

Electrochemistry

Two major electrochemical types:

Voltaic (galvanic) cells:

Using spontaneous chemical reactions to do work (i.e. provide electricity).

Electrolytic Cells:

Using electricity to force nonspontaneous reactions.

Purification of Metals
Electroplating

Electrochemistry is also tied to Gibbs Free Energy and Chemical Equilibrium

Oxidation-Reduction: The Heart of Electrochemistry

General Idea:

Since redox reactions involve the transfer of electrons from one component of a reaction to another, intercepting that transfer (flow) of electrons, allows useful "work" to be done (i.e. electrical circuits can be powered).

Don't Forget: *Leo Goes Ger*

Loses Electrons Oxidized

Gains Electrons Reduced

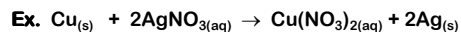
Expanded Definition of Redox Reactions

Oxidation:

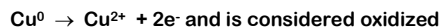
- Lose electrons
- Gain oxygen (special case)
- Lose hydrogen (special case)

Reduction:

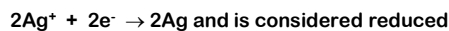
- Gain electrons
- Lose oxygen (special case)
- Gain hydrogen (special case)



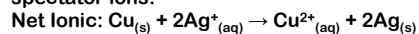
In this example copper loses two electrons and each silver atom gains an electron



This is the oxidation half-reaction. It only shows the component oxidized and does not include any spectator ions.



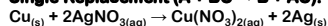
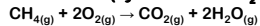
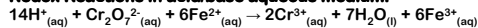
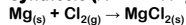
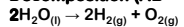
This is the reduction half-reaction. It only shows the component reduced and does not include any spectator ions.



Characteristics:

- Electrons are lost/gained by particles in the reaction
- There must be a change in "oxidation number".
- You must know the rules for assigning oxidation numbers
- Oxidation numbers are for "book keeping purposes" and may not represent actual charges
- Oxidations and reductions must occur in pairs (i.e. electron loss must be accompanied by electron gain)
- The oxidizing "agent" does the oxidizing and is itself reduced (agent refers to entire species)
- The reducing "agent" does the reducing and is itself oxidized.
- In a *disproportionation reaction*, an element in one oxidation state is simultaneously oxidized and reduced.

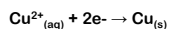
Common Redox Reactions

Single Replacement (A + BC → B + AC):**Combustion (hydrocarbon + O₂ → CO₂ + H₂O):****Redox Reactions in acid/base aqueous medium:****Synthesis (A + B → AB):****Decomposition (AB → A + B):**

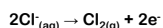
Not all of these take place in aqueous solutions but in each case electrons are lost and gained somewhere in the reaction equation.

Example:

Write the oxidation and reduction half reactions for cupric chloride decomposing to form copper metal and chlorine gas.
 $\text{CuCl}_{2(aq)} \rightarrow \text{Cu}_{(s)} + \text{Cl}_{2(g)}$

Answer:**Reduction:**

Cu goes from +2 to 0

Oxidation:

Cl goes from (-1 to 0)x2

Balancing Redox Reactions in Acidic and Basic Medium

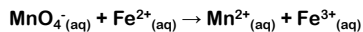
Many redox reactions take place in either acidic or basic solutions. Acidic solutions are a source of H⁺ ions and basic solutions provide OH⁻ when balancing equations.

You must balance both **elements AND charges** in redox reactions.

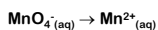
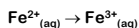
Generally, spectator ions are not included.

Example:

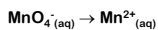
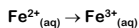
The permanganate ion, MnO₄⁻ is an oxidizing agent. A common laboratory analysis for iron is to titrate aqueous iron(II) ion with a solution of potassium permanganate of precisely known concentration. Use the half-reaction method to write the balanced net ionic equation for the reaction in acidic solution.



Step 1: Separate the reaction into oxidation/reduction half reactions.

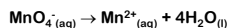
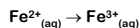


Step 2: Balance atoms other than oxygen and hydrogen.

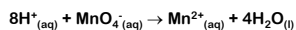
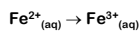


In this case the half-reactions are already balanced.

Step 3: For every oxygen, add an equivalent number of water molecules on the opposite side to balance them out.



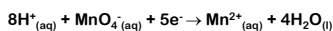
Step 4: Add H⁺ ions to balance the hydrogen added from water.



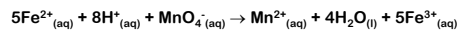
Step 5: Balance charges between reactants and products by adding electrons.



Step 6: Ensure that the number of electrons lost and gained is the same by multiplying half-reactions through where necessary.



