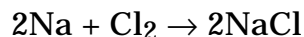


Chapter 18: Electrochemistry

Oxidation States

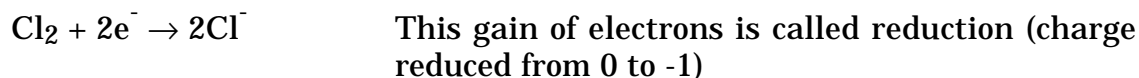
An oxidation-reduction reaction, or redox reaction, is one in which electrons are transferred.



Each sodium atom is losing one electron to form Na^+



Each chlorine atom is gaining 1 electron to form Cl^-



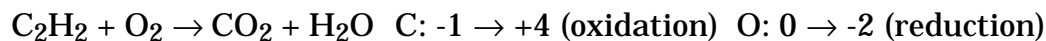
These equations are called half-reactions

In a redox reaction the number of electrons lost must equal the number of electrons gained.

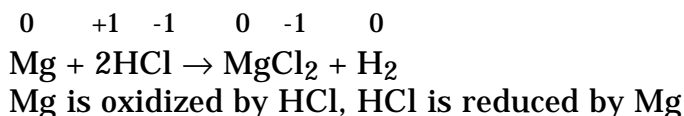
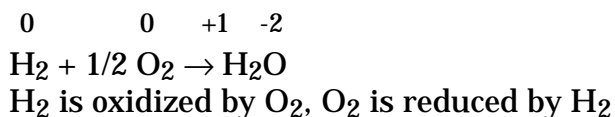
For ionic compounds, it is obvious that electrons are lost or gained. For covalent compounds, it is necessary to devise rules for counting electrons to determine if electrons are lost or gained, pg. 721. From a Lewis structure, oxidation numbers can be determined by assuming all shared electrons are on the more electronegative atom. (do H_2CO_3)

Rules for determining oxidation states

1. Oxidation states for atoms in uncombined elements is 0.
2. The oxidation state of a monatomic ion is equal to the charge of the ion.
3. In compounds, F is always -1. Other halogens are -1 unless combined with a more electronegative element.
4. In compounds, H is +1 except for metal hydrides where it is -1.
5. In compounds, oxygen is always -2 except for peroxides (O_2^{-2}) and with F
6. The sum of the oxidation states must equal zero in a neutral compound, or the charge of the ion for polyatomic ions.

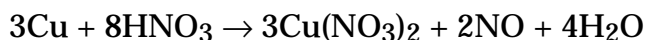
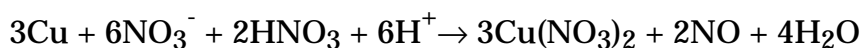
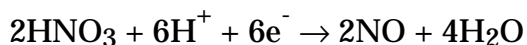
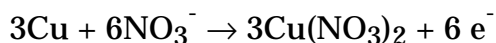
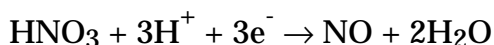
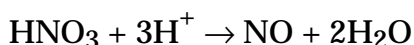
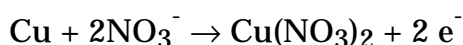
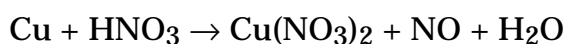


do KMnO_4 , FeSO_4 , CH_2O

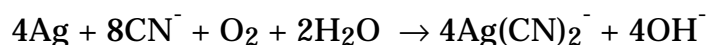
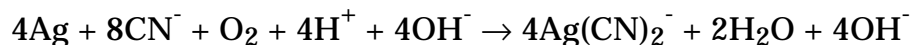
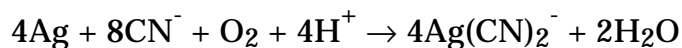
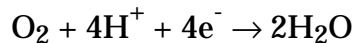
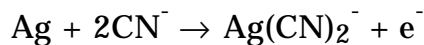
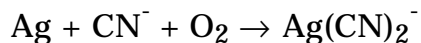
Balancing Oxidation-Reduction Equations

