Name ________________________ **AP CHEM** **__/__/__**

Chapter 17 Outline – Electrochemistry

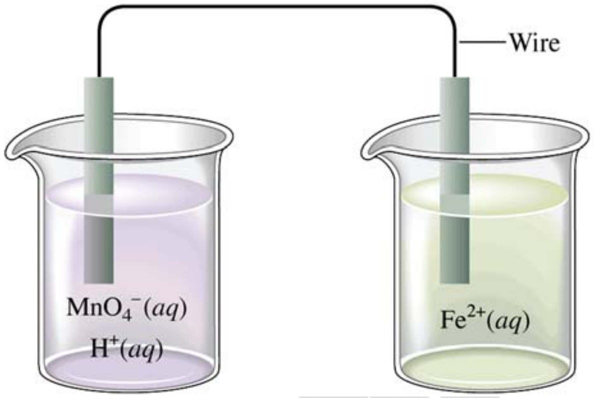
Electrochemistry is the study of the interchange of chemical and electrical energy. It is concerned with two processes that involve oxidation-reduction reactions: the generation of an electric current from a spontaneous chemical reaction and the opposite process, the use of a current to produce chemical change.

Galvanic Cells

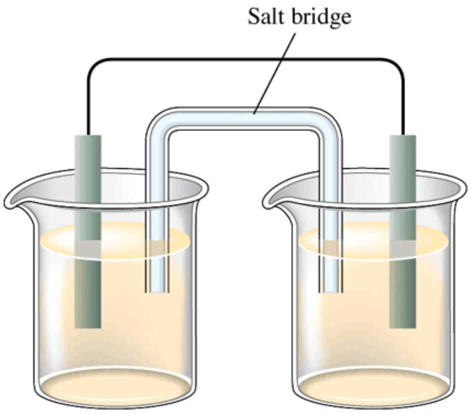
- An oxidation-reduction (redox) reaction involves a transfer of electrons from the reducing agent to the oxidizing agent.
- Oxidation involves a loss of electrons (and an increase in oxidation number). OIL
- Reduction involves the gain of electrons (and a decrease in oxidation number). RIG

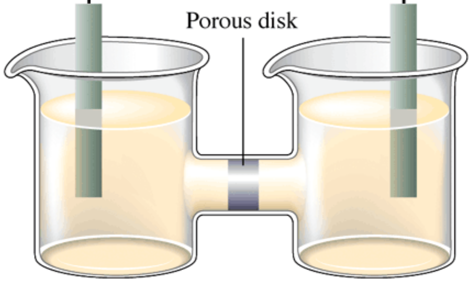
  Just for fun: Balance the following redox equation: $MnO_4^-(aq) + Fe^{2+}(aq) \xrightarrow{Acidic} Fe^{3+}(aq) + Mn^{2+}(aq)$
- Oh yeah, you forgot the steps:

  For an Acidic Solution:
    - Split into half reactions. (Indicate which is reduction and which is oxidation.)
    - Balance all elements except Hydrogen and Oxygen.
    - Balance Oxygen using H_2O.
    - Balance Hydrogen using H^+.
    - Balance the charge using electrons (e^-).
    - Equalize the electron transfer in the two half reactions.
    - Add the half reactions
- **For a Basic Solution:**
    - Add OH- ions to both sides of the balanced equation to eliminate the H^+ ions.
    - Eliminate excess water molecules.
    - Memorize these steps.
- OK, now try to balance it: $MnO_4^-(aq) + Fe^{2+}(aq) \xrightarrow{Basic} Fe^{3+}(aq) + Mn^{2+}(aq)$



- Consider the system illustrated to the right. When the wires are connected, the current flows for an instant and then ceases. The current stops flowing because of charge build up in the two compartments. Creating a charge separation requires a large amount of energy.
- To solve this problem, the solutions must be connected so that ions can flow to keep the net charge in each compartment zero. This connection might involve a **salt bridge** (a U-tube filled with an electrolyte) or a porous disc in a tube connecting the two solutions. Either of these devices (shown below) allows ions to flow without extensive mixing of the solutions.





- Electrons flow through the wire from reducing agent to oxidizing agent and ions flow from one compartment to the other to keep the net charge zero.
- A **galvanic cell** is a device in which chemical energy is changed to electrical energy. (The opposite process is called electrolysis.)
- **Oxidation occurs at the anode. Reduction occurs at the cathode.**

Cell Potential

- A galvanic cell consists of an oxidation agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment.
- The pull, or driving force, on the electrons is called the **cell potential ($\mathscr{E}_{cell}$)**, or the **electromotive force** (emf) of the cell.
- The unit of electrical potential is the **volt** (abbreviated V) which is defined as **1 joule of work per coulomb** of charge transferred.
- Cell potential is measured using a **voltmete**r. This is accomplished by inserting a variable-voltage device (powered by an external source) in opposition to the cell potential. The voltage on this instrument (called a **potentiometer**) is adjusted until no current flows in the circuit. The cell potential is equal in magnitude and opposite in sign to the voltage setting of the potentiometer.

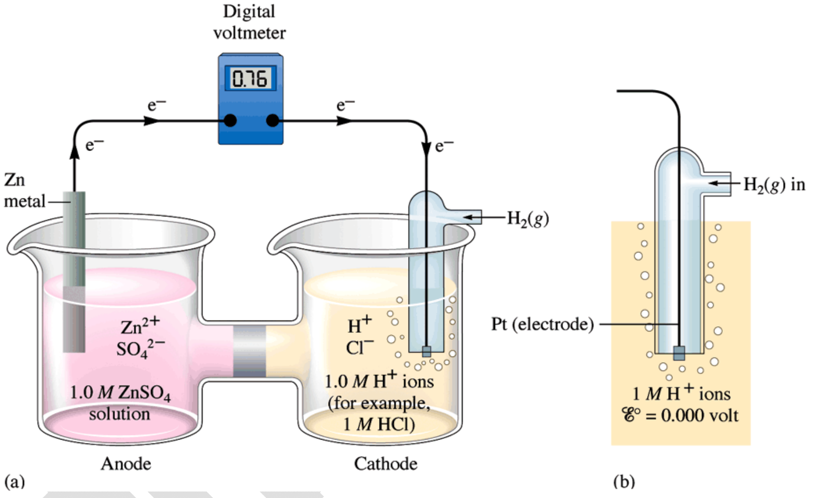
Standard Reduction Potentials

- The reaction in a galvanic cell is always an oxidation-reduction reaction that can be broken down into two half reactions.
- Consider the following redox reaction: $\mathbf{2H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)}$ with a measured cell potential of 0.76 V and the corresponding diagram below:

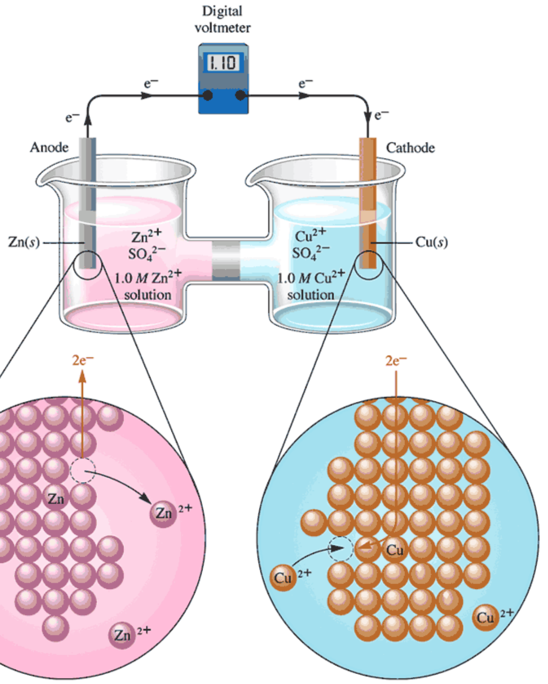
- The anode reaction is the oxidation half-reaction: $Zn \rightarrow Zn^{2+} + 2e^-$
- The zinc metal, in producing Zn^{2+} ions that go into the solution, is giving up electrons which flow through the wire.
- The cathode reaction of this cell is the reduction half reaction: $2H^+ + 2e^- \rightarrow H_2$
- The cathode consists of a platinum electrode (used because it is a chemically inert conductor) in contact with 1 M H^+ ions and bathed by hydrogen gas at 1 atm. Such an electrode, called the standard hydrogen electrode is shown below.
- **The reaction $2H^+ + 2e^- \rightarrow H_2$ is assigned a potential of exactly zero volts**. Then the reaction: $Zn \rightarrow Zn^{2+} + 2e^-$ would have a potential of 0.76 V because: $\mathscr{E}^\circ_{cell} = \mathscr{E}^\circ_{H^+ \rightarrow H_2} + \mathscr{E}^\circ_{Zn \rightarrow Zn^{2+}}$

$$0.76\ V = 0\ V + 0.76\ V$$

- By setting the standard potential for the half reaction: $2H^+ + 2e^- \rightarrow H_2$ equal to zero, we can assign values to all other half reactions.



- The ℰ° values corresponding to half reactions with all solutes at 1 M and all gases at 1 atm are called standard reduction potentials.
- The accepted convention is to give the potentials of half reactions as reduction processes. Combining two half reactions to obtain a balanced oxidation-reduction reaction often requires two manipulations:
  - One of the reduction half reactions must be reversed which means that the sign of the potential for the reversed half reaction must also be reversed.
  - Since the number of electrons lost must equal the number gained, the half-reactions must be multiplied by integers as necessary to achieve the balanced equation. However, the ℰ° value is not changed when a half reaction is multiplied by an integer. The standard reduction potential is an intensive property and is independent of the amount of times the reaction occurs.



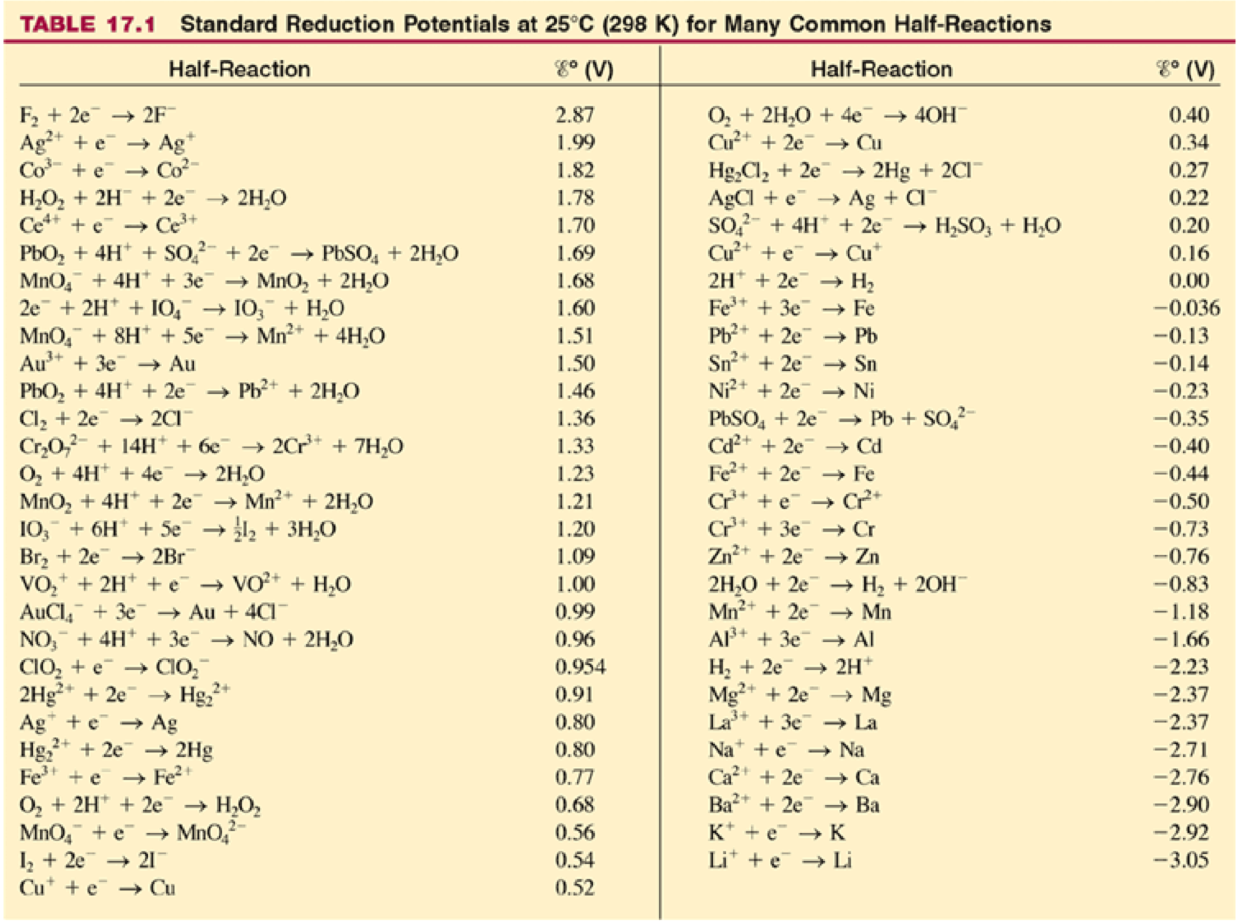


TABLE 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathscr{E}°$ (V)	Half-Reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3-} + e^- \rightarrow Co^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^+$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