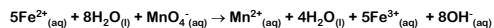
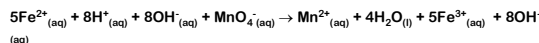
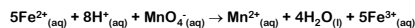
Now we can add the two reaction equations together. Note that the electrons cancel out so are not included in the final net reaction.



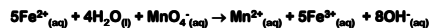
Notice that the Mn is reduced from +7 to +2 and each iron is oxidized from +2 to +3.

The permanganate ion, $\text{MnO}_4^-_{(\text{aq})}$, is said to be the oxidizing agent (because it oxidizes the iron), and the iron is the reducing agent.

As a final step, ~~if~~ the reaction were to have taken place in basic solution, the hydrogen ions must be removed and replaced by hydroxide ions. This is done by adding OH^- to each side of the equation.



Simplify the water molecules by removing 4 from both sides to end up with



Example:

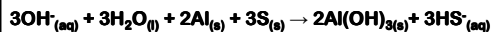
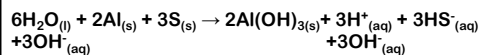
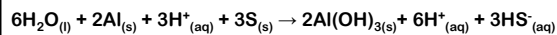
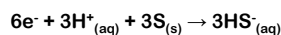
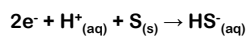
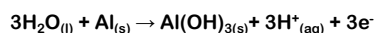
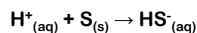
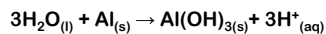
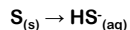
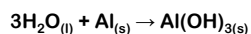
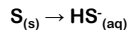
Voltaic cells based on the reduction of sulfur are under development. One such cell involves the reaction of sulfur with aluminum under basic conditions



a) Balance this equation

b) Identify the oxidizing and reducing agents, the substance oxidized and the substance reduced.

Answer:



Aluminum is the reducing agent and is oxidized.

Sulfur is the oxidizing agent and is reduced.

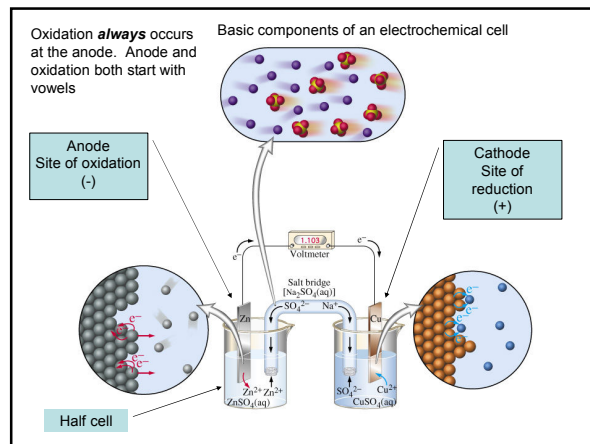
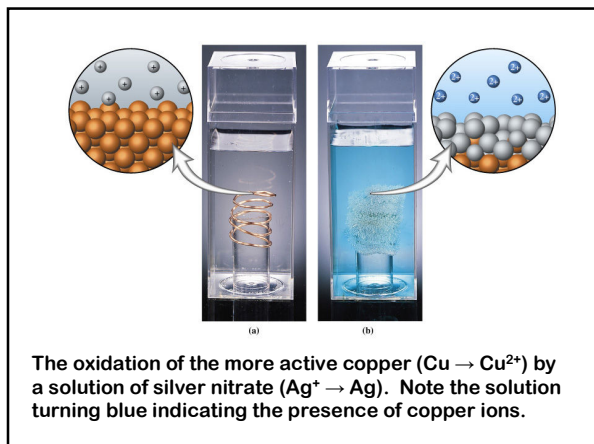
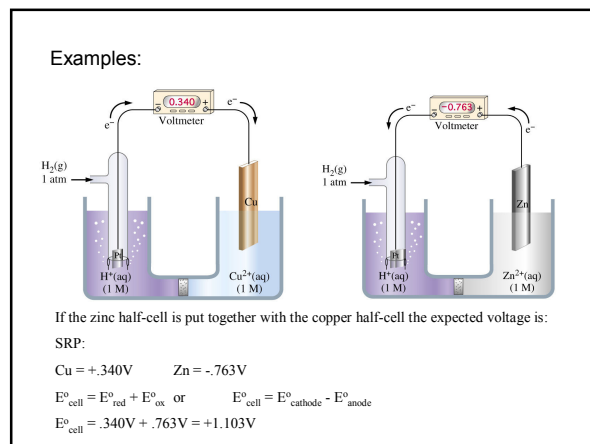
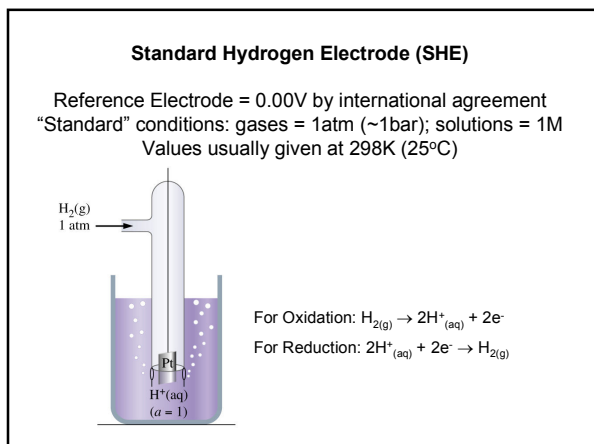
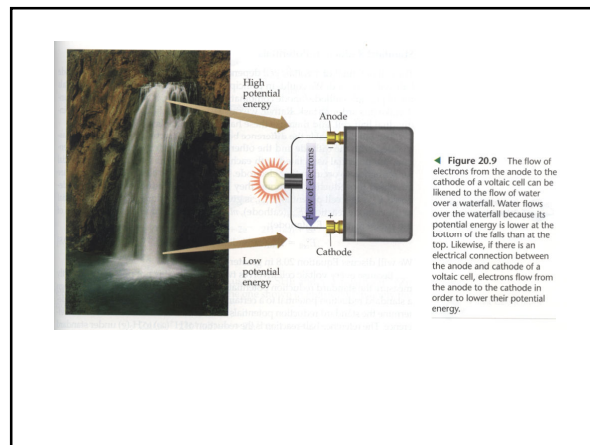


