

Section 17.1

Review of Redox Chemistry



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Learning Objectives



- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction
- Balance chemical equations for redox reactions using the half-reaction method

Oxidation Numbers



- A redox reaction entails changes in **oxidation number** for one or more of the elements.
- The oxidation number of an element in a compound is essentially an assessment of how the *electronic environment of its atoms is different in comparison to atoms of the pure element*.
 - The oxidation number of *an atom in an element is equal to zero*.
 - For an atom in a compound, the oxidation number is equal to the *charge the atom would have in the compound if the compound were ionic*.
- The sum of oxidation numbers for all atoms in a molecule is equal to the charge on the molecule.

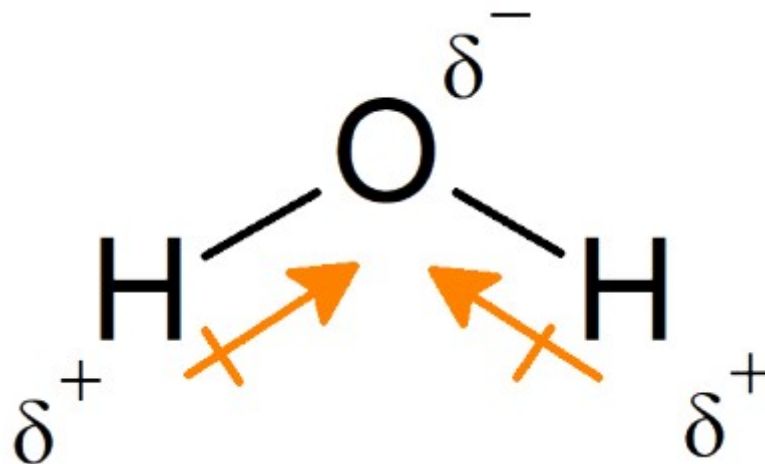
Oxidation Number of Ionics



Oxidation Number Ca = +2

Oxidation Number F = -1

Covalent Oxidation Numbers

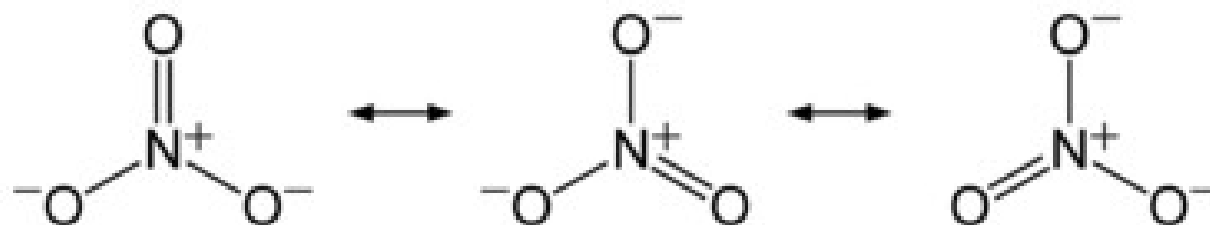


If it were ionic



Oxidation Number H = +1

Oxidation Number O = -2



$$(1 \text{ N atom}) \left(\frac{+5}{\text{N atom}} \right) + (3 \text{ O atoms}) \left(\frac{-2}{\text{O atom}} \right) = +5 + -6 = -1$$

Balancing Redox Reactions



- 1) Write skeletal equations for the oxidation and reduction half-reactions.
- 2) Balance each half-reaction for all elements except H and O.
- 3) Balance each half-reaction for O by adding H_2O .
- 4) Balance each half-reaction for H by adding H^+ .
- 5) Balance each half-reaction for charge by adding electrons.
- 6) If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
- 7) Add the two half-reactions and simplify.
- 8) If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

Section 17.2

Galvanic Cells



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Learning Objectives

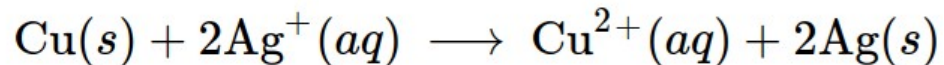


- Describe the function of a galvanic cell and its components
- Use cell notation to symbolize the composition and construction of galvanic cells

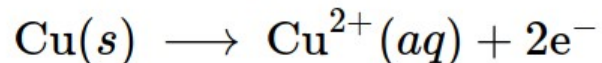
Redox Reaction Example



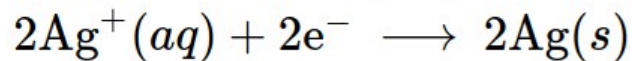
overall reaction:



oxidation half-reaction:



reduction half-reaction:



The direct transfer of electrons from the copper wire to the aqueous silver ions is spontaneous

Galvanic Cells



- Electrochemical cells are devices that contains all the reactants and products of a redox system but prevent physical contact between the reactants.
 - Direct transfer of electrons is prevented
 - Transfer takes place indirectly through an external circuit that contacts the separated reactants.
 - Devices based on spontaneous redox reactions are called **galvanic cells** (or **voltaic cells**).

Separating Electron Transfer



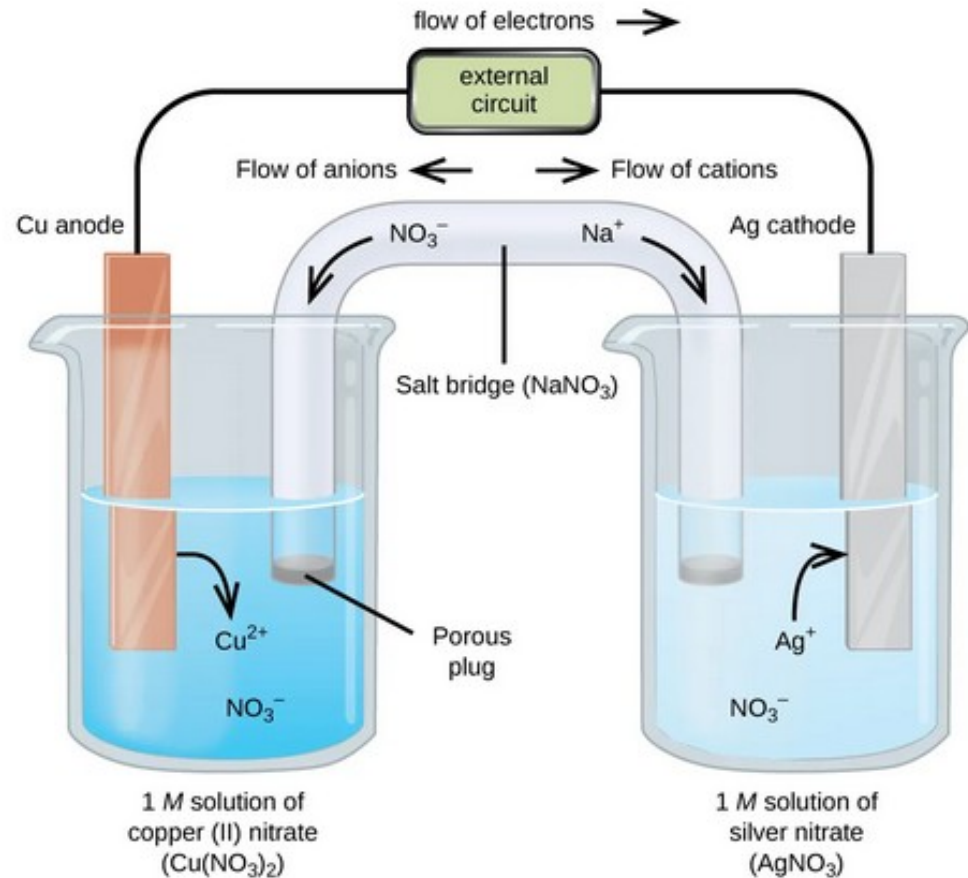
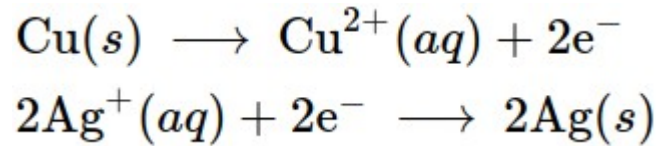
- Galvanic cells are comprised of two half-cells
 - Each containing the redox conjugate pair (“couple”) of a single reactant.
- An external circuit is connected to each half-cell at its solid electrode.
 - The **anode** of an electrochemical cell is the electrode at which oxidation occurs
 - The **cathode** is the electrode where reduction occurs.

The Salt Bridge



- To keep the reactants separate while maintaining charge-balance, the two half-cell solutions are connected by a tube filled with inert electrolyte solution called a **salt bridge**.
- The spontaneous reaction produces cations in the anode half-cell and consumes anions in the cathode half-cell
- A compensatory flow of inert ions from the salt bridge that maintains charge balance.

Picturing the Cell



Cell Notation

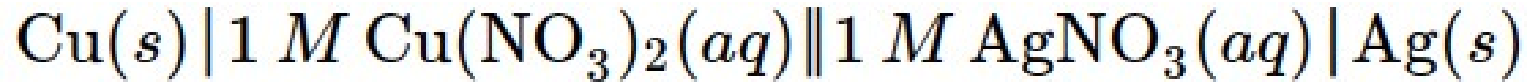


- **Cell notations** or **cell schematics** are an abbreviated symbolism commonly used to represent a galvanic cell by providing essential information on its composition and structure.
- They are written following a few guidelines:
 - 1) The relevant components of each half-cell are represented by their chemical formulas or element symbols
 - 2) All interfaces between component phases are represented by vertical parallel lines; if two or more components are present in the same phase, their formulas are separated by commas
 - 3) By convention, the schematic begins with the anode and proceeds left-to-right identifying phases and interfaces encountered within the cell, ending with the cathode

Cell Notation Example



- A galvanic cell consists of a solid copper anode immersed in an aqueous solution of copper(II) nitrate that is connected via a salt bridge to an aqueous silver(I) nitrate solution, immersed in which is a solid silver cathode.