- Consider a galvanic cell based on the following reaction: $Fe^{3+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Fe^{2+}(aq)$

  The half reactions:

  $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\mathscr{E}° = 0.77$ V (1)

  $Cu^{2+} + 2e^- \rightarrow Cu$ $\mathscr{E}° = 0.34$ V (2)

  To balance the cell reaction and calculate the standard cell potential, reaction (2) must be reversed.

  $Cu \rightarrow Cu^{2+} + 2e^-$ $\mathscr{E}° = -0.34$ V (2)

  Equation (1) needs to be multiplied by 2 to balance the number of electrons transferred.

  $2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$ $\mathscr{E}° = 0.77$ V (1)

  The balanced equation can be obtained by summing the appropriately modified half reactions.

  $2Fe^{3+} + \cancel{2e^-} \rightarrow 2Fe^{2+}$ $\mathscr{E}° = 0.77$ V (1)

  $\underline{Cu \rightarrow Cu^{2+} + \cancel{2e^-} \quad \mathscr{E}° = -0.34\ V \quad (2)}$

  $2Fe^{3+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$ $\mathscr{E}° = 0.43$ V

- You try: Calculate the $\mathscr{E}°$ and give the balanced cell reaction for a galvanic cell based on the reaction: $Al^{3+}(aq) + Mg(s) \rightarrow Al(s) + Mg^{2+}(aq)$

Line Notation

- Line notation is used to describe electrochemical cells.
- In this notation the anode components are listed on the left and the cathode components are listed on the right, separated by double vertical lines (indicating the salt bridge or porous disc).
- For example, the line notation for the example shown above is: $Cu(s)|Cu^{2+}(aq)||Fe^{3+}(aq),Fe^{2+}(aq)|Pt(s)$

- Note that in the answer above Pt is used to represent the cathode. Platinum is needed because Fe^{3+} and Fe^{2+} are both ions. Only solids can serve as cathodes or anodes. If neither ion is a solid an inert conductor, like platinum, is used.
- The general format is: anode|ions at anode||ions at cathode|cathode. or A|AI||CI|C
  You try: Write the line notation for the reaction you worked out above:
  $Al^{3+}(aq) + Mg(s) \rightarrow Al(s) + Mg^{2+}(aq)$

- A cell will always run spontaneously in the direction that produces a positive cell potential. The half reaction that has a larger E° value will always be the reduction reaction. The reaction with the smaller E° will be reversed (the sign of the E° is also switched) and will be the oxidation reaction.
- A complete description of a galvanic cell usually includes four items:
  - The cell potential (always positive for a galvanic cell) and the balanced cell reaction.
  - The direction of the electron flow. (Electrons travel from the anode to the cathode – indicate the ion that loses electrons and the ion that gains electrons).
  - The designation of the cathode and the anode.
  - The nature of each electrode and the ions present in each compartment. A chemically inert conductor is needed if none of the substances participating in the half reaction is a conducting solid. Line notation should be given.

- Here is a little summary I came up with so that I could get it straight.
  Anode – electrons leave – oxidation occurs to the substance with the smaller E°
  Cathode – electrons enter – reduction occurs to the substance with the bigger E°.

- You try: Describe completely (as outlined above) the galvanic cell based on the following half reactions under standard conditions:
  $Ag^+ + e^- \rightarrow Ag$ $E° = 0.80$ V
  $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E° = 0.77$ V

- Try another: Describe completely (as outlined above) the galvanic cell based on the following half reactions under standard conditions:
  $Mn^{2+} + 2e^- \rightarrow Mn$ $E° = -1.18$ V
  $Fe^{3+} + 3e^- \rightarrow Fe$ $E° = -0.036$ V

Cell Potential, Electric Work, and Free Energy

- The work that can be accomplished when electrons are transferred through a wire depends on the push (the thermodynamic driving force) behind the electrons.
- The driving force (the emf) is defined in terms of a potential difference (in volts) between two points in a circuit.

- Work is viewed from the point of view of the system. Thus, work flowing out of the system is indicated by a minus sign. When a cell produces a current, the cell potential is positive, and the current can be used to do work – to run a motor, for instance. Thus the cell potential, E, and work, w, have opposite signs.
  $-w = qE$ where q is the charge (more on q in a second)
- There is a problem with this equation because to obtain electrical work, current must flow. When current flows, some energy is inevitably wasted through frictional heating, and the maximum work is not obtained. In any real, spontaneous process some energy is always wasted – the actual work realized is always less than the calculated maximum. This is a consequence of the fact that for any spontaneous process to occur the entropy of the universe must increase.
- The charge on 1 mole of electrons is a constant called the faraday (abbreviated F), which has the value 96,485 coulombs of charge per mole of electrons. Thus q equals the number of moles of electrons times the charge per mole of electrons: $q = nF$
- By deriving the relationship between work and free energy, the following equation can be derived:
  $\boldsymbol{\Delta G^\circ = -nF\mathcal{E}^\circ}$
- The equation states that the maximum cell potential is directly related to the free energy difference between the reactants and the products in the cell. This relationship is important because it provides an experimental means to obtain ΔG° for a reaction. It also confirms that a galvanic cell will run in the direction that gives a positive value for $\mathcal{E}_{cell}$ (and thus ΔG° is negative), which is a condition for spontaneity.

- Example: Calculating ΔG° for a cell reaction. Using the data in the standard reduction potential table, calculate ΔG° for the reaction below. Is the reaction spontaneous?

  $$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$$

  Solution:

  The half reactions are:

  $Cu^{2+} + 2e^- \rightarrow Cu$ $\mathcal{E}^\circ = 0.34$ V

  $\underline{Fe \rightarrow Fe^{2+} + 2e^- \qquad \mathcal{E}^\circ = 0.44 \text{ V}}$

  $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$ $\mathcal{E}^\circ = 0.78$ V

  Note that 2 mole of electrons were transferred in the equation above.