Ion-electron method:

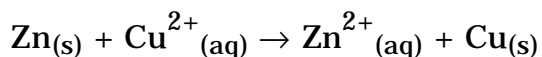
- assign oxidation states and determine what is being oxidized and what is being reduced
- write 2 skeleton half reactions
- Balance each half-reaction separately
 - balance each element except H and O
 - balance O by adding H₂O as needed
 - balance H by adding H⁺
 - add electrons to make charge balance
- multiply one or both half reactions by a small integer so the number of electrons lost is equal to the number of electrons gained.
- add the two half reactions, cancelling out the electrons and any ions or molecules which appear on both sides of the equation.



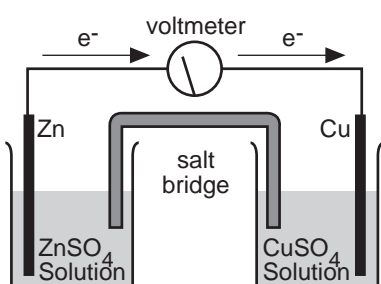
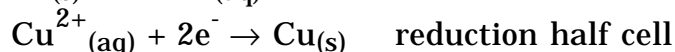
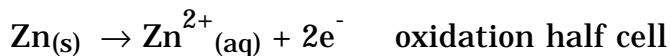
In basic solutions, balance as above and add OH^- to convert H^+ to H_2O



Voltaic Cells



Zn is oxidized, Cu^{2+} is reduced



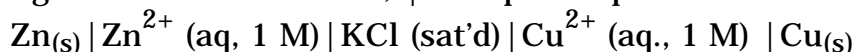
anode: electrode at which oxidation occurs

cathode: electrode at which reduction occurs

The two half reactions must be physically separated into **half cells**, otherwise Cu^{2+} will react directly with the Zn electrode. A salt bridge is a tube containing a gel of an inert salt such as KCl or NH_4NO_3 . Ions are able to move through the bridge and complete the circuit through the cell.

The voltage difference between the electrodes is called the **electromotive force** or **emf** (E), measured in volts.

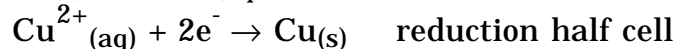
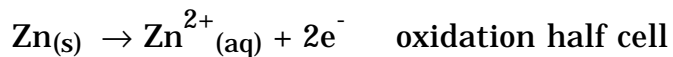
Cell diagram: anode to cathode, | to separate phases



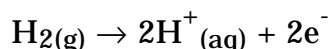
Electrodes may be active or inert (Pt, Au, C). Gas phase reactions and reactions such as $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + \text{e}^-$ may occur at an inert electrode.

Voltages of Voltaic Cells

Standard Electrode Potentials

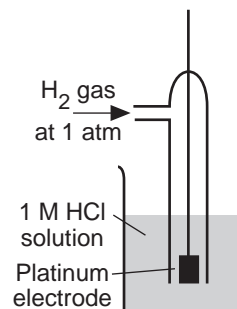


We can treat each half cell as if it has its own electrical potential, and so the cell EMF is equal to the sum of the half-cell EMFs. However, EMF has to be measured relative to a reference. We define the Standard Hydrogen Electrode (SHE)



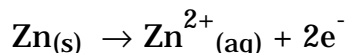
the potential for the SHE is defined to be exactly zero, or

$$E^{\circ}_{\text{H}_2/\text{H}^+} = 0 \text{ V}$$

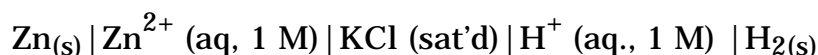


Standard reduction potential: reduction potential of a half cell when all solutes are at 1 M and all gases are at 1 ATM