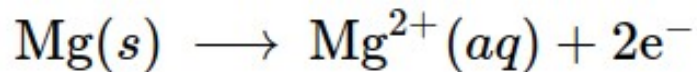


Interpreting Cell Descriptions

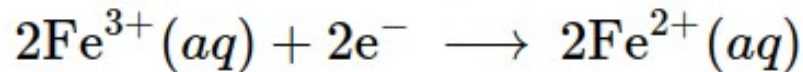


- A solid magnesium anode is immersed in an aqueous solution of magnesium chloride that is connected via a salt bridge to an aqueous solution containing a mixture of iron(III) chloride and iron(II) chloride, immersed in which is a platinum cathode.

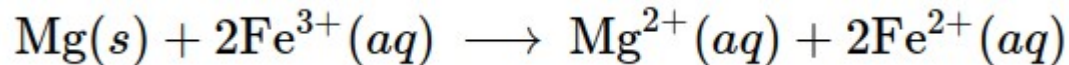
oxidation half-reaction:



reduction half-reaction:



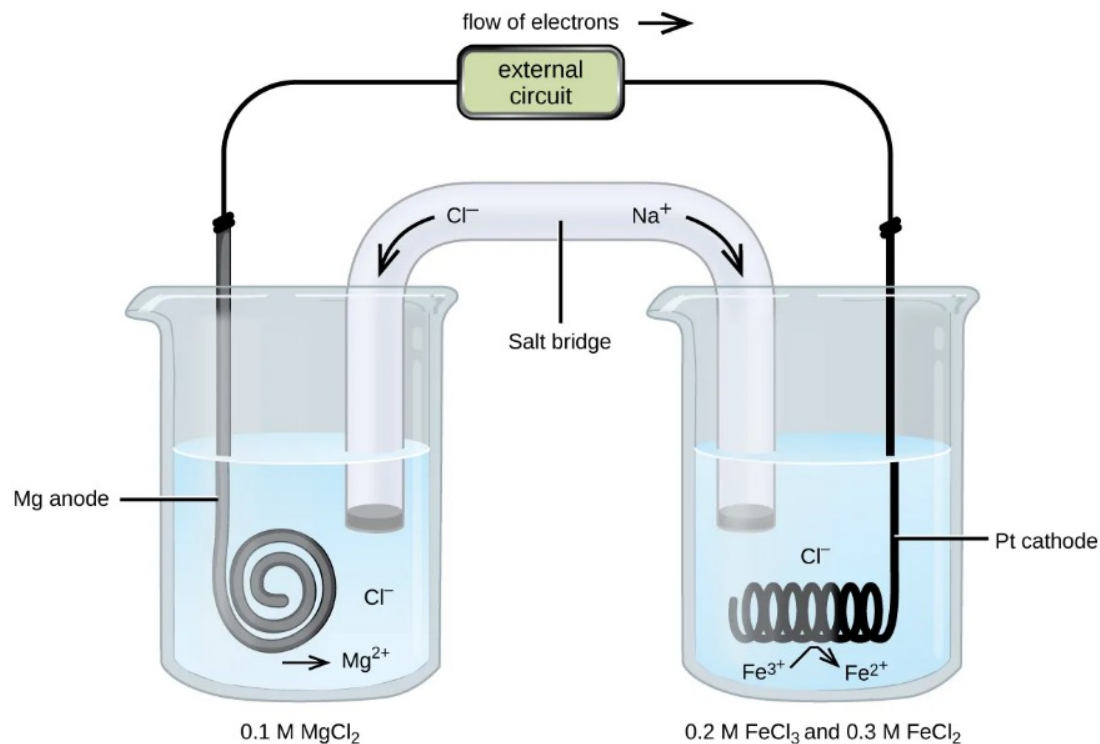
net cell reaction:



Interpreting Cell Descriptions



- Notice the cathode in this half-cell is neither a reactant nor a product.
- Its electrode is comprised of a substance (Pt)



Inert Electrodes



- **Inert Electrodes** are required when neither member of the half-cell's redox couple can reasonably function as an electrode.
 - Electrically conductive and in a phase separate from the half-cell solution.

Section 17.3

Electrodes and Cell Potentials



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Learning Objectives



- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Measuring Potential



- The activity of a redox reaction can be quantified by measuring a relatively easy property called **potential** or **voltage**.
 - It is a measure of energy accompanying the transfer of charge.
- Potentials are measured in the volt unit
 - Defined as one joule of energy per one coulomb of charge, $V = J/C$.
- A potential reflects the driving force for the transfer of electrons between redox reactants.

Cell Potentials



- The transfer of electrons requires two half cell reactions.
 - An oxidation reaction at the anode donating electrons
 - A reduction reaction at the cathode accepting electrons
 - *Electrons flow from the anode to the cathode*
- The difference in potential between two half-cells that may be measured
 - These measured potentials are called **cell potentials**, E_{cell} .

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Standard Cell Potentials



- E_{cathode} and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts.
- The **standard cell potential**, E°_{cell} , is a cell potential measured when both half-cells are under standard-state conditions
 - 1 M concentrations
 - 1 bar pressure
 - 298 K

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

SHE



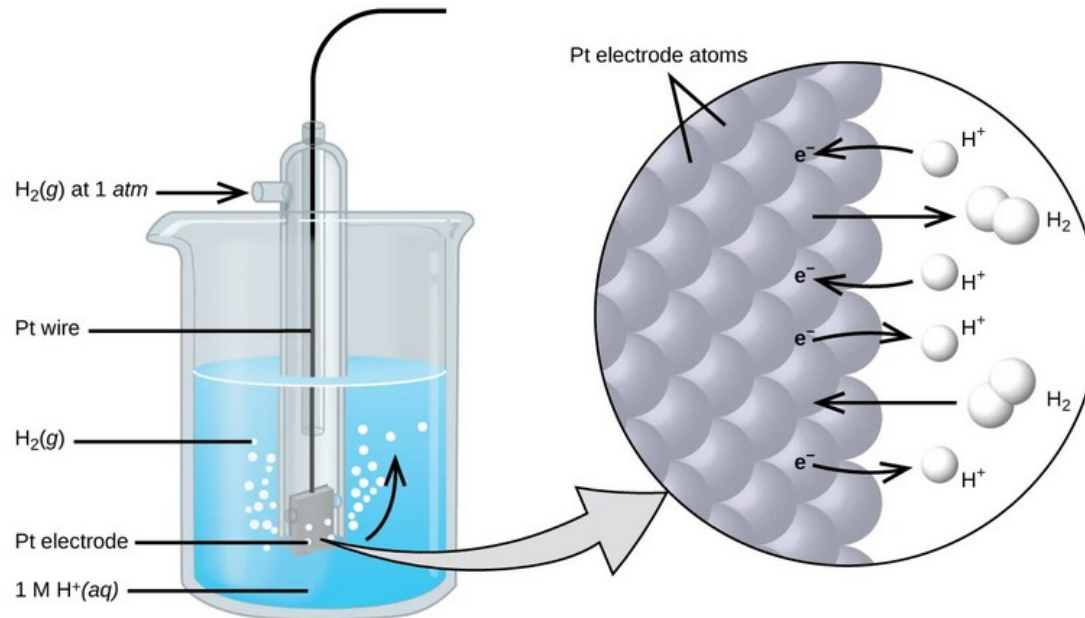
- To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements
 - Assigning it a potential of exactly 0 V.
- This half-cell is the **standard hydrogen electrode (SHE)** and it is based on half-reaction below:



SHE



- A typical SHE contains an inert platinum electrode immersed in precisely 1 M aqueous H^+ and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K.



Measuring Electrode Potential



- The **electrode potential (E_X)** for a half-cell X is defined as the potential measured for a cell comprised of X acting as cathode and the SHE acting as anode:

$$E_{\text{cell}} = E_X - E_{\text{SHE}}$$

$$E_{\text{SHE}} = 0 \text{ V (defined)}$$

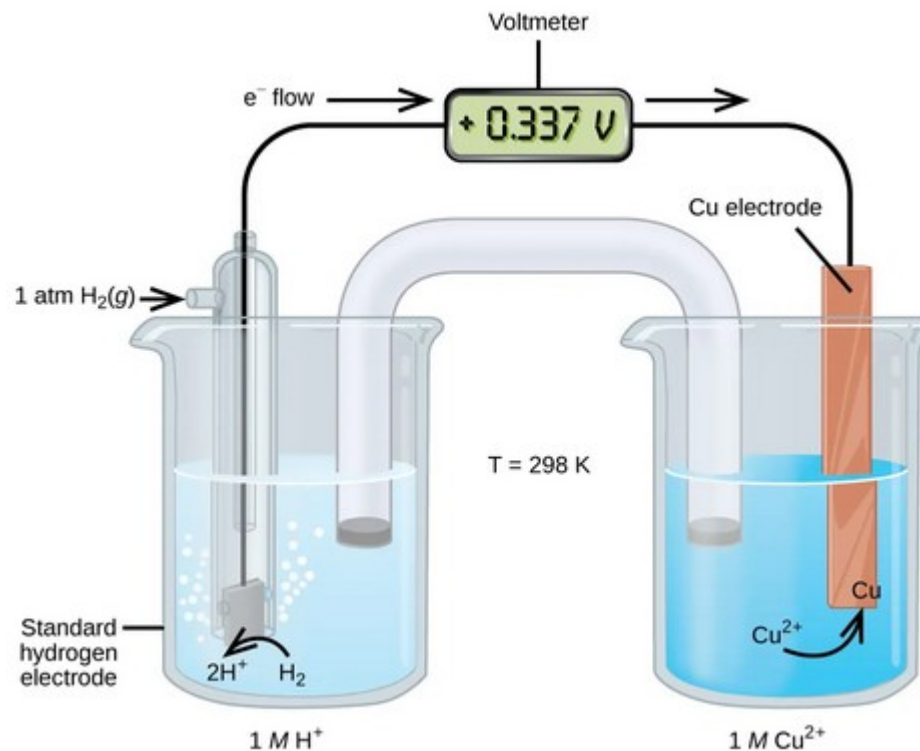
$$E_{\text{cell}} = E_X$$

- When the half-cell X is under standard-state conditions, its potential is the **standard electrode potential, E°_X** .