TABLE 18.1 Standard Reduction Potentials at 25 °C

Standard conditions are: 1M solutions, 1 atm for gases and a temperature of 25°C.

Reduction Half-Reaction	E° (V)
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.78
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.51
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	1.09
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	0.54
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$	0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.26
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.45
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04

Note the relationship to the activity series of metals



Calculating the Potential (voltage) for a Voltaic Cell

A table of *standard reduction (half-cell) potentials* must be used (p A-33 Appendix M)

The standard cell voltage (emf or electromotive force) for an electrochemical cell is

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} \quad \text{or} \quad E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

(This one doesn't require you to flip the sign)

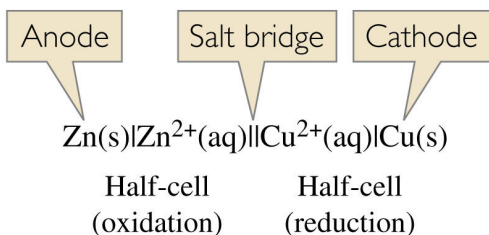
Don't forget, the table is a "reduction potential" table, so if you want oxidation you have to flip the sign on the number.

TABLE 18.1 Standard Reduction Potentials at 25°C. Standard conditions are: 1M solutions, 1 atm for gases and a temperature of 25°C.

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

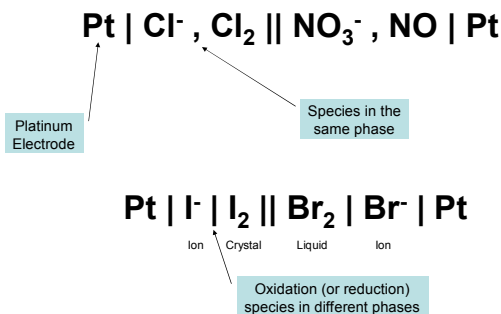
Note the relationship to the activity series of metals

Condensed (abbreviated) Cell Diagram



Note that the anode (oxidation) is listed on the left. A single vertical line represents a phase boundary and the double vertical line indicates the salt bridge. Normally spectator ions are not shown.

More complex abbreviated cell notations



Question:

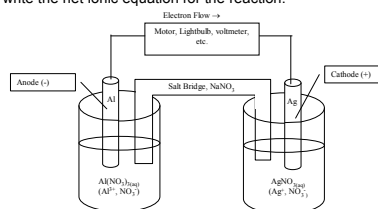
Draw a full cell diagram, a condensed cell diagram and determine the cell potential for a combination of silver/silver nitrate and aluminum/aluminum nitrate. Use sodium nitrate paste as the salt bridge. Also, identify the direction of electron flow and label the anode and the cathode.

Finally, write the net ionic equation for the reaction.

