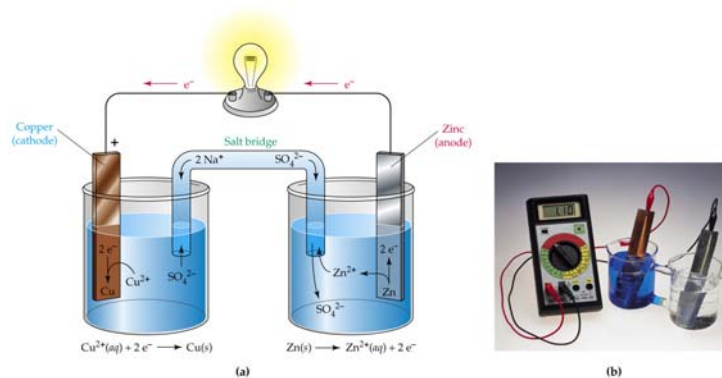


Chapter 18

Electrochemistry



Chapter 18

1

Electrochemical Cells

- **Electrochemical Cells** are of two basic types:
 - **Galvanic Cells** – a *spontaneous* chemical reaction generates an electric current
 - **Electrolytic Cells** – an electric current drives a *non-spontaneous* reaction
- Basically, the two cells are opposites of one another.
- We will be focused on the Galvanic cells for this Chapter.
- The spontaneous reaction that drives these cells is a redox reaction!

Chapter 18

2

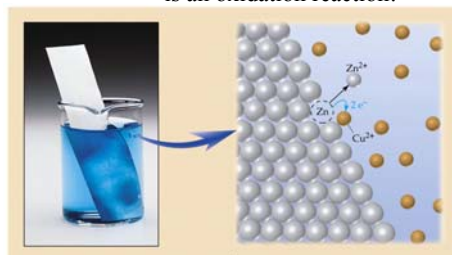
Oxidation–Reduction Reactions

LEO the lion goes **GER**

Lose $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^-$
Electrons
Oxidation

If the electron(s) is on the product side of the reaction, it is an oxidation reaction!

A substance which loses electrons (oxidized) is called a **reducing agent**. Its oxidation number **increases**.



Chapter 18

3

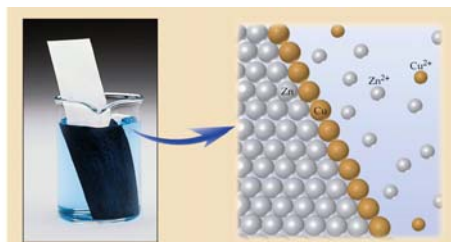
Oxidation–Reduction Reactions

LEO the lion goes **GER**

Gain $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu(s)}$
Electrons
Reduction

If the electron(s) is on the reactant side of the reaction, it is a reduction reaction!

A substance which gains electrons (reduced) is called the **oxidizing agent**. Its oxidation number **decreases**.

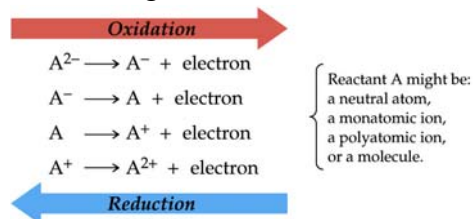


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Oxidation–Reduction Reactions

- The transfer of electrons between or among reactants is called the **oxidation** or **reduction** of species depending on which way the electrons are flowing.



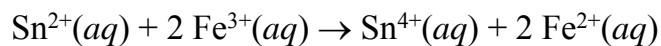
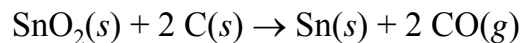
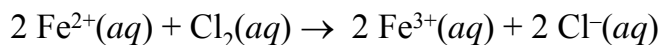
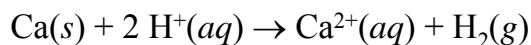
- Oxidation and reduction **must** occur together. They cannot exist alone.
- Therefore, a redox reaction can be broken into two half-reactions, one a reduction and the other an oxidation

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Oxidation–Reduction Reactions

For each of the following, write and balance the two half-reactions.
For each, identify which species is the reducing agent and which is the oxidizing agent:

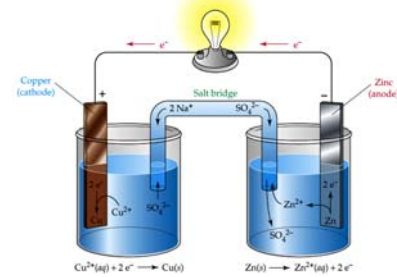


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Electrochemical Cells -Terms

- **Electrodes:** are usually metal strips/wires connected by an electrically conducting wire (the **anode** and the **cathode**).