  $\Delta G^\circ = -nF\mathcal{E}^\circ$

  $\Delta G^\circ = -(2 \text{ mol})(96{,}485 \text{ C/mol})(0.78 \text{ J/C})$

  $\Delta G^\circ = -1.5 \times 10^5$ J

  Since ΔG° is negative and $\mathcal{E}^\circ$ is positive, the reaction is spontaneous.

- You try: Chlorine dioxide (ClO_2) has been tested as a disinfectant for municipal water treatment. It is produced by the reaction:

  $$2NaClO_2(aq) + Cl_2(g) \rightarrow 2ClO_2(g) + 2NaCl(aq)$$

  Using the information below, calculate ΔG° and $\mathcal{E}^\circ$

  $ClO_2 + e^- \rightarrow ClO_2^-$ $\mathcal{E}^\circ = 0.954$ V

  $Cl_2 + 2e^- \rightarrow 2Cl^-$ $\mathcal{E}^\circ = 1.36$ V

Dependence of Cell Potential on Concentration

- Use Le Chatelier's principle. A larger concentration of the reactants shifts the reaction to the right. A larger concentration of product shifts the reaction to the left.

- A cell in which both compartments have the same components but at different concentrations is called a concentration cell. The difference in concentration is the only factor that produces a cell potential and the voltages are typically small.

The Nernst Equation

- The dependence of the cell potential on concentration results directly from the dependence on concentration.
- $\mathscr{E} = \mathscr{E}^\circ - \dfrac{RT}{nF}\ln(Q) = \mathscr{E}^\circ - \dfrac{0.0591}{n}\log(Q)$
- The potential calculated from the Nernst equation is the maximum potential before any current flow has occurred.
- The cell will spontaneously discharge until it reaches equilibrium, at which point: $Q = K$ and $\mathscr{E}^\circ = 0$.
- A dead battery is one in which the cell reaction has reached equilibrium, and there is no longer any chemical driving force to push electrons through the wire.
- At equilibrium, the components in the two cell compartments have the same free energy and $\Delta G=0$ for the cell reaction at the equilibrium concentration. The cell no longer has the ability to work.
- Example: Describe the cell based on the following half-reactions:

$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$ $\mathscr{E}^\circ = 1.00$ V
$Zn^{2+} + 2e^- \rightarrow Zn$ $\mathscr{E}^\circ = -0.76$ V
T= 25°C
$[VO_2^+] = 2.0$ M
$[H^+] = 0.50$ M
$[VO^{2+}] = 1.0 \times 10^{-2}$ M
$[Zn^{2+}] = 1.0 \times 10^{-1}$ M

Solution:

The first reaction is double to produce 2 e^-. The second reaction is flipped. Then the two reactions are added.

$$2VO_2^+ + 4H^+ + 2e^- \rightarrow 2VO^{2+} + 2H_2O \quad \mathscr{E}^\circ = 1.00\text{ V}$$
$$\underline{Zn \rightarrow Zn^{2+} + 2e^- \qquad\qquad \mathscr{E}^\circ = 0.76\text{ V}}$$
$$2VO_2^+ + 4H^+ + Zn \rightarrow 2VO^{2+} + 2H_2O + Zn^{2+} \qquad \mathscr{E}^\circ = 1.76\text{ V}$$

$$\mathscr{E} = \mathscr{E}^\circ - \frac{0.0591}{n}\log(Q)$$

$$\mathscr{E} = \mathscr{E}^\circ - \frac{0.0591}{2}\log([Zn^{2+}][VO^{2+}]^2 / [VO_2^+]^2[H^+]^4)$$

$$\mathscr{E} = 1.76 + 0.13 = 1.89\text{ V}$$

- You try: Can permanganate ion oxidize Fe^{2+} to Fe^{3+} at 25ºC under the following conditions?

$[Mn^{2+}] = 1 \times 10^{-6}$ M, $[MnO_4^-] = 0.01$ M,$[Fe^{2+}] = 1 \times 10^{-3}$, $[Fe^{3+}] = 1 \times 10^{-6}$ M, pH = 4.0

Ion-Selective Electrodes

- Because cell potential is sensitive to concentrations of reactants and products involved in the cell reaction, measured potentials can be used to determine the concentration of an ion.

- A pH meter is an example of an ion selective electrode.
- The glass electrode contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane. The electrical potential of the glass electrode depends on the difference in $[H^+]$ between the reference solution and the solution into which the electrode is dipped.
- Electrodes that are sensitive to the concentration of a particular ion are called ion-selective electrodes. Glass electrodes can be made sensitive to such ions as Na^+, K^+ or NH_4^+ by changing the composition of the glass. Other ions can be detected if an appropriate crystal replaces the glass membrane.

Calculation of Equilibrium Constants for Redox Reactions

- For a cell at equilibrium: $\mathscr{E}_{cell} = 0$ and Q = K
- Applying these to the **Nernst equation**: $\mathbf{\log(K)} = \dfrac{nE^\circ}{0.0591}$ **at 25ºC.**
- Example: Calculate the equilibrium constant for the following reaction:

$$S_4O_6^{2-} + Cr^{2+} \rightarrow Cr^{3+} + S_2O_3^{2-}$$

The half reactions are:

$$S_4O_6^{2-} + 2e^- \rightarrow S_2O_3^{2-} \qquad \mathscr{E}^\circ = 0.17V$$
$$Cr^{3+} + e^- \rightarrow Cr^{2+} \qquad \mathscr{E}^\circ = -0.50\ V$$

The second reaction is flipped and doubled.