Standard Reduction Potentials



- Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called **standard reduction potentials**.
- Tabulations of E° values for half-cells measured against a SHE are available in [Appendix L](#).



$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}} = +0.337 \text{ V}$$

Cell Potential and Spontaneity

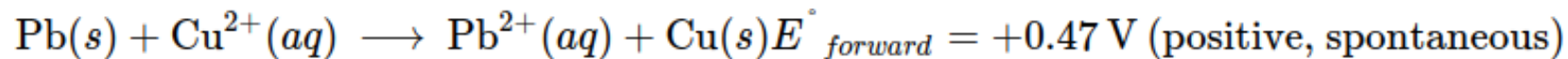
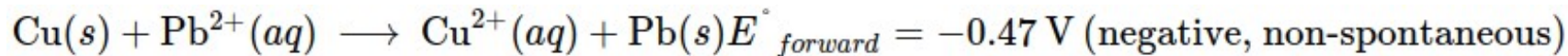


- *Spontaneous processes have positive cell potential, $E^\circ_{\text{cell}} > 0$, while the nonspontaneous process have negative cell potential, $E^\circ_{\text{cell}} < 0$.*
- Since electrode potentials are for reduction processes, an increased value of E° corresponds to an increased driving force behind the reduction of the species
 - Stronger oxidants (oxidizing agents) have greater standard electrode potential, E° .
- Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE.

Reversible Reactions



- If a process is spontaneous in one direction, it is non-spontaneous in the opposite direction.
- The potential of a cell reaction shows a consequential relationship in its arithmetic sign.



- Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions.

Section 17.4

Potential, Free Energy, and Equilibrium



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Learning Objectives



- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium
- Use the Nernst equation to determine cell potentials under nonstandard conditions

ΔG° and Electric Work



- The standard free energy change of a process, ΔG° is the maximum work that can be performed by a system, w_{\max} .
- In the case of a redox reactions essentially all the work is associated with transferring the electrons from reductant-to-oxidant, w_{elec}

$$\Delta G^\circ = w_{\max} = w_{\text{elec}}$$

E° and ΔG°



- The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\begin{aligned}\Delta G^\circ &= w_{\text{elec}} = -nFE_{\text{cell}}^\circ \\ \Delta G^\circ &= -nFE_{\text{cell}}^\circ\end{aligned}$$

- n is the number of moles of electrons transferred
- F is **Faraday's constant**, 96,485 C/mol.
- E°_{cell} is the standard cell potential.

E° and K



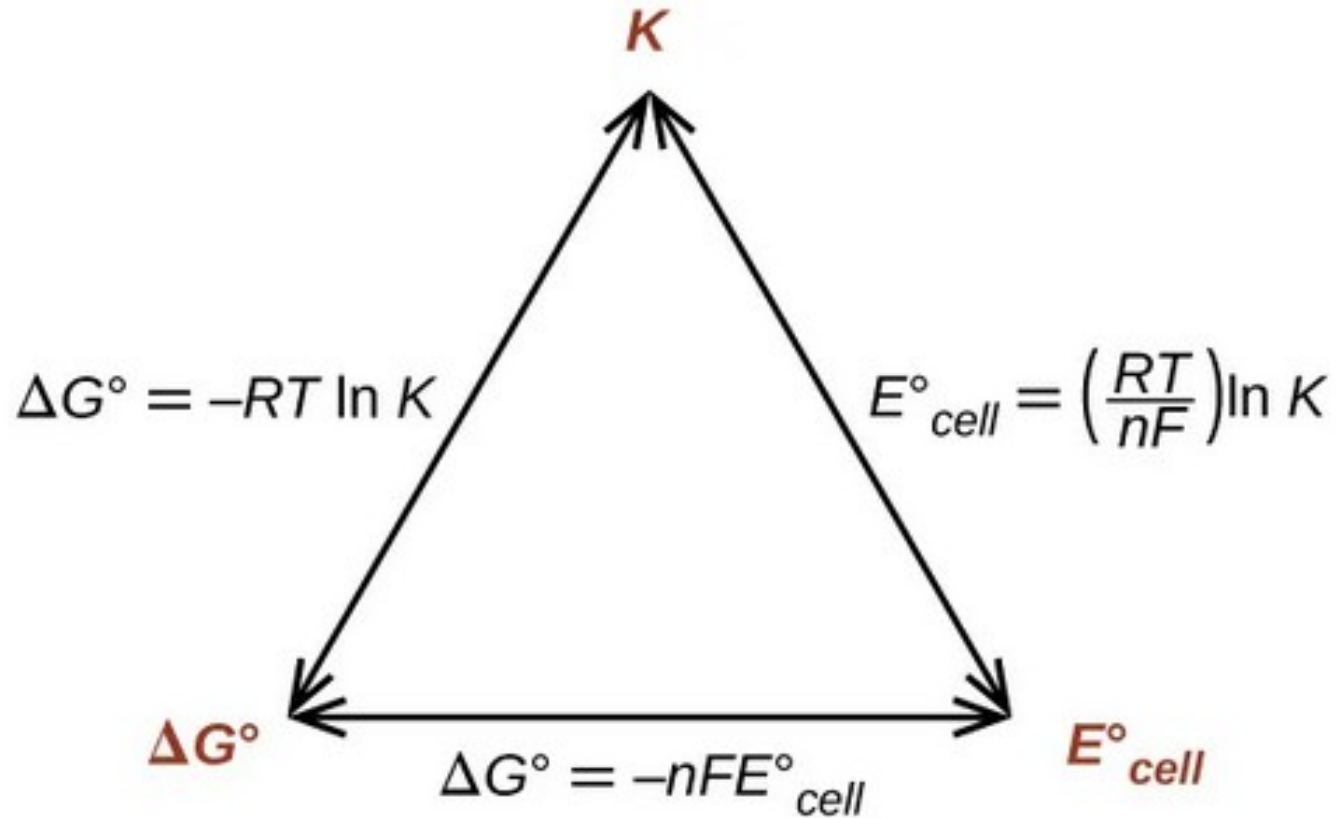
- Combining a previously derived relation between ΔG° and K and the equation relating ΔG° and E°_{cell} yields the following:

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

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF} \right) \ln K$$

- This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product.

Visualizing Relations



Summary



K	ΔG°	E°_{cell}	
> 1	< 0	> 0	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
$= 1$	$= 0$	$= 0$	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

The Nernst Equation



- Most of the redox processes do not occur under standard state conditions.
- The relationship between potential and free energy change combined with the equation for nonstandard state can be used to find the cell potential at nonstandard state.

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

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

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

A Convenient Simplification



- A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and standard temperature (298 K), along with a factor converting from natural to base-10 logarithms, have been included:

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

Concentration Cells



- A concentration cell is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode
- The potential of a concentration cell is determined only by the difference in concentration of the chosen redox species.



$$E_{\text{cell}} = 0.000\text{ V} - \frac{0.0592\text{ V}}{2} \log \frac{0.10}{0.50} = +0.021\text{ V}$$

Section 17.5

Batteries and Fuel Cells



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Learning Objectives

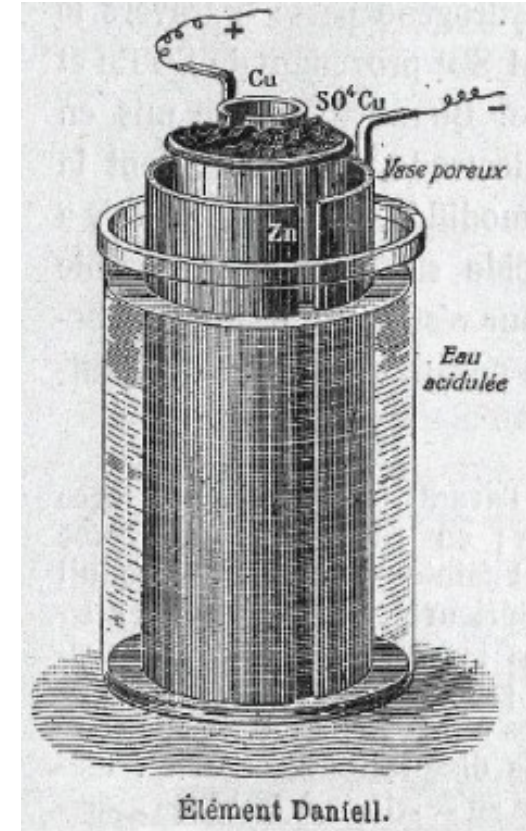


- Describe the electrochemistry associated with several common batteries
- Distinguish the operation of a fuel cell from that of a battery