Answer:

Draw a full cell diagram, a condensed cell diagram and determine the cell potential for a combination of silver/silver nitrate and aluminum/aluminum nitrate. Use sodium nitrate paste as the salt bridge. Also, identify the direction of electron flow and label the anode and the cathode.

Finally, write the net ionic equation for the reaction.



Electrode Potentials, Spontaneous Change and Equilibrium

The maximum amount of useful work that a system can do is $-\Delta G$.

$$-\Delta G = w_{\text{electric}} \text{ (useful work)} = nFE_{\text{cell}}$$

$$\Delta G = -nFE_{\text{cell}}$$

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

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

n = moles of electrons transferred in the balanced equation.

If E_{cell} is **positive**, the reaction in the forward direction (from left to right) is spontaneous.

If E_{cell} is **negative**, the reaction in the forward direction is nonspontaneous.

If $E_{\text{cell}} = 0$, the system is at equilibrium.

When a cell reaction is reversed, E_{cell} and ΔG change signs.

Activity Series and Reduction Potential

Activity Series of Metals

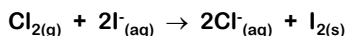
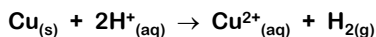
↑ increasing reactivity	potassium	Reacts violently with cold water
	sodium	Reacts slowly with cold water
	calcium	
	magnesium	Reacts very slowly with steam but quite reactive in acid
	aluminum	
	zinc	
	chromium	
	iron	Reacts moderately with high levels of acid
	nickel	
	tin	
	lead	< HYDROGEN comes here
	copper	Unreactive in acid
	silver	
	platinum	
gold		

The Activity Series of Metals

Metal Type	Pauling Electroneg.	S.R.P.	Activity
Very electro-positive metals	Below 1.4	-1.6 V or less	React with water
Electropositive metals	1.4 to 1.9	0.0 to -1.6 V	React with acids
Electronegative metals	1.9 to 2.54	positive	Not oxidized by H^+

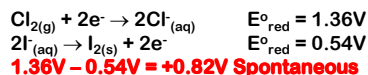
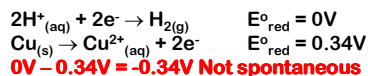
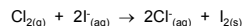
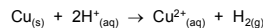
Question:

Using standard reduction potentials, determine whether the following reactions are spontaneous under standard conditions:



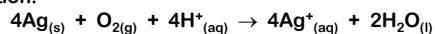
Answer:

Using standard reduction potentials, determine whether the following reactions are spontaneous under standard conditions:

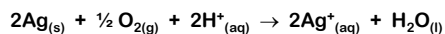


Question:

a. Use standard reduction potentials to calculate the standard free-energy change, ΔG° , for the following reaction:



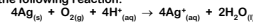
b. Suppose the reaction in part "a" were written as



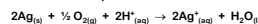
What are the values of E° and ΔG° when the reaction is written this way?

Answer:

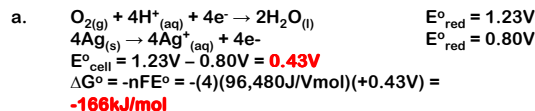
a. Use standard reduction potentials to calculate the standard free-energy change, ΔG° , for the following reaction:



b. Suppose the reaction in part "a" were written as



What are the values of E° and ΔG° when the reaction is written this way?



From thermodynamics

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

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

$$E^\circ_{\text{cell}} = RT \ln K_{\text{eq}} / nF \quad R = 8.3145 \text{ J/molK}$$

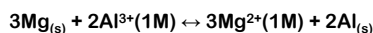
Since E°_{cell} is generally calculated at 25°C (298K)

$$E^\circ_{\text{cell}} = [0.025693 \text{ V/n}] \ln K_{\text{eq}} \quad @25^\circ\text{C}$$

(Where the label volts (V) = 1J/C)

Questions:

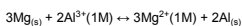
1. Calculate (using standard reduction potentials) the values of ΔG° and K_{eq} at 25°C for the reaction that follows.



2. Determine E°_{cell} and K_{eq} for the reaction of silver metal with nitric acid. The silver is oxidized to $\text{Ag}^+_{(aq)}$, and nitrate ion is reduced to $\text{NO}_{(g)}$.