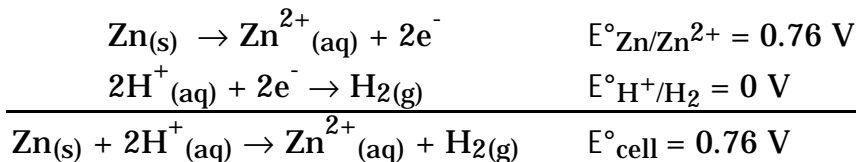
Standard reduction potentials are measured relative to the SHE and are listed in table 19.1 on pg. 785. Relative to SHE, the potential for the reaction



is +0.76, because the EMF of the cell



is 0.76 volts.



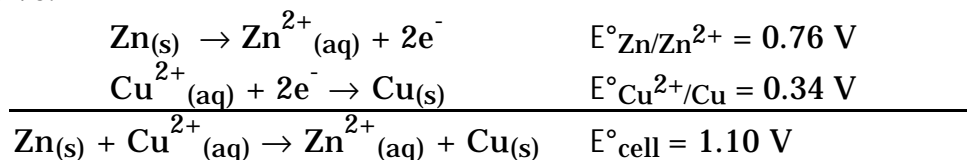
The standard cell potential is the sum of the standard oxidation potential and the standard reduction potential.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}$$

$$E^{\circ}_{\text{ox}} = -E^{\circ}_{\text{red}}$$

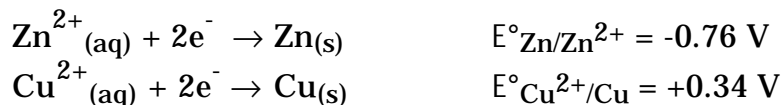
By convention, only standard reduction potentials are listed.

Under standard conditions, a reaction is spontaneous in the forward direction if the cell emf is positive, and spontaneous in the reverse direction if the cell emf is negative.



For Standard Reduction Potentials

- E° applies only to reaction as read in the forward (reduction) direction
- For oxidation potentials, $E^{\circ}_{\text{ox}} = -E^{\circ}_{\text{red}}$
- The more positive the SRP, the greater the tendency for the substance to be reduced, i.e., greater strength as an oxidizing agent. F_2 is the strongest oxidizing agent and Li is the weakest oxidizing agent.
- Oxidative and reductive strengths are relative. Strong oxidizing agents are weak reducing agents, and vice versa. Any given substance will act as an oxidizing agent when reacted with a substance above it in the SRP table, and will act as a reducing agent when reacted with a substance below it in the SRP table.
- Diagonal Rule: any species on the left side of a given half-cell reaction will react with a species on the right side of a half-cell located above it on the SRP table.



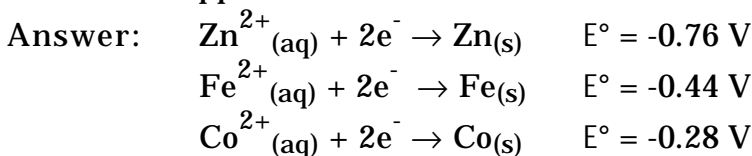
Zn reacts with Cu^{2+} but Cu does not react with Zn^{2+}

Conversely, any species on the right side of a given half-cell reaction will react with a species on the left side of a half-cell located below it on the SRP table.

Arrange in order of increasing oxidative strength: O_3 , Cl_2 , MnO_4^{-} , $\text{Cr}_2\text{O}_7^{2-}$

Answer: $\text{Cr}_2\text{O}_7^{2-}$, Cl_2 , MnO_4^{-} , O_3

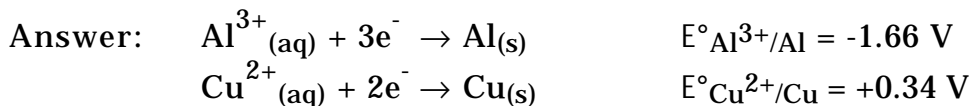
What will happen if Fe is added to a solution of 1 M $\text{Zn}(\text{NO}_3)_2$ and 1 M $\text{Co}(\text{NO}_3)_2$