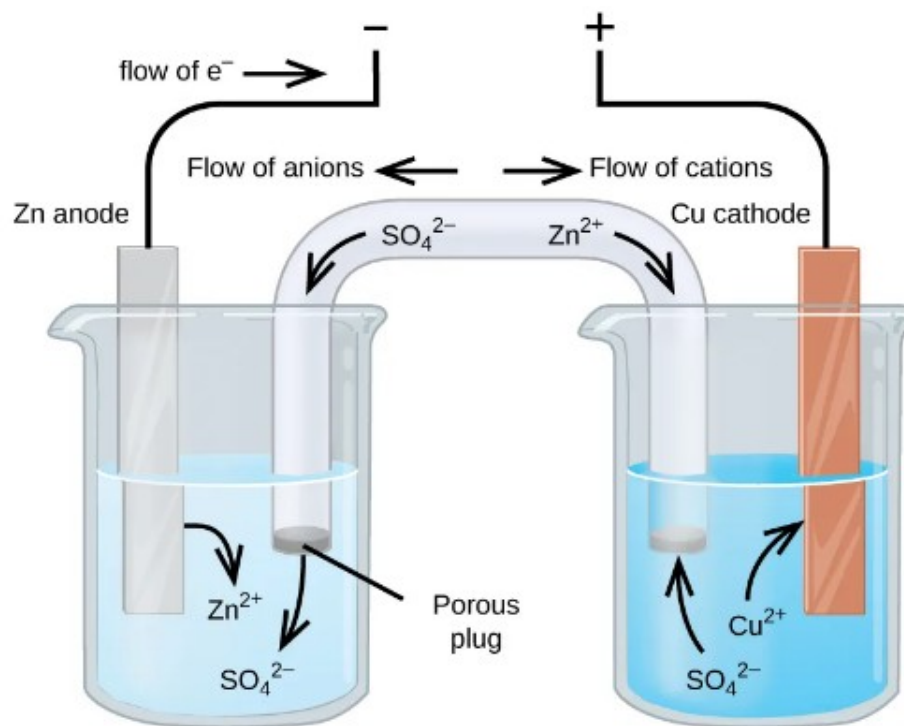
Batteries



- A **battery** is a galvanic cell that has been specially designed and constructed in a way that best suits its intended use as a source of electrical power for specific applications.
- Among the first successful batteries was the *Daniell cell*, which relied on the spontaneous oxidation of zinc by copper(II) ions.



Daniell cell



Modern Batteries

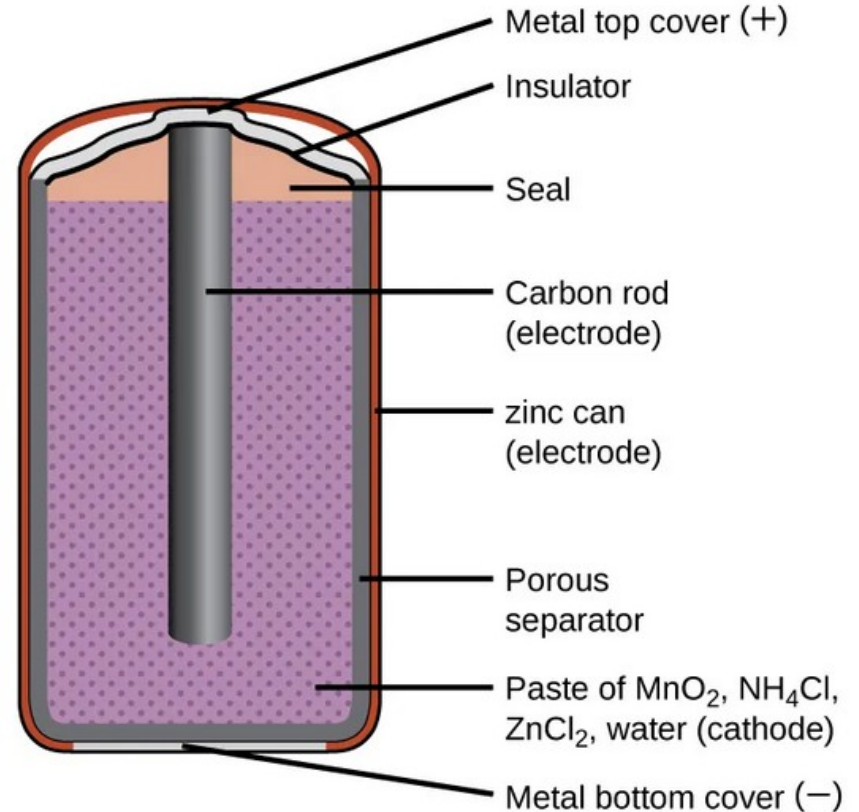


- Modern batteries exist in a multitude of forms to accommodate various applications.
 - Tiny button batteries that provide the power needs of a wristwatch
 - Very large batteries used to supply backup energy to municipal power grids.
- Some batteries are designed for single-use applications and cannot be recharged (**primary cells**).
- Others are based on conveniently reversible cell reactions that allow recharging (**secondary cells**).

Dry Cells



- A common primary battery is the **dry cell**.
 - zinc is used as both container and anode (“–” terminal)
 - A graphite rod as the cathode (“+” terminal)
 - An electrolyte paste containing manganese(IV) oxide, zinc(II) chloride, ammonium chloride, and water bridges the two electrodes.



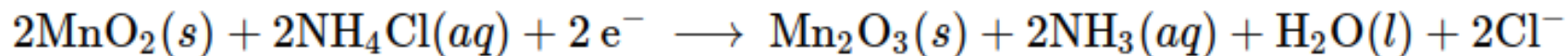
Dry Cell Voltage



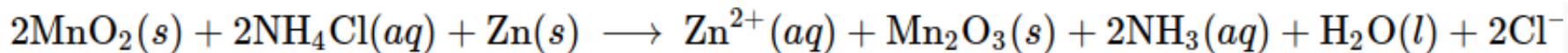
- Zinc is oxidized at the anode.



- Manganese (IV) is reduced within the paste.



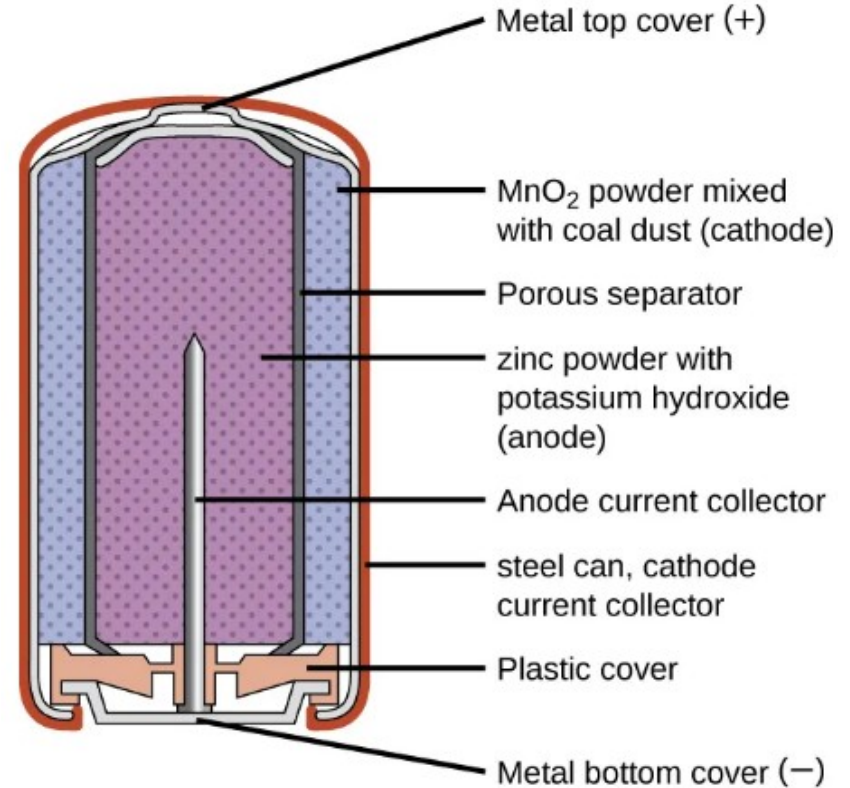
- The net reaction has a cell potential of 1.5 V.



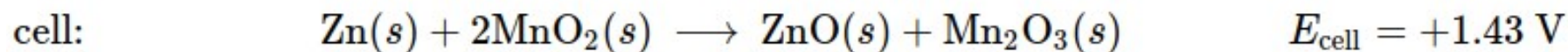
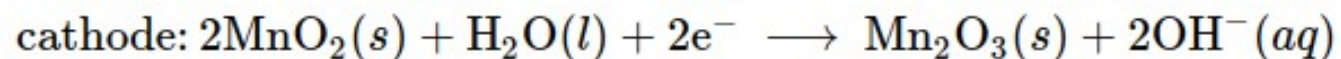
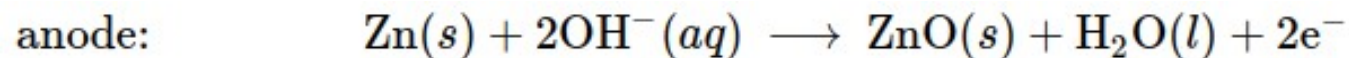
Alkaline batteries



- **Alkaline batteries** were developed in the 1950s to improve on the performance of the dry cell
- As their name suggests, these types of batteries use alkaline electrolytes
 - Often potassium hydroxide.
- An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size.



