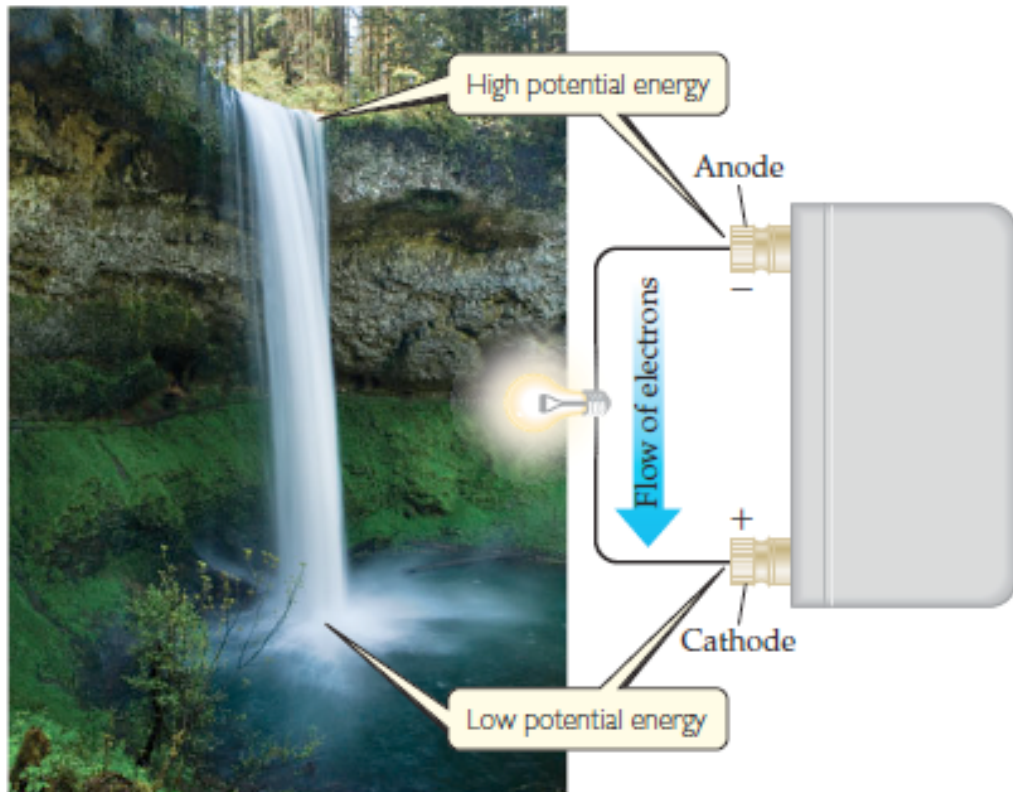
-
- Electrons flow from anode to cathode because the cathode has a lower electrical potential energy than the anode.
    - Potential difference: difference in electrical potential.
    - The potential difference is measured in volts.
    - One volt (V) is the potential difference required to impart one joule (J) of energy to a charge of one coulomb (C):

$$IV = 1 \frac{J}{C}$$

- **Electromotive force (emf)** is the force required to push electrons through the external circuit.
  - o **Cell potential:** E_{cell} is the emf of a cell.
  - o This is known as the cell voltage.
  - o E_{cell} is > 0 for a spontaneous reaction.
- For 1 *M* solutions or 1 atm pressure for gases at 25°C (standard conditions), the **standard emf (standard cell potential)** is called E^o_{cell}.
  - o For example, for the reaction:
    $$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
    - ▪ $E^o_{cell} = +1.10$ V

Oxidizing and Reducing Agents

- Consider a table of standard reduction potentials.
- We can use this table to determine the relative strengths of reducing (and oxidizing) agents.