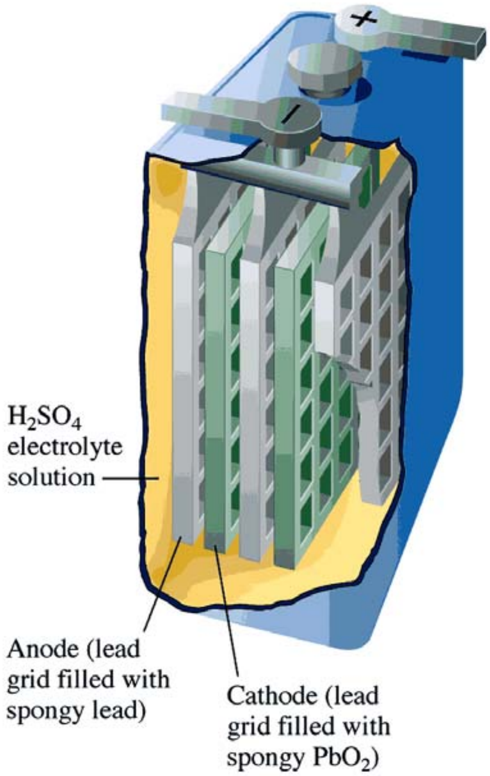
$$S_4O_6^{2-} + 2e^- \rightarrow S_2O_3^{2-} \qquad \mathscr{E}^\circ = 0.17V$$
$$\underline{2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^- \qquad \mathscr{E}^\circ = 0.50\ V}$$
$$S_4O_6^{2-} + 2Cr^{2+} \rightarrow 2Cr^{3+} + S_2O_3^{2-} \quad \mathscr{E}^\circ = 0.67\ V$$

$$\log(K) = \frac{2(0.67)}{0.0591}$$
$$K = 4 \times 10^{22}$$

A very large equilibrium constant is not unusual for a redox reaction.

- You try: Calculate ΔG and K at 25ºC for the reaction below:

$$Cr^{3+}(aq) + Cl_2(g) \rightleftharpoons Cr_2O_7^{2-}(aq) + Cl^-(aq)$$



Lead Storage Battery

- A battery is a galvanic cell, or more commonly, a group of galvanic cells connected in series, where the potentials of the individual cells add to give the total battery potential.
- The lead storage battery has been a major factor in making the automobile a practical means of transportation.
- In this battery, lead serves as the anode, and lead coated with lead dioxide serves as the cathode. Both electrodes dip into an electrolyte solution of sulfuric acid.

  Anode reaction: $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$

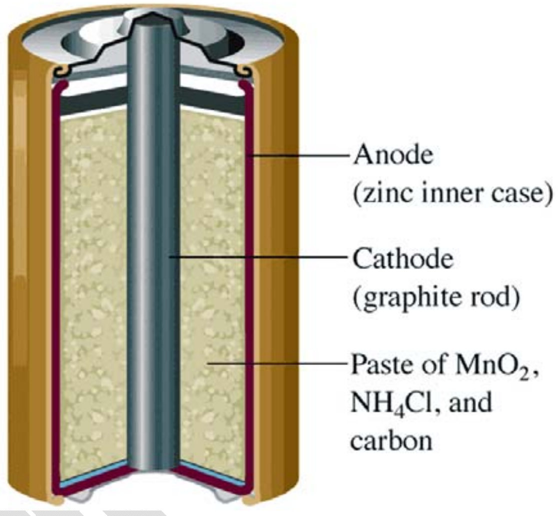
  Cathode Reaction: $PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

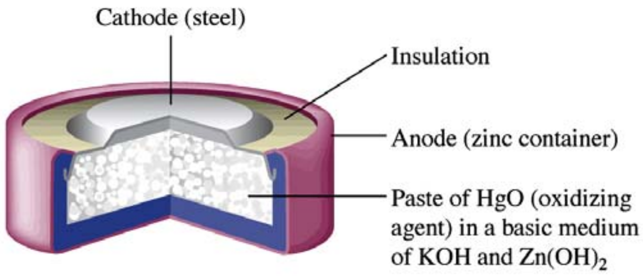
  Cell Reaction: $Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
- The typical automobile lead storage battery has six-cells connected in series. Each cell contains multiple electrodes in the form of grids and produces approximately 2V, to give a total battery potential of about 12V.
- Sulfuric acid is consumed as the battery discharges. This lowers the density of the electrolyte solution from its initial value of about 1.28 g/cm^3 in the fully charged battery. As a result, the condition of the battery can be monitored by measuring the density of the sulfuric acid solution.
- The battery is recharged by forcing current through it in the opposite direction to reverse the cell reaction. A car's battery is continuously charged by an alternator driven by the automobile engine.

- An automobile can be "jump-started" by connecting its battery to the battery in a running automobile. This process can be dangerous, however, because the resulting flow of current causes electrolysis of water in the dead battery, producing hydrogen and oxygen gases. Disconnecting the jumper cables after the disabled car starts causes an arc that can ignite the gaseous mixture. If this happens, the battery may explode, ejecting corrosive sulfuric acid. This problem can be avoided by connecting the ground jumper cable to a part of the engine remote from the battery. Any arc produced when this cable is disconnected will then be harmless.

Other Batteries

- The dry cell battery was invented more than 100 years ago by George Leclanché (1839-1882), a French chemist.
- In its acid version, the dry cell battery contains a zinc inner case that acts as the anode and a carbon rod in contact with the moist paste of solid MnO_2, solid NH_4Cl and carbon that acts as the cathode. In the alkaline version of the dry cell battery, the solid NH_4Cl is replaced with KOH or NaOH. The alkaline dry cell lasts longer mainly because the zinc anode corrodes less rapidly under basic conditions than under acidic conditions.
- Another type of battery, a silver cell, has a Zn anode and an Ag_2O cathode in a basic environment..
- A mercury cell, often used in calculators, has a Zn anode and an HgO cathode in a basic medium.
- In a nickel-cadmium battery the electrode reactions are:
  At Anode: $Cd + 2OH- \rightarrow Cd(OH)_2 + 2e^-$
  At Cathode: $NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$
- As in a lead storage battery, the products of a nickel-cadmium battery adhere to the electrodes. Therefore, a nickel-cadmium battery can be recharged an indefinite number of times.





Fuel Cells

- A fuel cell is a galvanic cell for which the reactants are continuously supplied.
- Cars powered by fuel cells are now being tested.