Answer:

1. Calculate (using standard reduction potentials) the values of ΔG° and K_{eq} at 25°C for the reaction that follows.



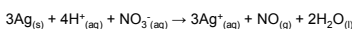
$$\Delta G^\circ = -nFE^\circ = -(6)(96,485 \text{ J/mol})(-1.66\text{V} - (-2.37\text{V})) = -411,026.1 \text{ J/mol} = -411 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad \ln K_{\text{eq}} = -411,026.1 \text{ J/mol} / (-8.314 \text{ J/molK})(298\text{K}) = 165.899$$

$$e^{165.899} = K_{\text{eq}} = 1.1 \times 10^{72}$$

2. Determine E°_{cell} and K_{eq} for the reaction of silver metal with nitric acid. The silver is oxidized to $\text{Ag}^+_{(aq)}$, and nitrate ion is reduced to $\text{NO}_{(g)}$.

The balanced equation is:



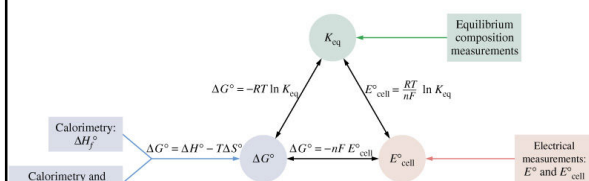
From the SRP chart : $\text{NO}_3^-_{(aq)} + 4\text{H}^+_{(aq)} + 3\text{e}^- \rightarrow \text{NO}_{(g)} + 2\text{H}_2\text{O}_{(l)} = +0.956\text{V}$ and



$$E^\circ_{\text{cell}} = [0.025693 \text{ V/n}] \ln K_{\text{eq}} \quad \ln K_{\text{eq}} = 3(.156\text{V}) / 0.025693\text{V} = 18.215$$

$$K_{\text{eq}} = e^{18.215} = 8.1 \times 10^7 \quad (\text{note that the coefficients of 3 for the silver half reaction did not alter the half cell potential})$$

Summary of Interrelationships Between Equilibrium, Thermodynamics and Electrochemistry

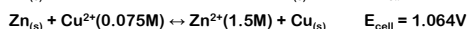
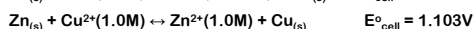
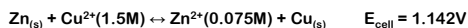


Effects of Concentration on cell voltage (E°_{cell} vs E_{cell})

Given the electrochemical cell between zinc and copper discussed earlier, it was identified that zinc (the more active metal) is oxidized to Zn^{2+} ions and copper is reduced from Cu^{2+} ions to $\text{Cu}_{(s)}$.

If the initial concentration of Cu^{2+} is increased and Zn^{2+} is decreased the effect is to raise the potential for the reaction in the forward direction.

You can think of this as the solution wanting "that much more" to reduce the copper ion concentration and increase the zinc ion concentration (Le Chatelier's Principle). Here are some examples:



The Nernst Equation

Used for calculating nonstandard cell potentials at 25°C.

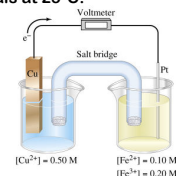
Given:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{substituting}$$

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

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/nF) \ln Q$$

At 25°C



$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.025693 \text{ V/n}) \ln Q \quad \text{or more commonly}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592 \text{ V/n}) \log Q$$

n is the number of electrons involved in the cell reaction.

Concentration Cells

The Nernst equation works even if the two half cells are identical.

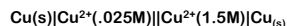


The standard potential (for 1M solutions) is expected to be zero.



$$E^\circ_{\text{cell}} = 0.340\text{V} - 0.340\text{V} = 0\text{V}$$

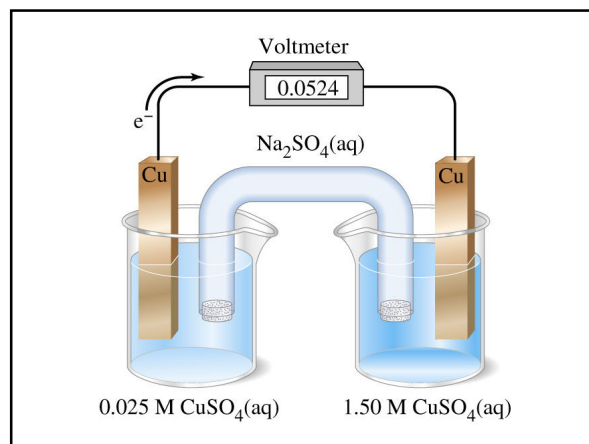
But if the solutions have nonstandard molarities, such as



$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592\text{V}/n)\log Q$$

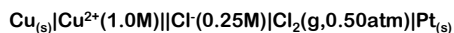
$$E_{\text{cell}} = 0\text{V} - (0.0592\text{V}/2)\log(0.025/1.50) = 0.0524\text{V}$$

The reaction progresses in such a way as to increase the ion concentration of the lower molarity solution and decrease the ion concentration of the higher molarity solution. This means in this case the copper at the .025M solution is oxidized.