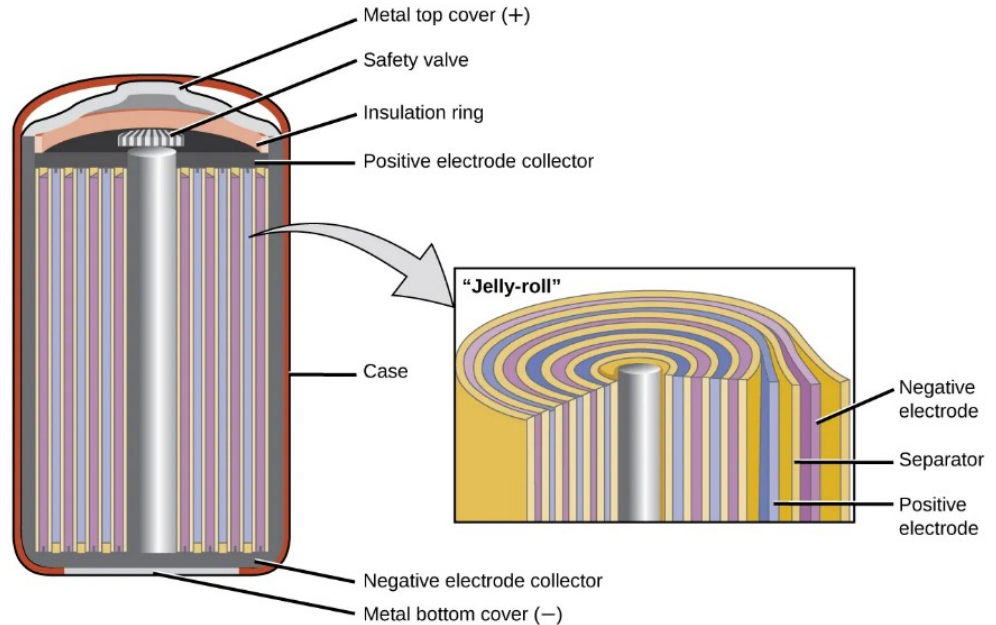
Alkaline Cell Voltage



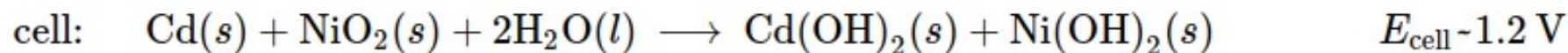
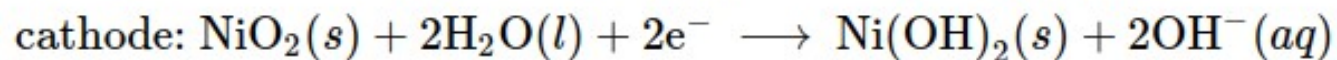
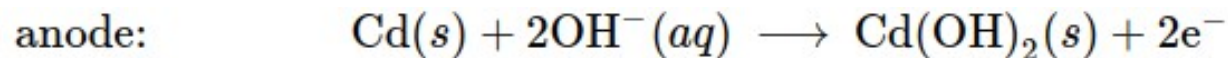
Nickel-Cadmium Cells



- **Nickel-cadmium, or NiCd,** batteries consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode.
 - A “jelly-roll” design and allows it to deliver more current than a similar-sized alkaline battery.
 - A NiCd battery can be recharged about 1000 times.
 - Cadmium is a toxic heavy metal



Nickel-Cadmium Cell Voltage



Lithium Ion Cells

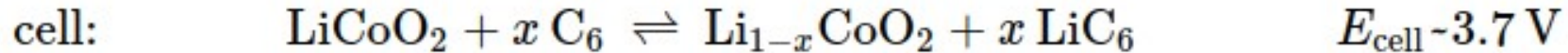
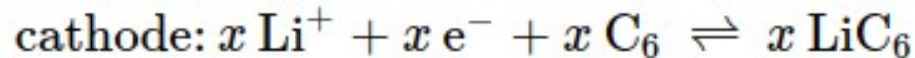
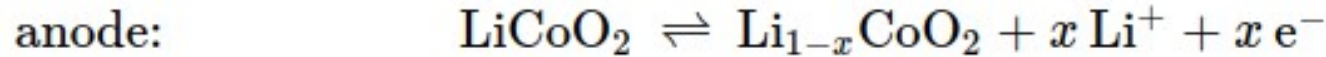


- **Lithium ion batteries** are among the most popular rechargeable batteries and are used in many portable electronic devices.
 - Provide a large amount current
 - Are lighter than comparable batteries of other types
 - Produce a nearly constant voltage as they discharge
 - Only slowly lose their charge when stored.

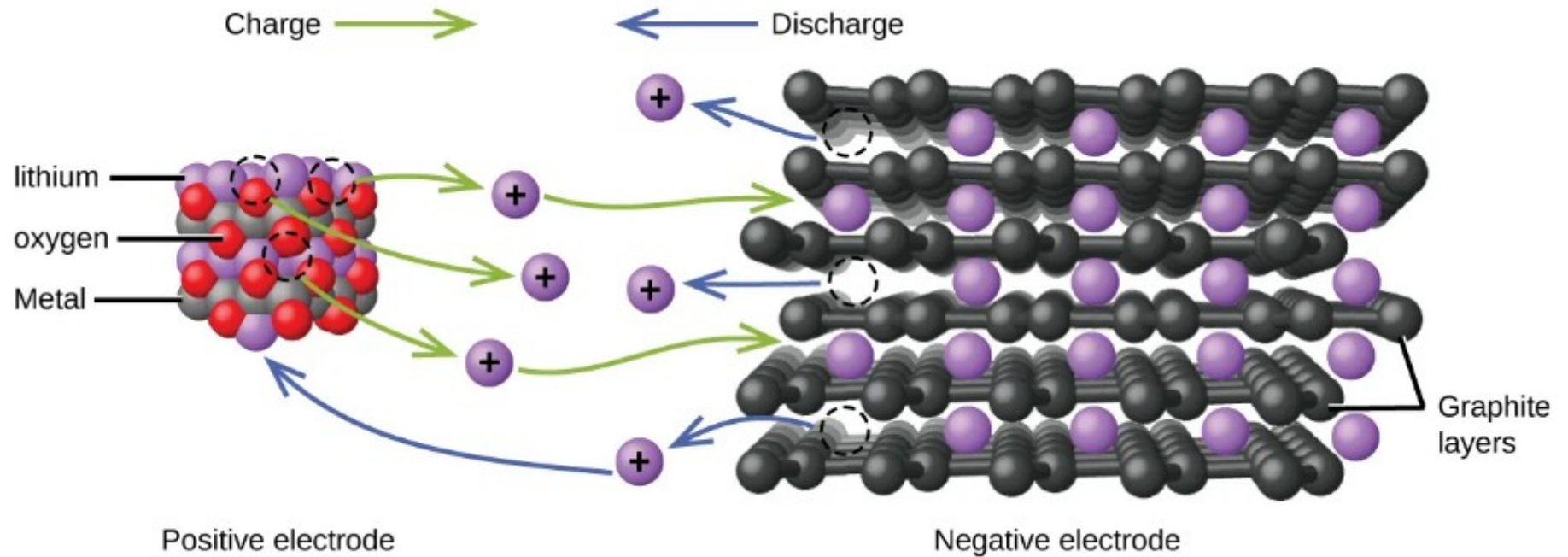
Lithium Cell Voltage



- The variable stoichiometry of the cell reaction leads to variation in cell voltages
 - x is usually no more than 0.5 and the cell voltage is 3.7 V.



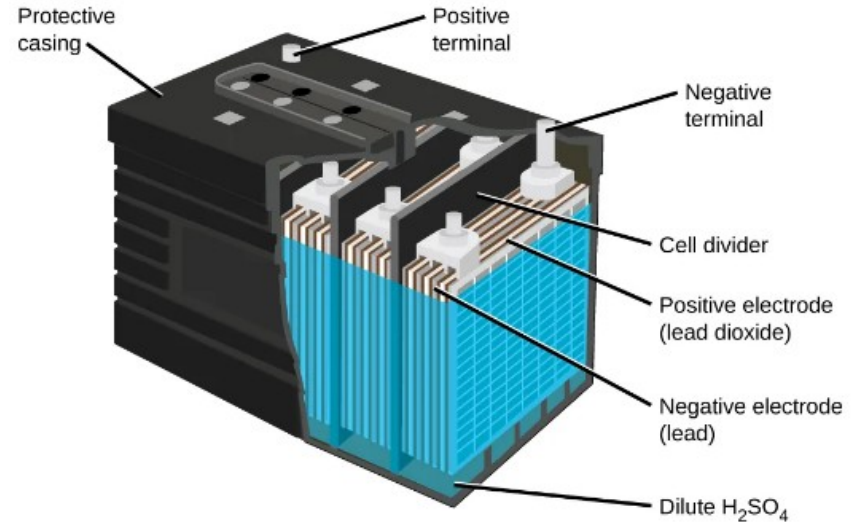
Lithium Ion Transfer



Lead Acid Batteries



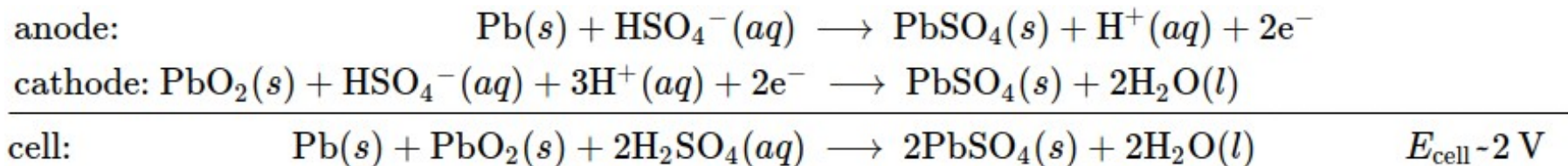
- The lead acid battery is the type of secondary battery commonly used in automobiles.
 - It is inexpensive and capable of producing high current.
 - Lead acid batteries are heavy and contain a caustic liquid electrolyte, H_2SO_4 (aq)
 - They must always be disposed of properly.