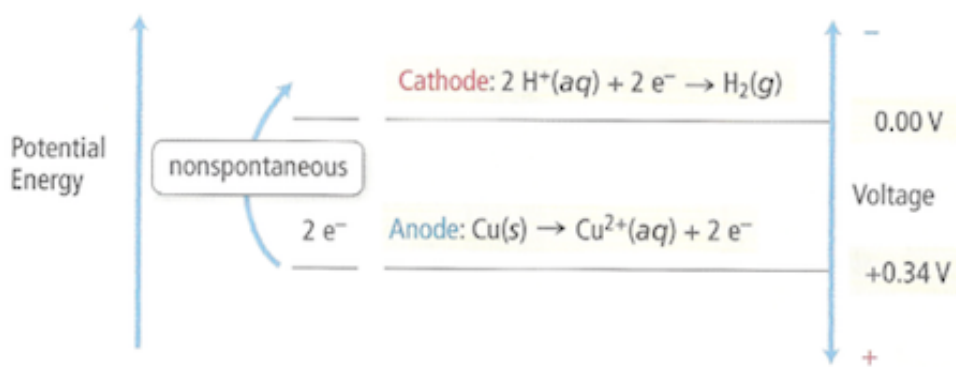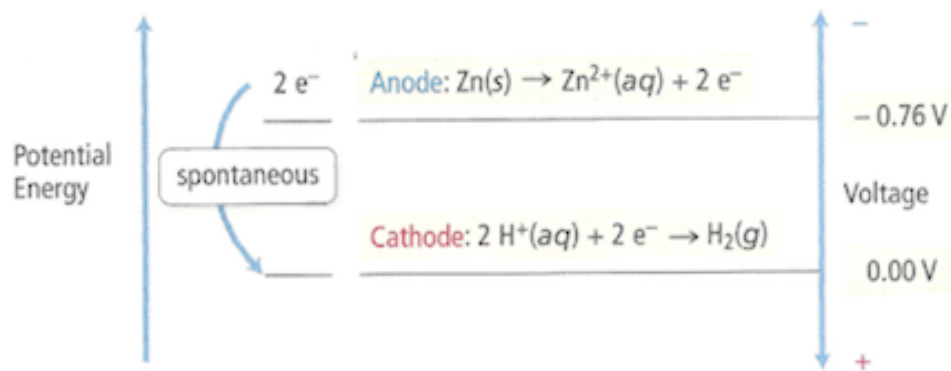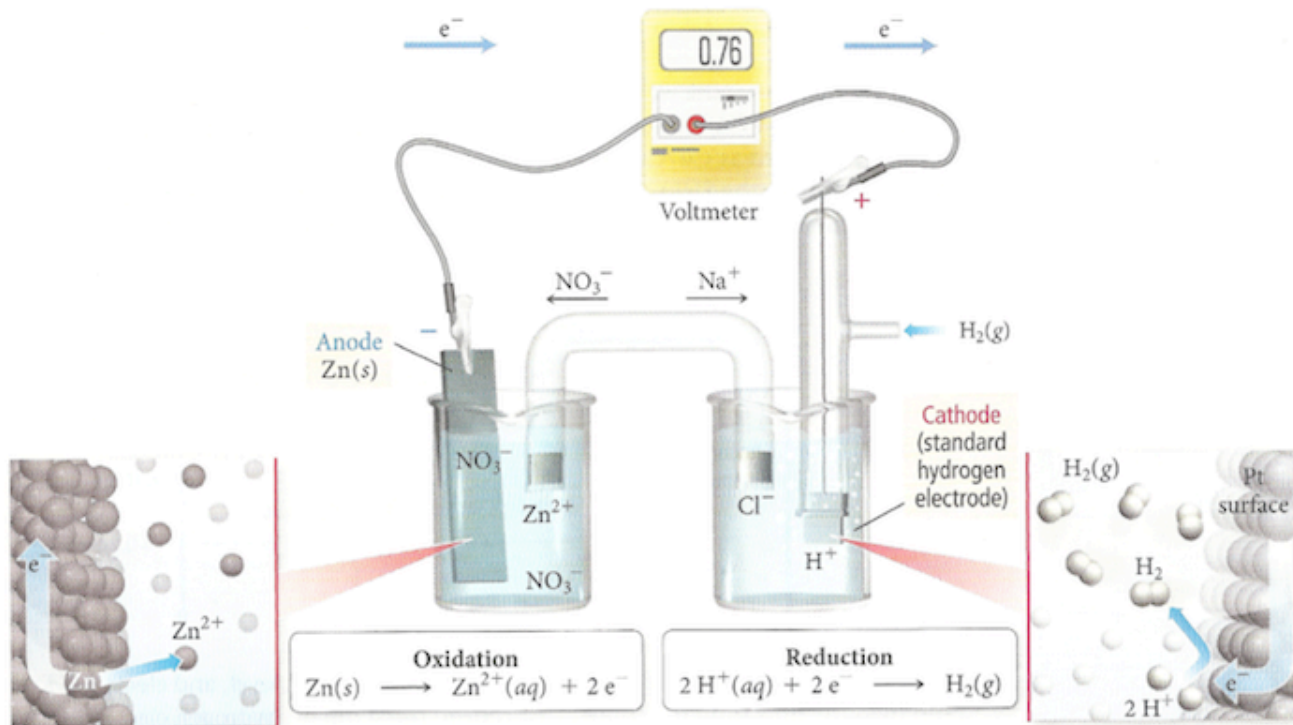### TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