Anode: {
Is where oxidation occurs
Is where electrons are produced
Is what anions migrate toward
Has a negative sign

Cathode: {
Is where reduction occurs
Is where electrons are consumed
Is what cations migrate toward
Has a positive sign

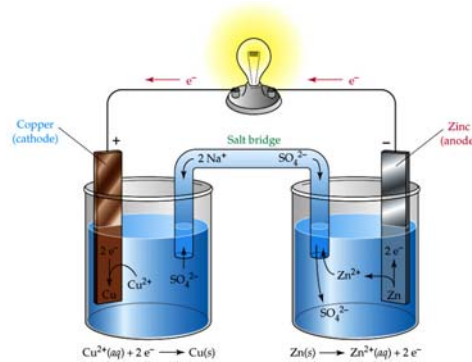
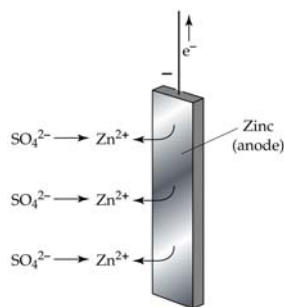


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Electrochemical Cells -Terms

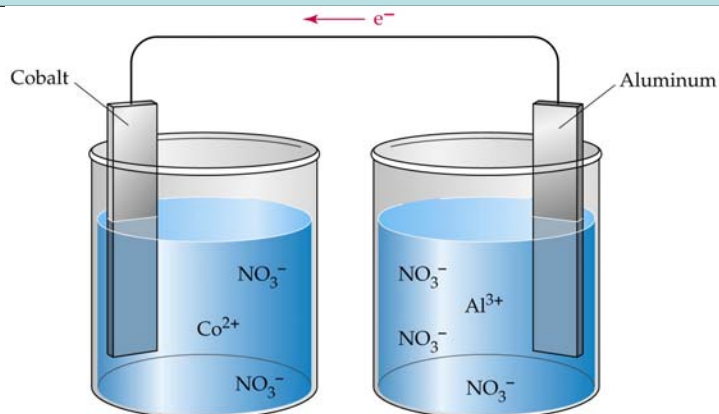
- **Salt Bridge:** is a U-shaped tube that contains a gel permeated with a solution of an inert
- These ions do not react with the other ions and they are not reduced or oxidized
- The salt bridge completes the electrical circuit by neutralizing any growing charge in the solutions.
- Anions flow into the anode and cations flow to the cathode



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Electrochemical Cells

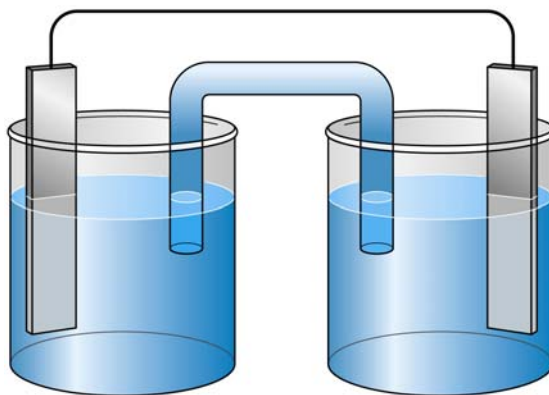


- Are any components essential for a functioning cell missing?
- Identify the anode and cathode and indicate the direction of the electron flow
- Write a balanced equation for the cell reaction.