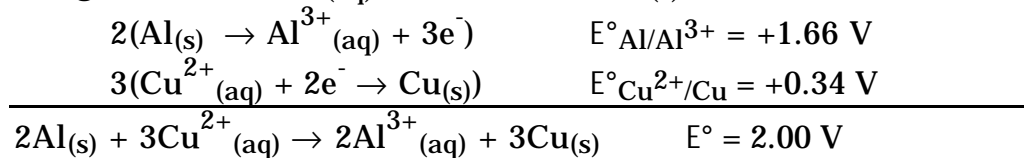
By the diagonal rule, Fe(s) will react with $\text{Co}^{2+}(\text{aq})$ but not with $\text{Zn}^{2+}(\text{aq})$

The reaction is $\text{Fe(s)} + \text{Co}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Co(s)}$

A galvanic cell is made up of an Al electrode in a 1 M solution of $\text{Al}(\text{NO}_3)_3$ and a Cu electrode in a 1 M solution of $\text{Cu}(\text{NO}_3)_2$. What is the cell emf, which electrode is the anode, which electrode is the cathode, what is the oxidizing agent, what is the reducing agent?



By the diagonal rule, $\text{Cu}^{2+}(\text{aq})$ will react with $\text{Al}(\text{s})$



Al is the anode, Cu is the cathode, Cu^{2+} is the oxidizing agent, Al is the reducing agent.

Cell Potentials, G, and K

Gibbs Free Energy $G = H - TS$

$$G = H - TS = w_{\text{max}}$$

at standard conditions, $G^\circ = H^\circ - TS^\circ$

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

at equilibrium, $G = 0$ and $Q = K$ so

$$G^\circ = -RT \ln K$$

In a galvanic cell, electrical energy = volts x coulombs = joules

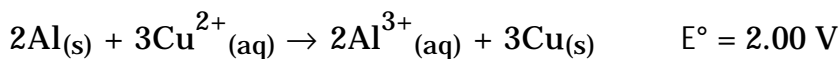
Total charge (coulombs) = nF where F , the Faraday, is 1 mole of electrons = 96,500 coulombs.

$$1 F = 96,500 \text{ coulombs/mol}$$

$$1 F = 96,500 \text{ J/V mol}$$

$$w_{\text{max}} = -nFE_{\text{cell}}$$

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



$$G = -nFE_{\text{cell}} = (-6)(96,500 \text{ J/V})(+2.00 \text{ V}) = 1,160 \text{ kJ}$$

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

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

at 298K,

$$E^\circ_{\text{cell}} = \frac{.0591}{n} \log K$$

Dependence of Voltage on Concentration: the Nernst Equation

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

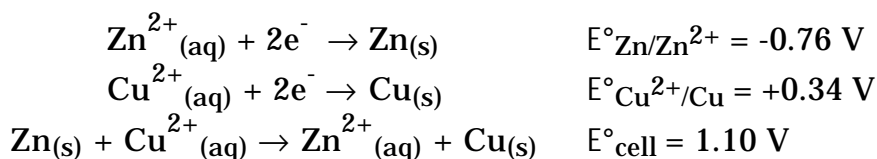
$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q$$

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

at 298 K

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{.0591}{n} \log Q \quad \text{this is the Nernst equation}$$

What is the cell potential for a cell made up of Zn, 0.500 M Zn(NO₃)₂, Cu, and 1.500 M Cu(NO₃)₂?