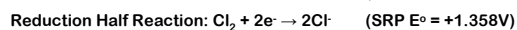
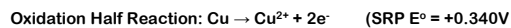
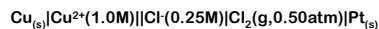
Question:

Use the Nernst equation to determine E_{cell} at 25°C for the following voltaic cell:



Answer:

Use the Nernst equation to determine E_{cell} at 25°C for the following voltaic cell:



$$E^\circ_{\text{cell}} = 1.358 - 0.34 = 1.018\text{V}$$

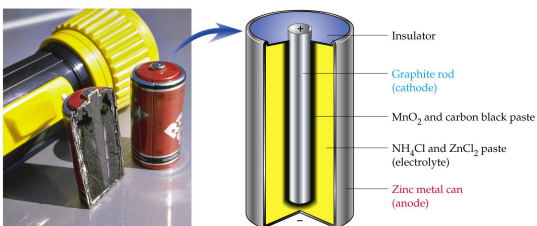
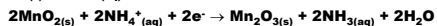
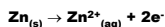
$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592\text{V}/n)\log Q$$

$$E_{\text{cell}} = 1.018\text{V} - (0.0592\text{V}/2)\log[(1.0)(0.25)^2/(0.50)]$$

$$E_{\text{cell}} = 1.018\text{V} - (-0.02673) = \mathbf{1.045\text{V}}$$

Primary (nonrechargeable) Batteries (1.5V)

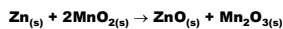
Le Clanché



Large currents cause build up of NH_3 gas at carbon cathode
Causes voltage drop from insulation

Alkaline Batteries

KOH is used instead of NH_4Cl

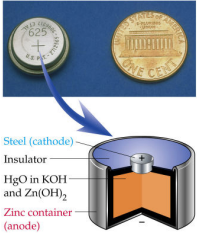


Mercury (HgO) "button" batteries (~1.3V)

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

$$\text{HgO}_{(s)} + \text{H}_2\text{O} + 2e^{-} \rightarrow \text{Hg}_{(l)} + 2\text{OH}^{-}_{(aq)}$$

Overall: $\text{Zn}_{(s)} + \text{HgO}_{(s)} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_{2(s)} + \text{Hg}_{(l)}$
Often Ag_2O is used in place of HgO



Steel (cathode)
 Insulator
 HgO in KOH and Zn(OH)₂
 Zinc container (anode)

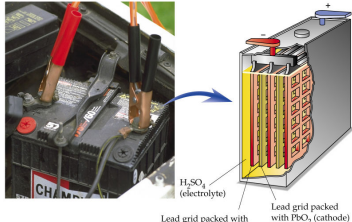
Lead-Acid Battery (12V)

$$\text{Pb}_{(s)} + \text{HSO}_4^{-}_{(aq)} \rightarrow \text{PbSO}_4(s) + \text{H}^{+}_{(aq)} + 2e^{-}$$

$$\text{PbO}_{2(s)} + 3\text{H}^{+}_{(aq)} + \text{HSO}_4^{-}_{(aq)} + 2e^{-} \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}$$

Overall: $\text{Pb}_{(s)} + \text{PbO}_{2(s)} + 2\text{H}^{+}_{(aq)} + 2\text{HSO}_4^{-}_{(aq)} \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}$

Recharging can cause electrolysis of H_2O : $2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{H}_{2(g)} + \text{O}_{2(g)}$



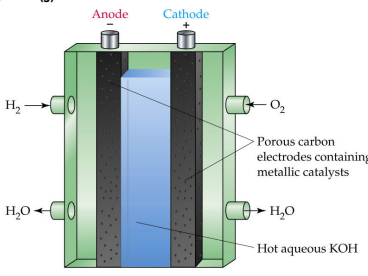
5 cells at 2.4V each
 H₂SO₄ (electrolyte)
 Lead grid packed with spongy lead (anode)
 Lead grid packed with PbO₂ (cathode)

Fuel Cells:

$$2\text{H}_{2(g)} + 4\text{OH}^{-}_{(aq)} \rightarrow 4\text{H}_2\text{O} + 4e^{-}$$

$$\text{O}_{2(g)} + 2\text{H}_2\text{O} + 4e^{-} \rightarrow 4\text{OH}^{-}_{(aq)}$$

Overall: $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}$



Anode Cathode
 H₂ O₂
 H₂O H₂O
 Porous carbon electrodes containing metallic catalysts
 Hot aqueous KOH

Other types of batteries:

Ni-Cad (Nickel-Cadmium)