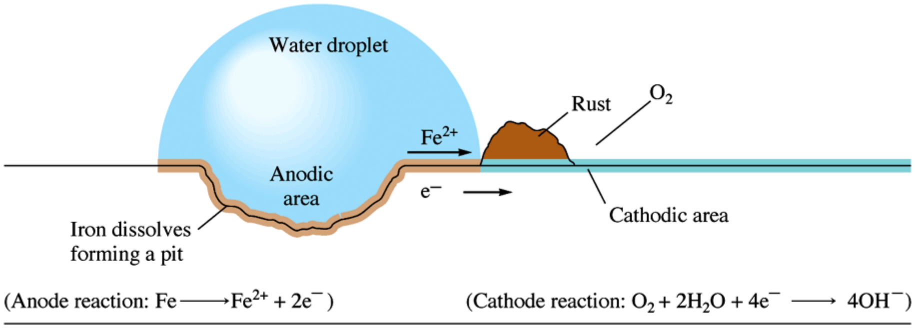
Corrosion

- Corrosion can be viewed as the process of returning metals to their natural state- the ores from which they were originally obtained. Corrosion involves the oxidation of the metal.
- Metals corrode because they oxidize easily. The oxidation of most metals by oxygen is spontaneous (although we cannot tell from the potential how fast it will occur…that's for kinetics).
- Some metals, such as copper, gold, silver, and platinum, are relatively difficult to oxidize. These are called noble metals.
- The problem of corrosion does not completely prevent the use of metals in air. Most metals develop a thin oxide coating, which tends to protect their internal atoms against further oxidation. The metal that best demonstrates this phenomenon is aluminum.
- According to the apparent thermodynamics of the reaction, an aluminum airplane could dissolve in a rainstorm. The fact that this very "active" metal(reduction potential of -1.66V) can be used as a structural material is due to the formation of a thin, adherent layer of aluminum oxide (Al_2O_3), more properly represented as $Al_2(OH)_6$, which greatly inhibits further corrosion. The potential of the "passive" oxide coated aluminum is -0.6 V, a value that causes it to behave much like a noble metal.

- Iron also forms a protective oxide coating. This coating tends to flake off and expose new metal surfaces to corrosion.

Corrosion of Iron

- The corrosion of iron is an electrochemical reaction as shown below.



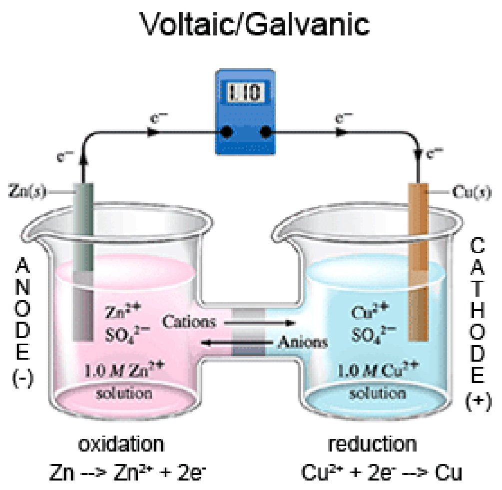
- Steel has a nonuniform surface because the chemical composition is not completely homogeneous. Also, physical strains leave stress points in the metal. These nonuniformities cause areas where the iron is more easily oxidized (anodic regions) than it is at others (cathodic regions). In the anodic regions each iron atom gives up two electrons to form the Fe^{2+} ion: $Fe \rightarrow Fe^{2+} + 2e^-$
- The electrons that are released flow through the steel, as they do through a wire of a galvanic cell, to a cathodic region, where they react with oxygen:
  $$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
- The Fe^{2+} ions formed in the anodic regions travel to the cathodic regions through the moisture on the surface of the steel, just as ions travel through a salt bridge in a galvanic cell. In the cathodic regions Fe^{2+} ions react with oxygen to form rust, which is hydrated iron(III) oxide of variable composition.
  $$4Fe^{2+} + O_2 + (4+ 2n)H_2O(l) \rightarrow 2Fe_2O_3 * nH_2O(s) + 8H^+(aq)$$
- The electrochemical nature of rusting of iron explains the importance of moisture in the corrosion process. Moisture must be present to act as a kind of salt bridge between anodic and cathodic regions. Steel does not rust in dry air. As a result, cars last longer in the arid Southwest than in the relatively humid Midwest.
- Salt accelerates rusting.

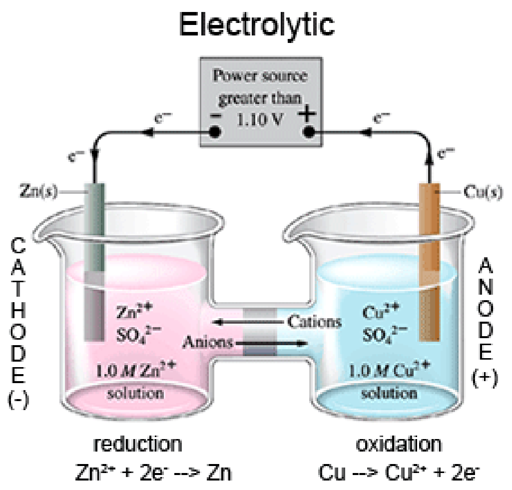
Prevention of Corrosion

- The primary means of protection is the application of a coating most commonly paint or metal plating to protect the metal from oxygen and moisture.
- Chromium and tin are often used to plate steel because they oxidize to form a durable, effective outer coating.
- Zinc is also used to coat steel in a process called galvanizing, forms a mixed oxide-carbonate coating. Since zinc is a more active metal than iron any oxidation that occurs dissolves zinc rather than iron.
- Alloying is also used to prevent corrosion. Stainless steel contains chromium and nickel, both of which form oxide coatings that change steel's reduction potential to that of the noble metals.

Electrolysis

- An electrolytic cell, uses electrical energy to produce chemical change.
- The process of electrolysis involves forcing a current through a cell to produce a chemical change for which the cell potential is negative; that is electrical work causes an otherwise nonspontaneous chemical reaction to occur.
- The figure (b) below shows an external power source forcing electrons through the cell in the opposite direction to that in (a). This requires an external potential greater than 1.10 V, which must be applied in opposition to the natural cell potential. This device is called an electrolytic cell. Notice that since electron flow is opposite in the two cases, the anode and cathode are reversed between (a) and (b). Also, ion flow through the salt bridge is opposite in the two cells.