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{.0591}{n} \log Q = 1.10 - \frac{.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.10 - .0295 \log \frac{0.500}{1.500} = 1.11 \text{ V}$$

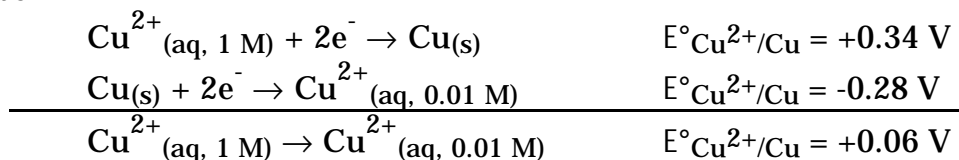
As LeChatelier's principle predicts, increasing [reactant] and decreasing [product] drives reaction harder to the right.

Concentration Cells

For a half-cell with [Cu²⁺] = 0.0100 M, $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{.0591}{n} \log Q$

$$= 0.34 - \frac{.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.34 - .0295 \log \frac{1}{0.0100} = 0.28 \text{ V}$$

For a cell made up of one 1 M half cell and one 0.0100 M half cell, the cell emf would be



The system would tend to move toward an intermediate concentration. As the concentrations change, the half-cell potentials would converge on a common value and the cell potential would drop to zero.

Applications of Voltaic Cells in Chemistry

Ion-selective electrodes

Reference electrode: Calomel $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-$ (sat'd KCl)

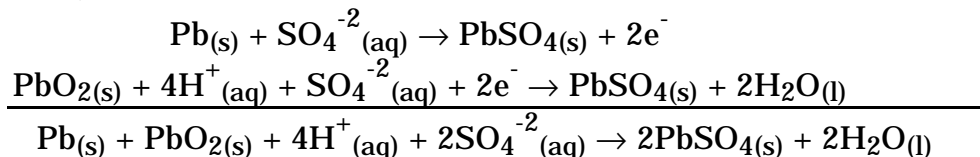
Determination of K

$$RT \ln K = nFE \quad \text{measure } E, \text{ determine } K$$

Commercial Voltaic Cells

Battery: a galvanic cell (or series of cells) which are designed to be self-contained.

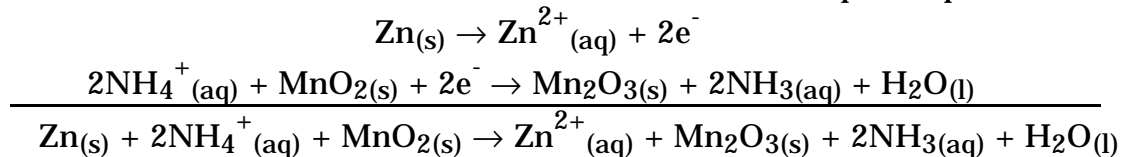
Lead Storage Battery: Six cells in series. Each cell has a lead anode, 38% H_2SO_4 (sulfuric acid), and a PbO_2 /metal cathode.



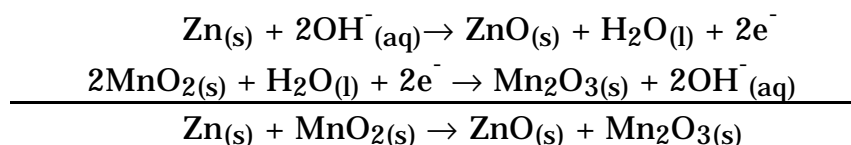
The battery is rechargeable because both reactions are reversible.

The battery can be checked by testing the density of the electrolyte; H_2SO_4 is replaced by water as the battery discharges.

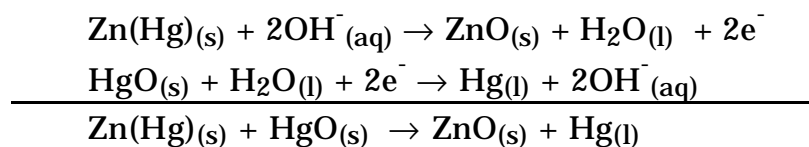
Dry Cell: Zn can is anode, in contact with moist paste of MnO_2 , NH_4Cl , and ZnCl_2 in starch. A carbon rod cathode is in contact with the metal cap on top of the cell.