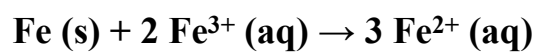
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Electrochemical Cells



- Design a galvanic cell that uses the redox reaction:

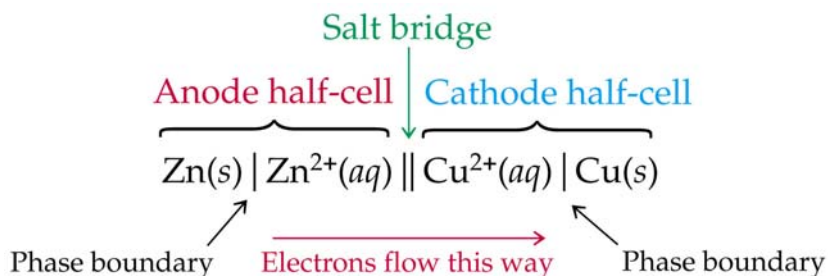
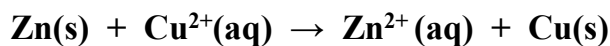


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Electrochemical Cells – Shorthand Notation

- The shorthand notation for describing the cell:



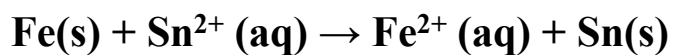
- Electrons flow from anode to cathode.
- Anode is placed on left by convention.

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Electrochemical Cells

- Write the shorthand notation for a galvanic cell that uses the reaction:



- Write the balanced equation for the overall cell reaction and give a brief description of a galvanic cell represented by the following shorthand notation:



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Electromotive Force (EMF)

- The driving force to move the electrons from the anode towards the cathode is an electrical potential called the **electromotive force (EMF)**
 - This is also known as the cell potential (E) or the cell voltage
- This force is the natural tendency of one substance to lose electrons and a second substance to gain electrons
- The greater this tendency, the higher the cell voltage
- The SI unit of EMF is the **volt (V)**
 - The relationship between the volt, the joule (energy) and the coulomb (electric charge) is:

$$1 \text{ J} = 1 \text{ C} \cdot 1 \text{ V}$$

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Standard Reduction Potentials

- The standard cell potential of any galvanic cell is the sum of the standard half-reaction potentials for the oxidation and reduction half-cells.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$$

- Standard half-cell potentials are always quoted as a **reduction process** (See Table 18.1).
- If your half-reaction is an oxidation, the numerical value is the same as in the Table but the **sign must be changed**.

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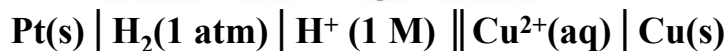
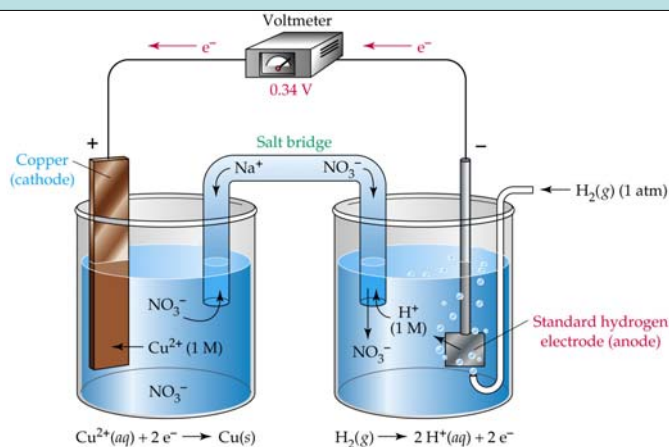
Standard Reduction Potentials

- It is not possible to measure the potential of a single half reaction (remember, you must always have both $\frac{1}{2}$ rxns!)
- The **standard half-cell potentials (E°)** have been determined experimentally by measuring the **difference** between two electrodes, the target electrode and a standard or reference electrode.
- The reference electrode is called the **standard hydrogen electrode (SHE)** and consists of a platinum electrode in contact with H_2 gas (1 atm) and aqueous H^+ ions (1 M).
- The **standard hydrogen electrode** is assigned an arbitrary value of exactly **0.00 V**.