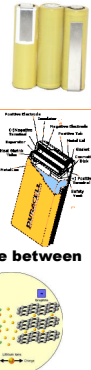
$$2\text{Ni(OH)}_{(s)} + 2\text{H}_2\text{O}_{(l)} + 2e^{-} \rightarrow 2\text{Ni(OH)}_{2(s)} + 2\text{OH}^{-}_{(aq)}$$

$$\text{Cd}_{(s)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{Cd(OH)}_{2(s)} + 2e^{-}$$

Suffers from: weight, toxic metals and "memory"

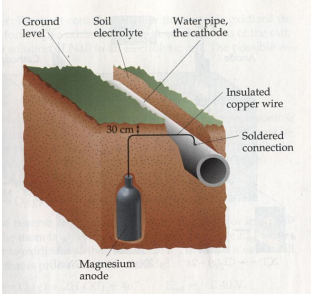
In NiMH (Nickel-Metal Hydride)
Anode consists of metal alloy (e.g. ZrNi₂)

In Li-ion (Lithium Ion) batteries, lithium ions migrate between layered materials.



Cathodic Protection

Using a more active metal (sacrificial anode) to protect a less active metal



Ground level
 Soil electrolyte
 Water pipe, the cathode
 Insulated copper wire
 Soldered connection
 Magnesium anode

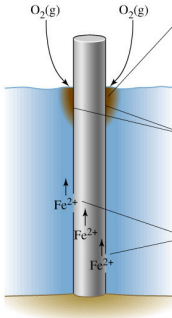
◀ Figure 20.27 Cathodic protection of an iron water pipe. The magnesium anode is surrounded by a mixture of gypsum, sodium sulfate, and clay to promote conductivity of ions. The pipe, in effect, is the cathode of a voltaic cell.

Corrosion of an Iron Piling

Rust formation:
 $\text{Fe}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{Fe(OH)}_{2(s)}$
 $4\text{Fe(OH)}_{2(s)} + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{Fe(OH)}_{3(s)}$

Cathode:
 $\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^{-} \rightarrow 4\text{OH}^{-}_{(aq)}$

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



Example:

Two electrochemical cells are connected as shown. Specifically, the zinc electrodes of the two cells are joined, as are the copper electrodes. Will there be
 a) no current,
 b) a flow of electrons in the direction of the red arrows,
 or
 c) a flow of electrons in the direction of the blue arrows?



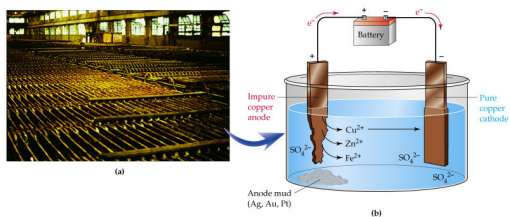
Answer:

Since these connected cells have opposing current flow, the one that "wins" will be the one with the greater cell potential.

From the Nernst equation, $[E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592V/n)\log Q]$, the cell with the smaller anode molarity and higher cathode molarity will have the greater nonstandard cell potential. Therefore, electrons will flow from the zinc electrode that is immersed in the 0.10M Zn^{2+} ion solution which is consistent with the red arrows.

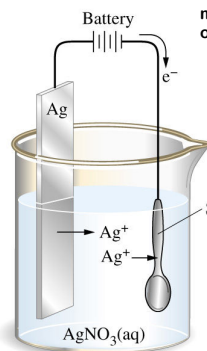
Electrolysis

Using electrical energy to drive a reaction in a nonspontaneous direction.



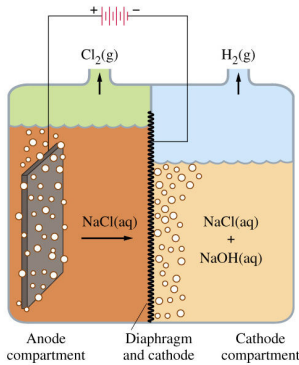
Purification of copper process
 Copper ions are more "reducible" than zinc or iron ions

Electroplating: Plating a more "precious" metal onto the surface of a base metal or other object.

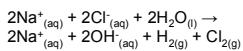


Important Note: In electrolytic cells, the anode is still the site of oxidation (as always), but is considered to be positive (+), while the cathode is negative (-).

In the schematic of the battery in the diagram (the series of long and short vertical lines [that represent battery "cells"], the long line at the outer edge is positive and the short line at the opposite outer edge is negative.



Chlor-alkali Process for producing $Cl_{2(g)}$, $H_{2(g)}$ and $NaOH_{(aq)}$



The $NaOH$ must stay separate from the Cl_2 to prevent disproportionation to ClO^- and Cl^-

H_2 must remain separate from Cl_2 (mixture can be explosive).