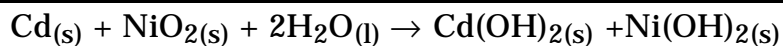
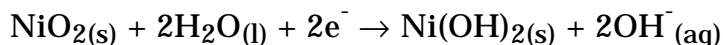
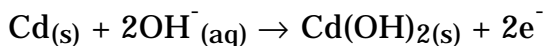
Alkaline Battery: NH_4Cl is replaced with KOH or NaOH . Zn anode corrodes less under alkaline conditions and cell voltage is more constant because net reaction contains all condensed-phase species.



Mercury Battery: Zn/Hg amalgam anode in contact with a paste containing KOH , $\text{Zn}(\text{OH})_2$, and HgO , in contact with a steel cathode.

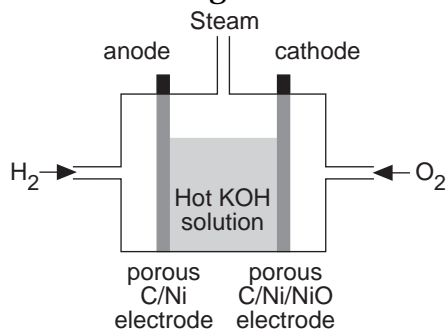


Since all reactants and products are in condensed phases, the cell voltage remains constant until the reactants are spent.

Ni-Cad Battery:

The battery is rechargeable because both reactions are reversible.

Fuel Cell: A galvanic cell in which the reactants are continuously supplied.



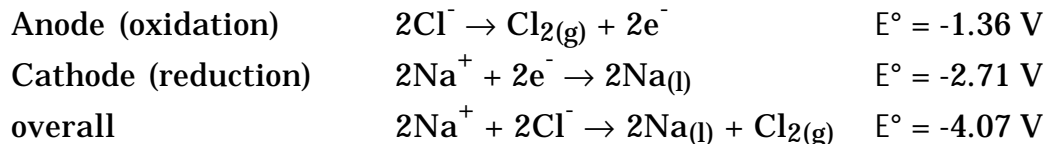
Ni and NiO are catalysts. $E^{\circ} = 1.23 \text{ V}$

steam generated by cell is condensed to water for use as drinking water

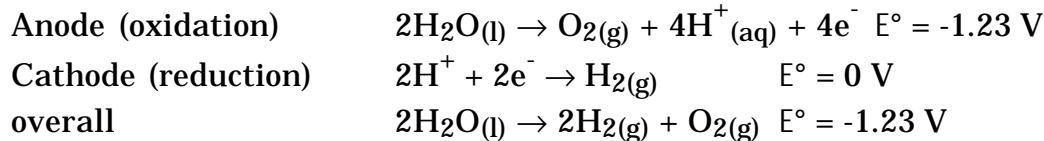
Electrolysis

Electrolysis: process in which electrical energy is used to make a non-spontaneous chemical reaction occur.

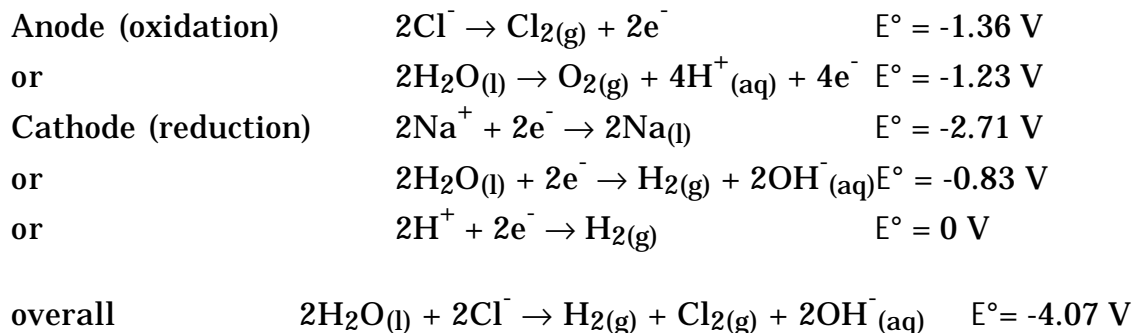
Electrolysis of molten NaCl



Electrolysis of water (in acid solution)



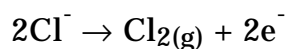
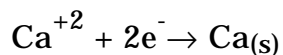
Electrolysis of aqueous NaCl



Overtoltage: difference between calculated potential and actual potential needed to cause the reaction.