- An ampere [amp], abbreviated A, is 1 coulomb of charge per second.
- Plating means depositing the neutral metal on the electrode by reducing metal ions in solutions.
- The above information can be used to calculate time for electroplating.
- If you are just calculating the mass that would plate out, you can use my formula:

  $$\frac{AtM}{Fe^-} = \text{Mass Plated out}$$

  A = amps, t = time (in seconds), M= molar mass of metal being plated out,
  F = Faraday (96485 C/mole of e^-), e^- = mole of electrons transferred
- You need to know the units associated with each of the following in case a different variable is being solved for: Volt = Joule/ Coulomb, Faraday = 96485 Coulombs/ mol e^-
  Ampere = Coulomb/ second
- You can also go through the factor label method. For example: How long must a current of 5.00 A be applied to a solution of Ag^+ to produce 10.5 g silver metal?
  1. Convert grams to moles:
     10.5 g ÷107.868 g/mol = 9.73×10^{-2} mol Ag
  2. Each Ag^+ ion requires one electron to become a single atom:
     $Ag^+ + e^- \rightarrow Ag$; so 9.73×10^{-2} mol electrons is required.
  3. The quantity of charge can be calculated by multiplying by the number of moles by 96,485 C/mol e^- (farday):
     9.73×10^{-2} mol e^- x 96,485 C/mol e^- = 9.39×10^3 C
  4. Time can be calculated by converting the given amperage to C/s and solving for seconds:
     9.39×10^3 C = (5.00 C/s) x (Time in seconds)
     time = 1.88×10^3 sec = 31.3 min
- You try: How long will it take to plate out each of the following with a current of 100.0 A?
  a. 1.0 kg Al from aqueous Al^{3+}
  b. 1.0 g Ni from aqueous Ni^{2+}
  c. 5.0 mol Ag from aqueous Ag^+

Electrolysis of Water

- In practice, when electrodes connected to a 6-V battery are dipped into pure water, no reaction is observed because pure water contains so few ions that only a negligible current can flow. The addition of a soluble salt causes an immediate evolution of bubbles of hydrogen and oxygen.
- You should know the anode and cathode reactions for the electrolysis of water.

Anode reaction:	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$\mathscr{E}^\circ = -1.23V$
Cathode reaction:	$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$	$\mathscr{E}^\circ = -0.83$ V
	$6H_2O \rightarrow 2H_2 + O_2 + 4\{H^+ + OH^-\}$	
Reduced to:	$2H_2O \rightarrow 2H_2 + O_2$	$\mathscr{E}^\circ = -2.06$ V

Electrolysis of Mixtures of Ions

- Consider a solution that contains Cu^{2+}, Ag^+ and Zn^{2+}. If the voltage is initially very low and is gradually turned up, in which order will the metals be plated out onto the cathode?

$Ag^+ + e^- \rightarrow Ag$	$\mathscr{E}^\circ = 0.80$ V
$Cu^{2+} + 2e^- \rightarrow Cu$	$\mathscr{E}^\circ = 0.34$ V
$Zn^{2+} + 2e^- \rightarrow Zn$	$\mathscr{E}^\circ = -0.76$ V

- The more positive the $\mathscr{E}^\circ$ value, the more the reaction has a tendency to proceed in the direction indicated.
- The answer for the above question in order of plating: Ag^+, Cu^{2+}, Zn^{2+}
- You try: An acidic solution contains Sn^{2+}, Fe^{2+}, and Co^{2+}. Using the $\mathscr{E}^\circ$ values listed on your Standard Reduction Potentials determine the order of oxidizing ability (the order in which each would plate out).

- **In all electrochemical reactions in water, the oxidation of water to produce oxygen gas,**
  $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

only occurs if the anion in the solution can't be oxidized. For example, in nitrate, NO_3^{1-}, nitrogen has an oxidation number of +5. Nitrogen has no more valence electrons to lose, so it can't be oxidized. Other substances that can't be oxidized include sulfate, SO_4^{2-} (oxidation number +6), and phosphate, PO_4^{3-} (oxidation number +5). That is why a solution of sodium sulfate is used in the electrolysis of water. The ions allow for the movement of electricity and since sulfate can't be oxidized, oxygen and hydrogen would be produced.

- Consider the electrolysis of a potassium chloride solution.
  - $K^+ + 1e^- \rightarrow K$ — $\mathscr{E}^\circ = -2.92$ V — reduction
  - $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ — $\mathscr{E}^\circ = -1.23$ V — oxidation
  - $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ — $\mathscr{E}^\circ = -0.83$ V — reduction
  - $2Cl^- \rightarrow Cl_2 + 2e^-$ — $\mathscr{E}^\circ = -1.36$ V — oxidation

  The half reactions are adjusted to represent what exists in solution – K^+, Cl^- & H_2O

  1. Pick the most positive half reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $\mathscr{E}^\circ = -0.83$ V
  2. Since the most positive half reaction is a reduction, you must choose an oxidation for the other reaction. Chloride CAN be oxidized, so it will be the oxidation half reaction: $2Cl^- + \rightarrow Cl_2 + 2e^-$ $\mathscr{E}^\circ = -1.36$ V
  3. The overall reaction is: $2H_2O + 2Cl^- \rightarrow H_2 + Cl_2 + 2OH^-$ $\mathscr{E}^\circ = -2.19$ V

- Consider the electrolysis of a potassium sulfate solution.
  - $K^+ + 1e^- \rightarrow K$ — $\mathscr{E}^\circ = -2.92$ V — reduction
  - $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ — $\mathscr{E}^\circ = -1.23$ V — oxidation
  - $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ — $\mathscr{E}^\circ = -0.83$ V — reduction
  - Sulfate can't be oxidized because sulfur has no more electrons to lose.

  The half reactions are adjusted to represent what exists in solution – K^+, SO_4^{2-} & H_2O

  1. Pick the most positive half reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $\mathscr{E}^\circ = -0.83$ V
  2. Since the most positive half reaction is a reduction, you must choose an oxidation for the other reaction. The only other oxidation is: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $\mathscr{E}^\circ = -1.23$ V oxidation
  3. The overall reaction is: $2H_2O \rightarrow H_2 + O_2$ $\mathscr{E}^\circ = -2.06$ V