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Standard Reduction Potentials



$$E^\circ_{\text{cell}} = E^\circ_{H_2 \rightarrow H^+} + E^\circ_{Cu^{2+} \rightarrow Cu}$$

$$0.34 \text{ V} = 0 \text{ V} + E^\circ_{Cu^{2+} \rightarrow Cu}$$

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Standard Reduction Potentials

TABLE 18.1 Standard Reduction Potentials at 25°C

Reduction Half-Reaction	E° (V)
$F_2(g) + 2 e^- \rightarrow 2 F^-(aq)$	2.87
$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \rightarrow 2 H_2O(l)$	1.78
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51
$Cl_2(g) + 2 e^- \rightarrow 2 Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33
$O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$	1.23
$Br_2(l) + 2 e^- \rightarrow 2 Br^-(aq)$	1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2 H^+(aq) + 2 e^- \rightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2 e^- \rightarrow 2 I^-(aq)$	0.54
$O_2(g) + 2 H_2O(l) + 4 e^- \rightarrow 4 OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2 e^- \rightarrow Sn^{2+}(aq)$	0.15
$2 H^+(aq) + 2 e^- \rightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2 e^- \rightarrow Pb(s)$	-0.13
$Ni^{2+}(aq) + 2 e^- \rightarrow Ni(s)$	-0.26
$Cd^{2+}(aq) + 2 e^- \rightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2 e^- \rightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2 e^- \rightarrow Zn(s)$	-0.76
$2 H_2O(l) + 2 e^- \rightarrow H_2(g) + 2 OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3 e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2 e^- \rightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

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Many more in
Appendix D in
your book

Spontaneity of a Reaction

- The value of E°_{cell} is also related to the thermodynamic quantity of ΔG° .

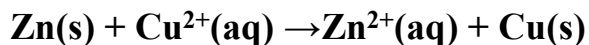
$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

n = # of moles of e^- transferred

F = the Faraday constant (96,485 C/mol e^-)

- For spontaneous reactions, ΔG° is **negative** and E°_{cell} is **positive**
- Calculate the free energy change at 25°C for the following reaction. The standard cell potential is 1.10V.

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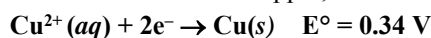


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Standard Reduction Potentials

- Remember, a positive value for E° means that the reaction is spontaneous.
- When deciding which half cell is the cathode and which is the anode, the half-cell reaction with the **more negative value** will form the **oxidation half-cell (the anode)**.
- If the half reactions do not have the same number of electrons, you must balance to get the correct cell reaction, however, you **DO NOT** change the standard reduction potential!

- Consider the reaction between zinc and copper, then zinc and silver:



Identify the oxidation and the reduction half-cells

What are the two half-cell standard potentials?

What is the standard potential of the cell?

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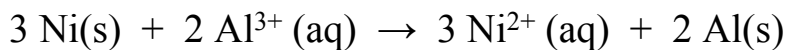
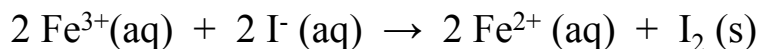
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Standard Reduction Potentials

- Using the standard reduction potentials, predict whether $\text{Pb}^{2+}(\text{aq})$ can oxidize $\text{Al}(\text{s})$ or $\text{Cu}(\text{s})$



- Using the standard reduction potentials, predict whether the following reactions can occur:



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The Nernst Equation

- Cell potentials can be modified by **temperature** and **composition** changes according to the Nernst equation:

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

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

$$E = E^\circ - \frac{2.303 RT}{nF} \log Q$$

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

Chapter 18

At 25°C

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The Nernst Equation

- Consider the reaction of metallic zinc with hydrochloric acid. Calculate the cell potential at 25°C when $[\text{H}^+] = 1.0 \text{ M}$, $[\text{Zn}^{2+}] = 0.0010 \text{ M}$, and $P_{\text{H}_2} = 0.10 \text{ atm}$.

- Consider the reaction of metallic copper with iron(III) to give copper(II) and iron(II). What is the potential of a cell when $[\text{Fe}^{3+}] = 0.0001 \text{ M}$, $[\text{Cu}^{2+}] = 0.25 \text{ M}$, and $[\text{Fe}^{2+}] = 0.20 \text{ M}$?