Lead Acid Cell Voltage



- Each cell produces 2 V, six cells are connected in series to produce a 12-V car battery.



Battery Capacity

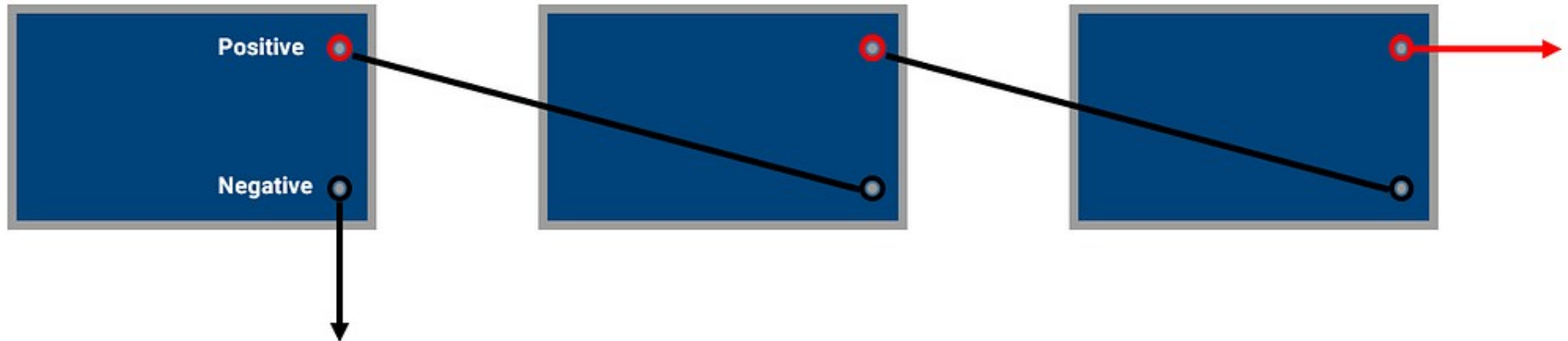


- Batteries come in different sizes. Sometimes this is combine multiple cells or contain one larger cells.
 - Dry cells are available in various sizes (e.g., D, C, AA, AAA).
- Larger cells contain greater amounts of the redox reactants and therefore are capable of transferring correspondingly greater amounts of charge before being spent.
- Larger cells will not be able to deliver more current or greater voltage.
 - Increasing E or i requires combining multiple cells.

Batteries in Series



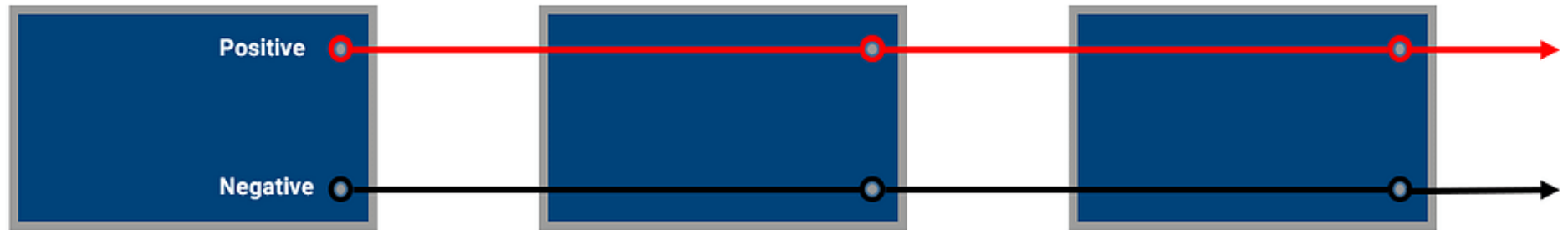
- Cells can be combined in series to increase the voltage of the overall battery.
- Each cell in series will increase the battery's voltage by the potential of a cell.
 - Each dry cell is 1.5 V, four dry cells in series would produce 6 V



Batteries in Parallel



- Cells can be combined in parallel to increase the capacity and maximum current available.
- Each cell in parallel will increase the battery capacity by the capacity of a single cell.
 - Wiring three 30 AH lead acid batteries will result in a 90 AH battery pack.



Fuel Cells

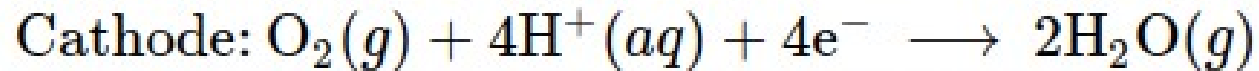


- A **fuel cell** is a galvanic cell that uses traditional combustible fuels that are continuously fed into the cell along with an oxidant.
 - Typical fuels include hydrogen, methane, and methanol
- Within the cell, fuel and oxidant undergo the same redox chemistry as when they are combusted
 - The catalyzed electrochemical process is much more efficient than traditional combustion.

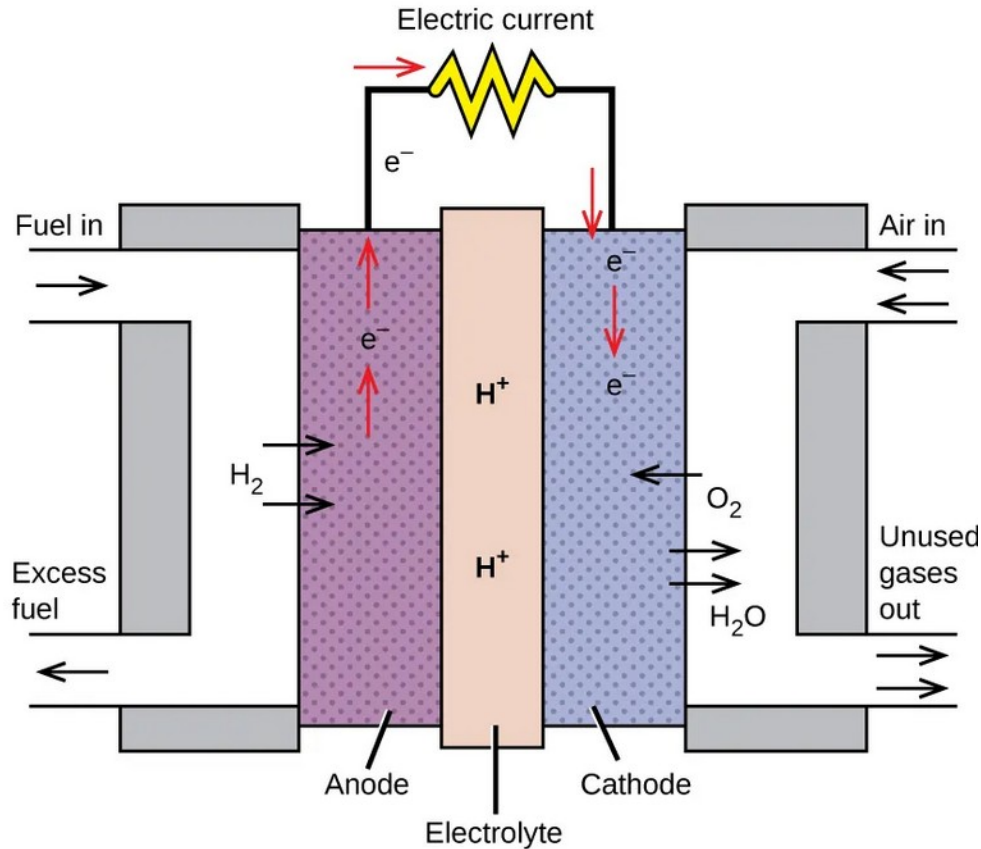
Fuel Cell Example



- A typical hydrogen fuel cell uses graphite electrodes embedded with platinum-based catalysts to accelerate the two half-cell reactions



Fuel Cell Example



- These types of fuel cells generally produce approximately 1.2 V.
- The energy efficiency is 20%–25% for an engine versus ~50%–75% for a fuel cell

Section 17.6

Corrosion



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Learning Objectives



- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion

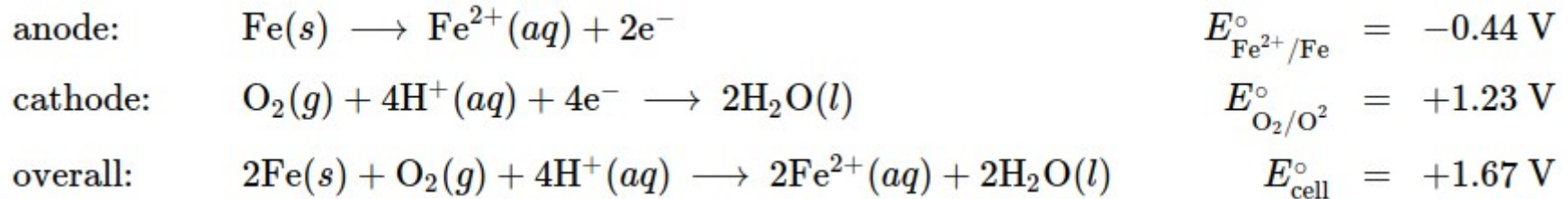


- **Corrosion** is usually defined as the degradation of metals by a naturally occurring electrochemical process.
 - Rust on iron
 - Tarnish on silver
 - The blue-green patina on copper
- The total cost of corrosion remediation in the United States is estimated to be in excess of half a trillion dollars a year.