Identifying the Cathode an Anode in Galvanic and Electrolytic Cells

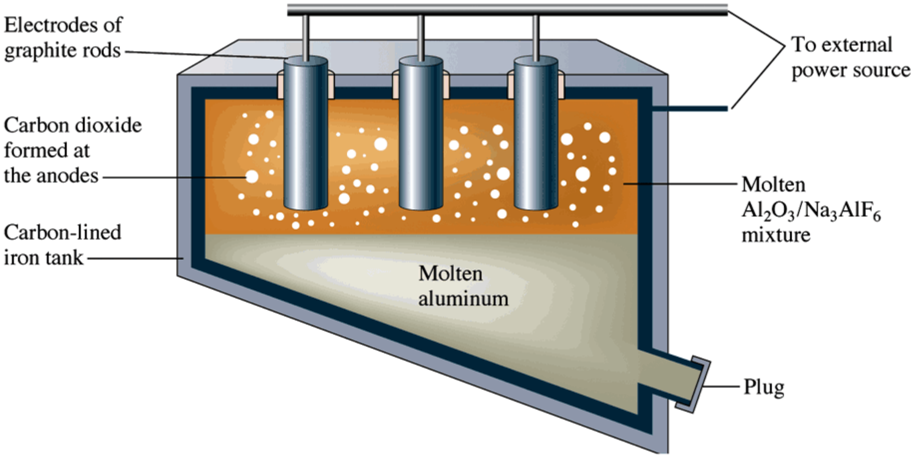
- Galvanic Cell using Cu^{2+} and Zn^{2+}:
  - Overall reaction: $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$
  - Anode reaction: $Zn \rightarrow Zn^{2+} + 2e^-$, oxidation, negative electrode
  - Cathode reaction: $2e^- + Cu^{2+} \rightarrow Cu$, reduction, positive electrode
- Electrolysis of a potassium iodide solution:
  - Overall reaction: $2H_2O + 2I^- \rightarrow H_2 + 2OH^- + I_2$
  - Anode reaction: $2I^- \rightarrow I_2 + 2e^-$, oxidation, positive electrode
  - Cathode reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, reduction, negative electrode

Production of Aluminum

- Aluminum is one of the most abundant elements on earth, ranking third behind oxygen and silicon.
- Since aluminum is a very active metal, it is found in nature as its oxide in an ore called bauxite (named for Les Baux, France where it was first discovered).
- Production of aluminum from its ore proved to be very difficult.
- In 1886, Charles Hall (US) and Paul Heroult (France) almost simultaneously discovered an electrolytic process for producing aluminum. The key factor in the Hall-Heroult process is in the use of molten cryolite (Na_3AlF_6) as the solvent for the aluminum oxide.
- Electrolysis is only possible if ions can move to electrodes. A common method for producing ion mobility is dissolving the substance to be electrolyzed in water. This is not possible in the case of aluminum because water is more easily reduced that Al^{3+}:

  $Al^{3+} + 3e^- \rightarrow Al$ $\qquad \mathscr{E}^\circ = -1.66$ V

  $2H_2O^{2+} + 2e^- \rightarrow H_2 + 2OH^-$ $\qquad \mathscr{E}^\circ = -0.83$ V
- Ion mobility also can be produced by melting the salt. The melting point of solid Al_2O_3 is 2050°C, much too high to allow for practical electrolysis of the molten oxide. A mixture of Al_2O_3 and Na_3AlF_6 has a melting point of 1000°C. The resulting molten mixture can be used to obtain aluminum metal electrolytically.
- The production of aluminum consumes 5% of all the electricity used in the United States.

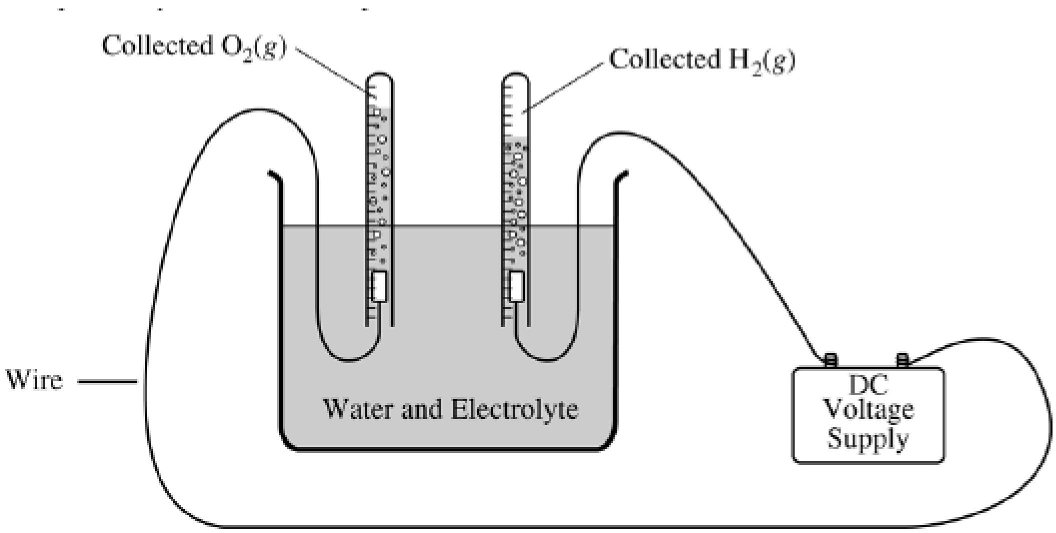


Electrolysis of Sodium Chloride

- Sodium metal is mainly produced by the electrolysis of molten sodium chloride.
- Because sodium chloride has a high melting point, solid calcium chloride is usually mixed in to lower the melting point.
- Sodium liquid is drained off, then cooled, and cast into blocks. Because it is so reactive, sodium must be stored in an inert solvent, such as mineral oil, to prevent oxidation.

- Electrolysis of aqueous sodium chloride (brine) is an important industrial process for the production of chlorine and sodium hydroxide. In fact, this process is the second largest consumer of electricity in the United States, after the production of aluminum. Hydrogen is produced at the cathode (not sodium due to the reduction potentials of sodium and water – water's reduction potential is greater).

And we end with an AP Free Response Question: 2005 Form B



Water was electrolyzed, as shown in the diagram above, for 5.61 minutes using a constant current of 0.513 ampere. A small amount of nonreactive electrolyte was added to the container before the electrolysis began. The temperature was 298 K and the atmospheric pressure was 1.00 atm.

(a) Write the balanced equation for the half reaction that took place at the anode.
(b) Calculate the amount of electric charge, in coulombs, that passed through the solution.
(c) Why is the volume of $O_2(g)$ collected different from the volume of $H_2(g)$ collected, as shown in the diagram?
(d) Calculate the number of moles of $H_2(g)$ produced during the electrolysis.
(e) Calculate the volume, in liters, at 298 K and 1.00 atm of dry $H_2(g)$ produced during the electrolysis.
(f) After the hydrolysis reaction was over, the vertical position of the tube containing the collected $H_2(g)$ was adjusted until the water levels inside and outside the tube were the same, as shown in the diagram below. The volume of gas in the tube was measured under these conditions of 298 K and 1.00 atm, and its volume was greater than the volume calculated in part (e). Explain.