Anode made from treated Ti metal. Cathode is an asbestos/polymer mixture deposited on steel wire mesh.

Electrolysis reactions can be predicted by analyzing possible oxidation reduction reactions and choosing the one that can be accomplished with the lowest voltage.

Factors can affect the voltages required for electrolysis and the species oxidized and reduced such as:

Nonstandard solutions

Interactions at the electrodes (particularly with gases) that require a greater voltage than necessary for electrolysis (such as with oxygen). This is known as **overvoltage**.

Electrodes that take part in electrolysis are known as **active**. Those that do not (such as Pt) are known as **passive**.

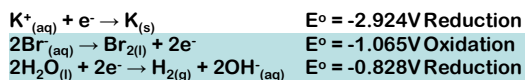
Questions:

Predict the electrolysis reaction when $\text{KBr}_{(aq)}$ is electrolyzed using platinum electrodes.

Predict the electrolysis reaction when $\text{AgNO}_{3(aq)}$ is electrolyzed using a silver anode and a copper cathode. What is the approximate external voltage required for the electrolysis?

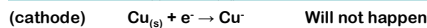
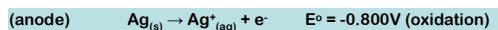
Answer:

Predict the electrolysis reaction when $\text{KBr}_{(aq)}$ is electrolyzed using platinum electrodes.



Answer:

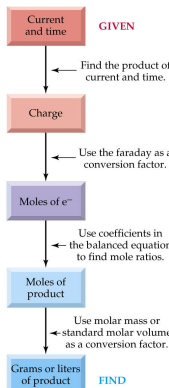
Predict the electrolysis reaction when $\text{AgNO}_{3(aq)}$ is electrolyzed using a silver anode and a copper cathode. What is the approximate external voltage required for the electrolysis?



$\text{NO}_3^-_{(aq)}$ will not be reduced w/o the presence of H^+ . It will not be oxidized as N is in its highest oxidation state, +5.

The applied voltage must overcome the natural tendency for the reaction $\text{Cu}_{(s)} + 2\text{Ag}^+_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$ which has an $E^\circ_{\text{cell}} = +0.800 + (-0.340) = .460\text{V}$, therefore **the voltage must be > .460V**

Current, Voltage and Electrochemistry



Faraday Constant (F) = 96,480 C/mol e⁻

Gives the amount of charge (in coulombs that exist in 1 mole of electrons passing through a circuit.

Another Useful Equation:

Ohm's Law: $V = I \times R$

(Also written as $E = I \times R$)

Where V (or E) = voltage (electrical potential)

I is current (in amperes (coulomb/sec))

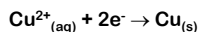
And R is the resistance (in ohms)

$$1\text{volt} = 1\text{joule/coulomb}$$

Example problem:

How many grams of copper are deposited on the cathode of an electrolytic cell if an electric current of 2.00A is run through a solution of CuSO_4 for a period of 20min?

Answer:



$$2.00\text{A} = 2.00\text{C/s}$$

$$20\text{min} (60\text{s/min}) = 1200\text{s}$$

$$\text{Coulombs of e}^- = (2.00\text{C/s})(1200\text{s}) = 2400\text{C}$$

$$\text{mol e}^- = (2400\text{C})(1\text{mol}/96,480\text{C}) = .025\text{mol}$$

$$(.025\text{mol e}^-)(1\text{mol Cu}/2\text{mol e}^-) = .0125\text{mol Cu}$$

$$\text{g Cu} = (.0125\text{mol Cu})(63.55\text{g/mol}) = .79\text{g}$$

Example problem:

How many hours would it take to produce 75.0g of metallic chromium by the electrolytic reduction of Cr^{3+} with a current of 2.25A?

Answer:

$$75.0\text{g Cr}/(52.0\text{g/mol}) = 1.44\text{mol Cr}$$

$$\text{mol e}^- = (1.44\text{mol Cr})(3\text{mol e}^-/1\text{mol Cr}) = 4.32\text{mol e}^-$$

$$\text{Coulombs} = (4.32\text{mol e}^-)(96,480\text{C/mol}) = 416,793.6\text{C} (4.17 \times 10^5\text{C})$$

$$\text{Seconds} = (4.17 \times 10^5\text{C})/(2.25\text{C/s}) = 1.85 \times 10^5\text{s}$$

$$\text{Hours} = (1.85 \times 10^5\text{s})(1\text{hr}/3600\text{s}) = 51.5 \text{ hours}$$