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

The more positive the E^o_{red}, the stronger the oxidizing agent (written in the table as a reactant)

- o The more negative the E^o_{red}, the stronger the reducing agent (written as a product in the table).
- o We can use this to predict if one reactant can spontaneously oxidize another.
    - ▪ For example:
        - • F_2 can oxidize H_2 or Li.
        - • Ni^{2+} can oxidize AI(*s*).
- We can use this table to predict if one reactant can spontaneously reduce another.
    - o For example:
        - ▪ Li can reduce-F_2.

20.5 Spontaneity of Redox Reactions

- For any electrochemical process
    $$E^o = E^o_{red} \text{ (reduction process) - } E^o_{red} \text{ (oxidation process).}$$
    - o A positive E^o indicates a spontaneous process (galvanic cell).
    - o A negative E^o indicates a nonspontaneous process. .
- The above equation is used to understand the activity series of metals.
- Consider the reaction of nickel with silver ion:
    $$Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$$
    - o The standard cell potential is:
        $$E^o_{cell} = E^o_{red} (Ag^+/Ag) - E^o_{red} (Ni^{2+}/ Ni)$$
        $$= (0.80 \text{ V}) - (-0.28 \text{ V})$$
        $$= 1.08 \text{ V}$$
    - o This value indicates that the reaction is spontaneous.
- Any reduction half-reaction listed is spontaneous when paired with the reverse of a half-reaction that appears below it in table 20.1
-

0.76

Voltmeter

NO_3^- Na^+

$H_2(g)$

Anode
$Zn(s)$

NO_3^-

Zn^{2+}

Cl^-

Cathode
(standard
hydrogen
electrode)

$H_2(g)$

Pt
surface

NO_3^-

H^+

H_2

e^-

Zn^{2+}

Zn

Zn^{2+}

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

Reduction
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$

$2H^+$

e^-

e^- e^-

Potential
Energy

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

-0.76 V

spontaneous

Voltage

Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

0.00 V

Potential
Energy

Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

0.00 V

nonspontaneous

Voltage

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

$+0.34$ V

EMF and Free-Energy Change

- We can show that:

$$\Delta G = -nFE$$

- Where ΔG is the change in free energy, n is the number of moles of electrons transferred, F is Faraday's constant and E is the emf of the cell.
- We define a **faraday** (F) as:

$$1F = 96{,}500 \ \frac{C}{\text{mol } e^-} = 96{,}500 \ \frac{J}{(V)(\text{mol } e^-)}$$

- Since n and F are positive, if $\Delta G < 0$ then $E > 0$, and the reaction will be spontaneous

20.6 Effect of Concentration on Cell EMF

- A voltaic cell is functional until $E = 0$ at which point equilibrium has been reached.
    - o The cell is then "dead."
- The point at which $E = 0$ is determined by the concentrations of the species involved in the redox reaction.