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The Nernst Equation and pH

- A particularly important use of the Nernst equation is in the electrochemical determination of pH
- Consider a cell with a hydrogen electrode as the anode and second electrode as the cathode



$$E_{\text{cell}} = E_{\text{H}_2 \rightarrow \text{H}^+} + E_{\text{ref}}$$

- The Nernst equation relates the concentration of any chemical species, including H^+ to the cell potential.
- This relationship is used in a pH meter which measures a cell potential and displays its value in terms of pH
- The Nernst equation can be applied to the half-reaction:



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The Nernst Equation and pH

- The Nernst equation can be applied to the half-reaction :



$$E_{\text{H}_2 \rightarrow \text{H}^+} = E_{\text{H}_2 \rightarrow \text{H}^+}^{\circ} - \frac{0.0592 \text{ V}}{n} \log \left(\frac{[\text{H}^+]^2}{P_{\text{H}_2}} \right)$$

- $E^{\circ} = 0 \text{ V}$ for this reaction (standard hydrogen electrode), $n = 2$ and P_{H_2} is 1 atm.

$$E_{\text{H}_2 \rightarrow \text{H}^+} = 0 - \frac{0.0592 \text{ V}}{2} \log([\text{H}^+]^2)$$

$$E_{\text{H}_2 \rightarrow \text{H}^+} = -0.0592 \text{ V} \cdot \log([\text{H}^+])$$

$$E_{\text{H}_2 \rightarrow \text{H}^+} = 0.0592 \text{ V} \cdot \text{pH}$$

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The Nernst Equation and pH

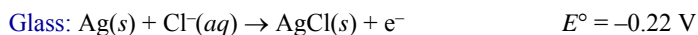
- So, for the overall cell potential:

$$E_{\text{cell}} = E_{\text{H}_2 \rightarrow \text{H}^+} + E_{\text{ref}}$$

$$E_{\text{Cell}} = (0.0592 \text{ V} \cdot \text{pH}) + E_{\text{Ref}}$$

$$\text{pH} = \frac{E_{\text{Cell}} + E_{\text{Ref}}}{0.0592 \text{ V}}$$

- A higher cell potential indicates a higher pH, therefore we can measure pH by measuring E_{cell} .
- A glass electrode (Ag/AgCl wire in dilute HCl) with a calomel reference is the most common arrangement.

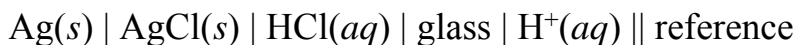


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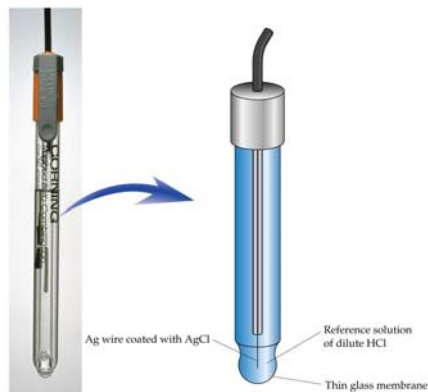
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The Nernst Equation and pH

- The glass pH probe is constructed as follows:



- The difference in $[\text{H}^+]$ from one side of the glass membrane to the other causes a potential to develop, which adds to the measured E_{cell} .

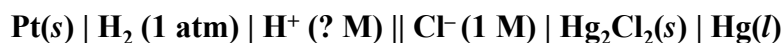


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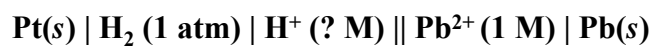
The Nernst Equation and pH

- The following cell has a potential of 0.55 V at 25°C:



What is the pH of the solution at the anode?

- The following cell has a potential of 0.28 V at 25°C:



What is the pH of the solution at the anode?