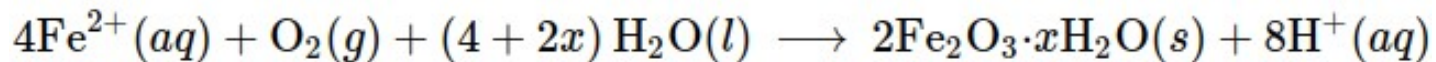
Rust



- Iron will rust when it is exposed to oxygen and water.
- The process begins with the following redox reactions:



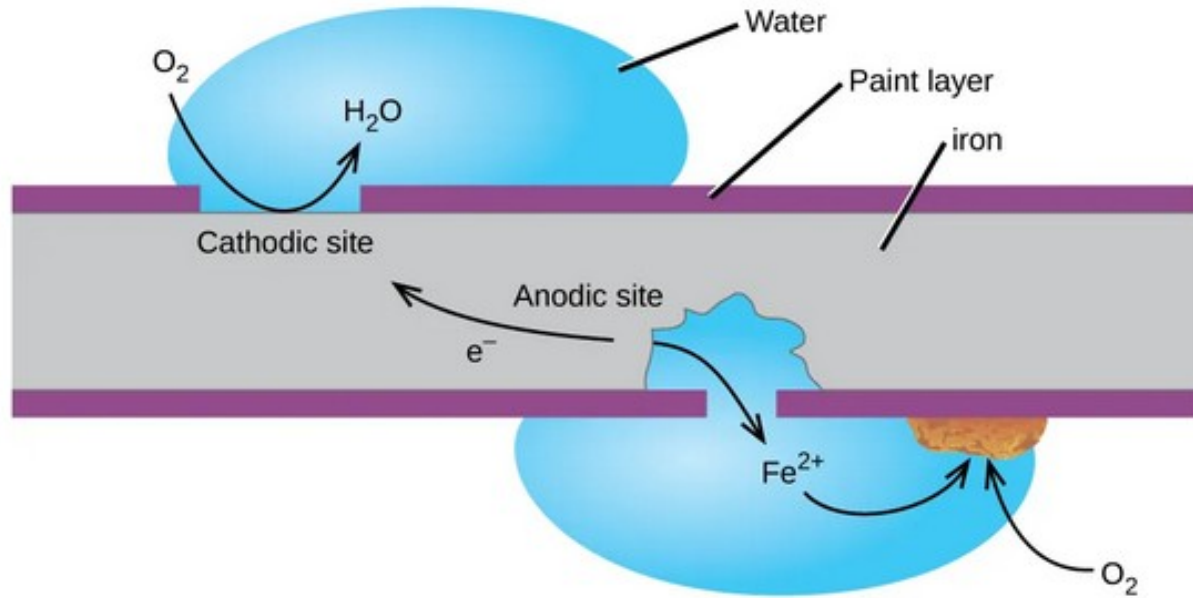
- Further reaction of the iron(II) product in humid air results in the production of an iron(III) oxide hydrate known as rust:



Rust



- Rust formation involves the creation of a galvanic cell at an iron surface



Protective Layers



- Corrosive layers on some metals form a protective layer preventing air from reaching metal below the corrosion layer.
 - The patina on copper
 - The oxidation layer on aluminum
- The formation of rust on iron does not create a protective layer
- Corrosion continues as the rust flakes off and exposes fresh iron to the atmosphere.
- This is a big problem due to the ubiquity of steel.

Preventing Rust

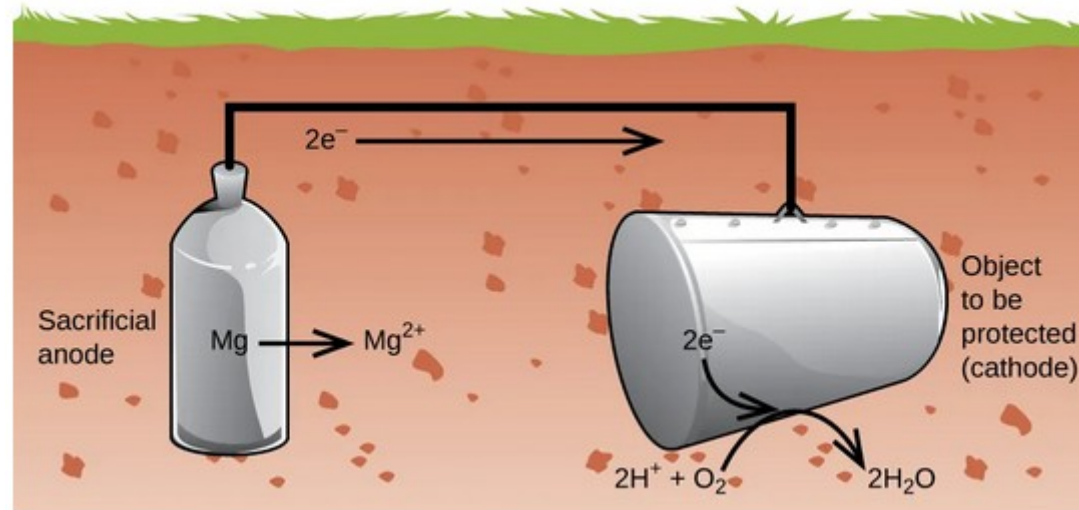


- There are many ways to control the formation of rust.
- Painting the surface
 - The paint will prevent air from reaching the metals surface
- Alloying iron with another metal
 - Stainless steel is an alloy containing chromium, iron, and carbon
- **Galvanization**, a process in which the metal to be protected is coated with a layer of a more readily oxidized metal, usually zinc.
 - Even when the protective coating is compromised the iron may still be protected from corrosion by a **cathodic protection process**

Cathodic Protection



- **Cathodic Protection** is a method of protecting metal by making it the cathode in a galvanic cell.
- This done by exposing the metal to metal with a lower reduction potential called a **sacrificial anode**.



Section 17.7

Electrolysis



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Learning Objectives



- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrolysis

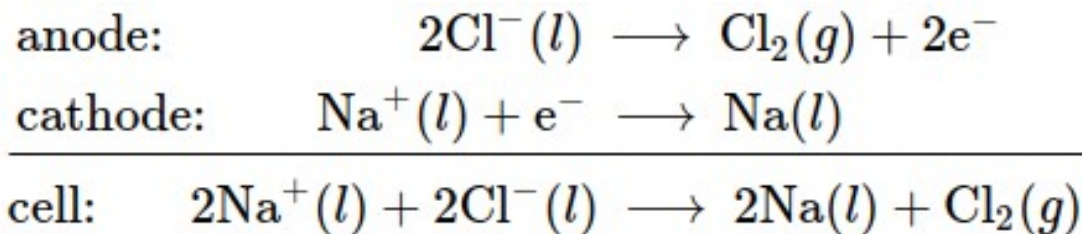


- Electrolysis is a process where *an external circuit does work on a redox system by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction*
 - Recharging a battery
 - Refinement of metallic ores
 - Manufacture of commodity chemicals,
 - Electroplating of metallic coatings on various products

NaCl Electrolysis



- Metallic sodium, Na, and chlorine gas, Cl₂, are used in numerous applications
- Their industrial production relies on the large-scale electrolysis of molten sodium chloride, NaCl