Quantitative Aspects of Electrolysis

A current of 0.452 A is passed for 1.50 hrs through a cell containing molten CaCl_2 . What masses of product is formed?



$$0.452 \text{ A} \times 1.50 \text{ hr} \times 3600 \text{ s/hr} = 2,440 \text{ coul}$$

$$2,440 \text{ coul} \times \frac{1 \text{ F}}{96500 \text{ coul}} = 0.0253 \text{ F} \times \frac{1 \text{ mol Ca or Cl}_2}{2\text{F}} = 0.0126 \text{ mol}$$

$$0.0126 \text{ mol Ca} \times 40.08 \text{ g/mol} = 0.507 \text{ g Ca}$$

$$0.0126 \text{ mol Cl}_2 \times 70.90 \text{ g/mol} = 0.897 \text{ g Cl}_2$$

Energy consumed $E = Q \times V$ What is the energy used above if the cell voltage was 5.0 V?

$$E = Q \times V = (2440 \text{ coul})(5.0 \text{ V}) = 12,200 \text{ J} \quad (1 \text{ V} = 1 \text{ J/coul})$$

$$1 \text{ kw-hr} = 3.60 \times 10^6 \text{ J} \quad \text{so } 12,200 \text{ J} \times 1 \text{ kw-hr}/3.60 \times 10^6 \text{ J} = 0.0034 \text{ kw-hr}$$

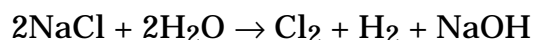
Electrolysis in Industry

Aluminum - the Hall process. Al_2O_3 is mixed with Na_3AlF_6 (cryolite) to lower the mp to 980° . Carbon electrodes are used at 4.2 V to form Al at the cathode and O_2 at the anode, which reacts with the electrodes to form CO_2 .

Sodium - NaCl is mixed with CaCl_2 to lower the mp and electrolyzed to form Na metal and Cl_2 gas

Fluorine - mixture of HF and KF is electrolyzed to form H_2 and F_2

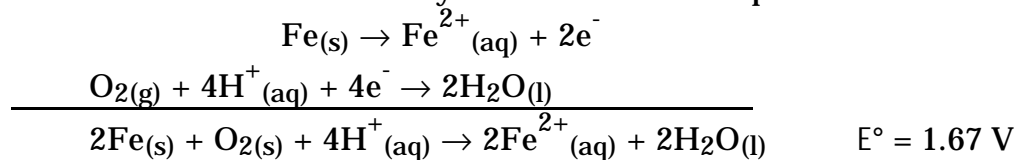
Chlorine - mostly produced by electrolysis of brine



Electrorefining of Cu - Cu is dissolved at the anode and pure Cu is deposited at the cathode

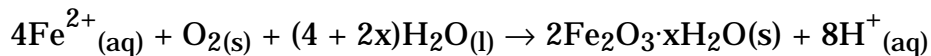
Corrosion

Corrosion: deterioration of metal by an electrochemical process.



H^{+} is supplied by reaction of CO_2 with water to form H_2CO_3

Fe^{2+} is further oxidized



iron (III) oxide is rust.

Some metals, such as Al, oxidize to form a hard, non-porous coating which is then resistant to additional oxidation.

Cathodic Protection: connecting the metal to be protected to a more electropositive metal (such as Fe to Zn or Mg), which makes the protected metal the cathode in the electrochemical cell.