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Cell Potentials and Equilibrium

- The value of K_{eq} is related to ΔG° by:

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

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$-nFE^\circ = -RT \ln K_{\text{eq}}$$

$$E^\circ_{\text{Cell}} = \frac{RT}{nF} \ln K_{\text{eq}}$$

$$E^\circ_{\text{Cell}} = \frac{0.0592 \text{ V}}{n} \log K_{\text{eq}}$$

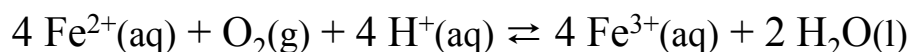
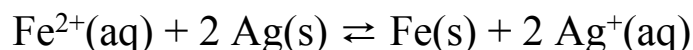
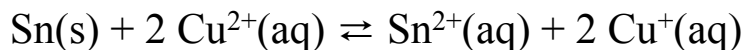
↑
At 25°C

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Cell Potentials and Equilibrium

- Calculate the standard free energy change (ΔG°) and the equilibrium constant (K) for the following reactions at 25°C :



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Electrolysis

- Electrolysis** is the process in which electrical energy is used to drive a *non-spontaneous* chemical reaction.
- An **electrolytic cell** has two electrodes that dip into an electrolyte and are connected to a battery of some other source of direct electric current.
- Processes in an electrolytic cell are the *reverse* of those in a galvanic cell.

TABLE 18.2 Relationship Between Cell Potentials E and Free-Energy Changes ΔG

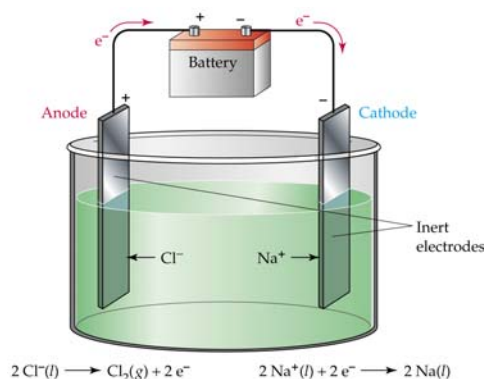
Reaction Type	E	ΔG	Cell Type
Spontaneous	+	-	Galvanic
Nonspontaneous	-	+	Electrolytic
Equilibrium	0	0	Dead battery

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Electrolysis of Molten NaCl

- Here, the battery (not a chemical reaction) serves as the electron pump
- The negative electrode (Cathode) attracts the molten Na^+ ions which are combined with the electrons producing $\text{Na}(l)$
- The positive electrode (Anode) attracts the Cl^- ions which replenish the electrons by being oxidized to $\text{Cl}_2(g)$



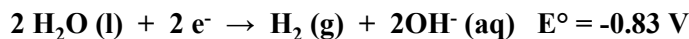
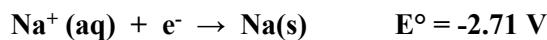
Anode is still the site of Reduction but it is positively charged
 Cathode is still the site of Oxidation but it is negatively charged

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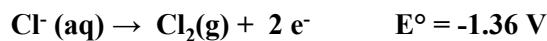
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Electrolysis of Aqueous NaCl

- When an aqueous salt solution is electrolyzed, the electrode reactions may be different than those of electrolysis the molten salt because water may be involved.



- Based on cell potentials, water (-0.83 V) would be preferentially reduced over sodium ions (-2.71 V).



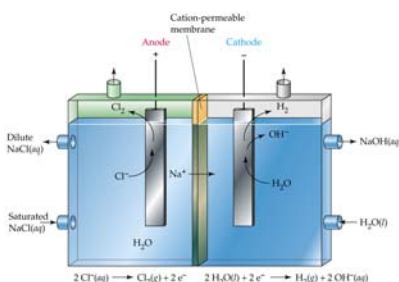
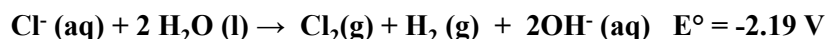
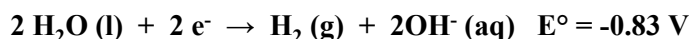
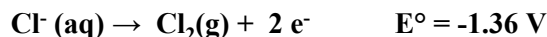
- Based on cell potentials, water ($+1.23 \text{ V}$) should be preferentially oxidized over chloride ions ($+1.36 \text{ V}$).