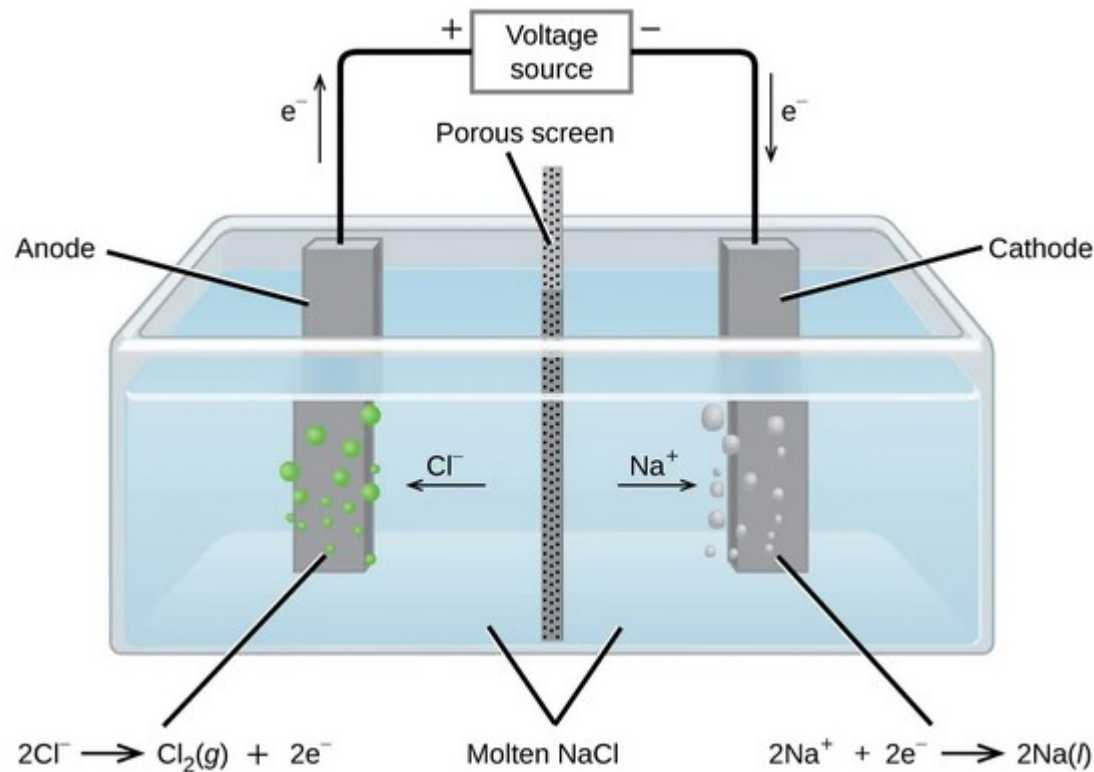


- To force this reaction, *a positive potential of magnitude greater than the negative cell potential must be applied to the cell.*

Downs Cell



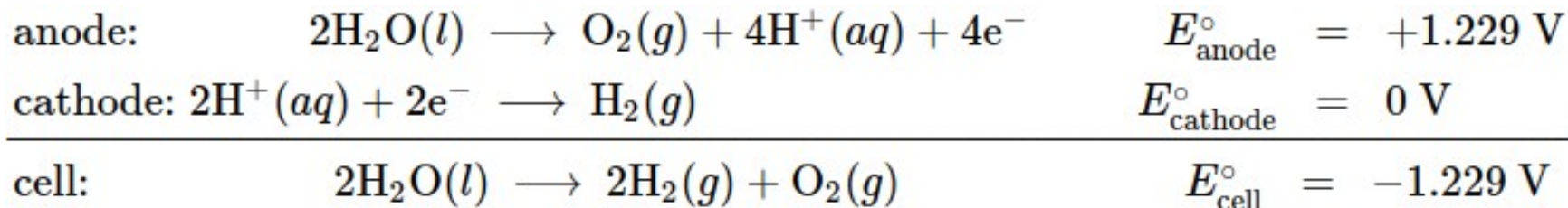
- The industrial process typically uses a *Downs Cell*



Water Electrolysis



- The redox processes associated with the electrolysis of water are:

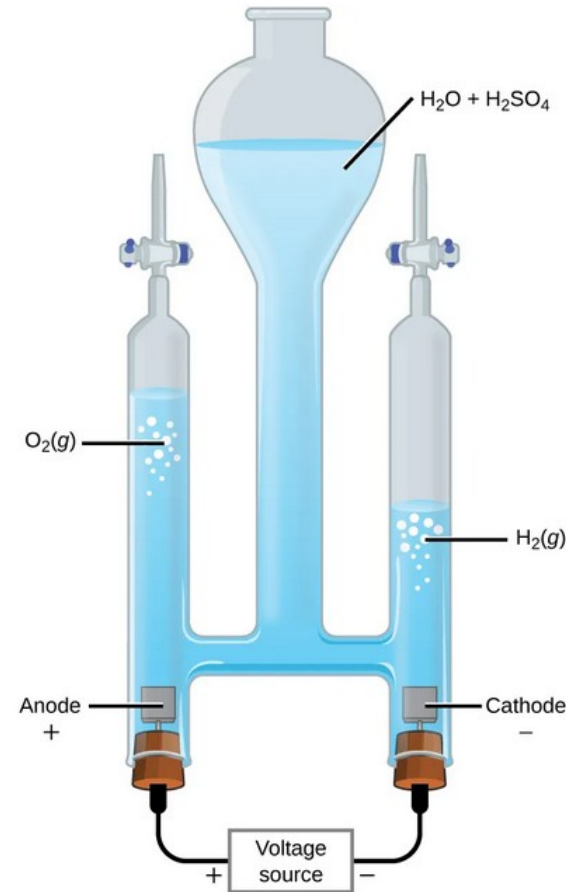


- To improve electrical conductivity without introducing a different redox species, strong acid is usually added.

Hoffman Apparatus



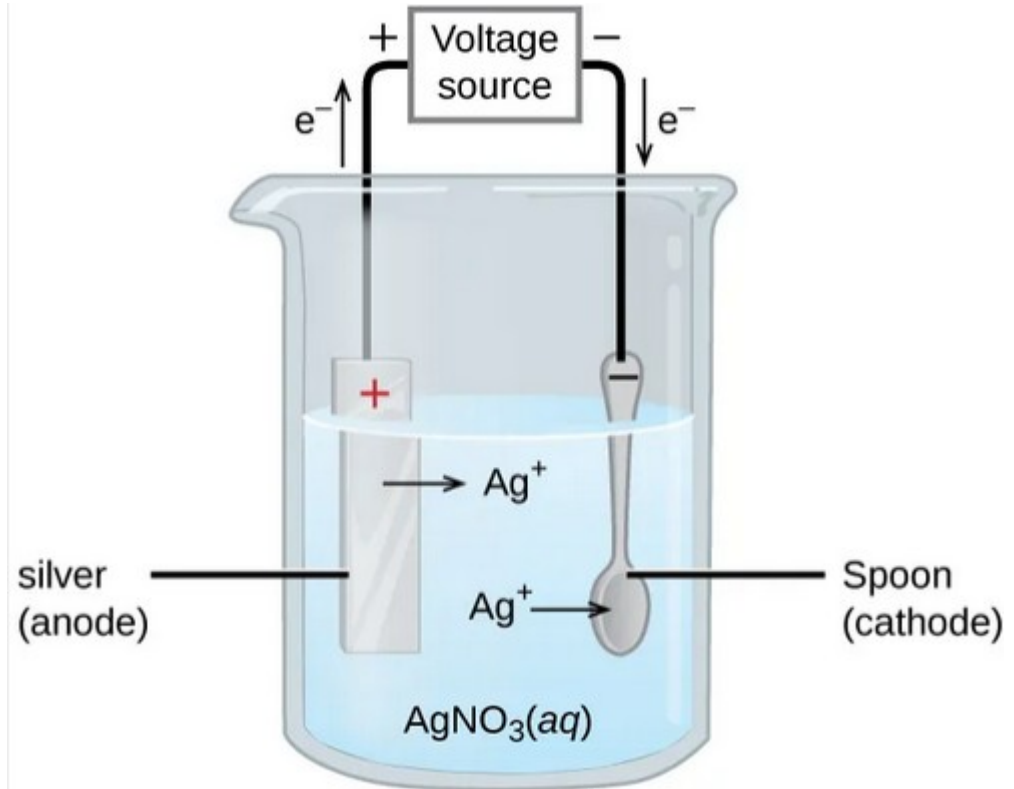
- Under standard conditions the reaction must be driven by imposing a cell voltage greater than +1.229 V.
- Keep in mind that under nonstandard conditions the required voltage will vary.



Electroplating



- **Electroplating** results in a thin coating of one metal on top of a conducting surface.
 - Used to make objects more corrosion resistant
 - Strengthen surfaces against abrasion
 - Produce attractive finishes
 - Purifying metal



Calculating Current



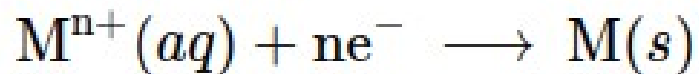
- Electrical current is defined as the rate of flow for any charged species.
 - Current is measured in a composite unit called an ampere defined as one coulomb per second, $A = 1 \text{ C/s}$.
- The charge transferred, Q , by passage of a constant current, I , over a specified time interval, t , is

$$Q = It$$

Stoichiometry of Electron Transfer



- When electrons are transferred during a redox process, the stoichiometry of the reaction may be used to derive the total amount of (electronic) charge involved.



$$Q = nF$$

- Where F is Faraday's constant, the charge in coulombs for one mole of electrons.

Example Problem



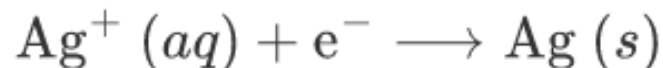
- While electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour.
 - How many moles of electrons passed through the cell?
 - What mass of silver was deposited at the cathode from the silver nitrate solution?

$$n = \frac{Q}{F} = \frac{it}{F}$$
$$= \frac{10.23 \frac{\text{C}}{\text{s}} \times 3600 \text{ s}}{96,485 \frac{\text{C}}{\text{mol e}^-}} = 0.3817 \text{ mol e}^-$$

Stoichiometry



- Mols of electrons can be treated using stoichiometric ratios just like chemical species.



$$\text{mole Ag} (s) = 0.3817 \text{ mol } e^- \left(\frac{1 \text{ mol Ag}}{1 \text{ mol } e^-} \right) = 0.3817 \text{ mol Ag}$$

$$0.3817 \text{ mol Ag} \left(\frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} \right) = 41.19 \text{ g Ag}$$