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Electrolysis of Aqueous NaCl

- Sodium ions act as a spectator ion and is not involved in the electrode reactions.
- The observed product at the anode is Cl_2 , not O_2 , because of a phenomenon called **overtoltage**.



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Electrolysis - Overtoltage

- Experiments have indicated that the applied voltage required for an electrolysis is always greater than the voltage calculated from the standard oxidation and reduction potentials.
- This additional voltage (**Overtoltage**) is needed to maintain the rate of electron transfer at the electrode–solution interface.
- We are unable to predict the magnitude of the overvoltage, therefore, it's sometimes difficult to predict which half-reaction will occur when E° values are similar for competing half-reaction.
- Overtoltage is most important for those systems involving gases that impede the flow of electrons between the electrode surfaces and the reactants in solution.
- Overtoltage is also required when a half-reaction has a significant activation energy, and so a slow rate.

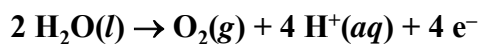
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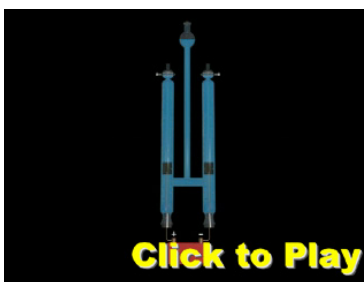
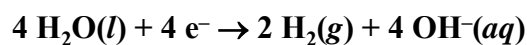
Electrolysis of Water

- **Electrolysis of Water:** Requires an electrolyte species, that is less easily oxidized and reduced than water, to carry the current.

Anode: Water is oxidized to oxygen gas.



Cathode: Water is reduced to hydrogen gas.

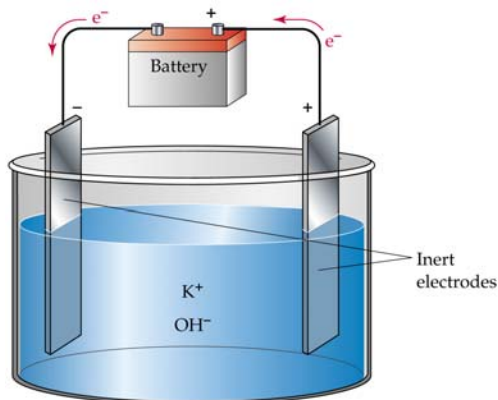


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Electrolysis

- Metallic potassium was first prepared by the electrolysis of molten potassium hydroxide:



- Label the anode and cathode, and show the direction of ion flow
- Write the balanced equations for the anode, cathode and overall cell reactions.

Chapter 18

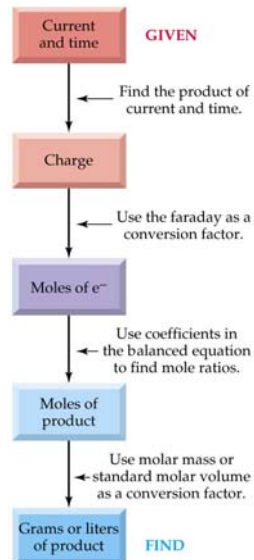
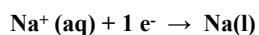
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Quantitative Electrolysis

- **Quantitative Electrolysis** describes the amount of substance produced at an electrode by electrolysis
- This value depends on the quantity of charge passed through the cell.
 - The quantity of charge is equal to the product of the current and time.
 - This charge can be converted to moles of electrons with the equality:

$$1 \text{ mol } e^- = 96500 \text{ C}$$

- From here, the problem is a straight stoichiometry problem
- Reduction of 1 mol of sodium ions requires 1 mol of electrons to pass through the system.



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Quantitative Electrolysis

- A constant current of 30.0 A (1 A = 1 C/s) is passed through an aqueous solution of NaCl for a time of 1.00 hour. How many grams of Na and how many liters of Cl₂ gas at STP are produced?
-
- A layer of silver is electroplated on a coffee server using a constant current of 0.100 A. How much time is required to deposit 3.00 g of Ag?

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