Electrochemistry

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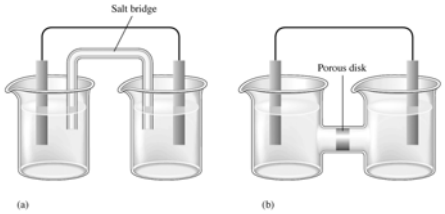
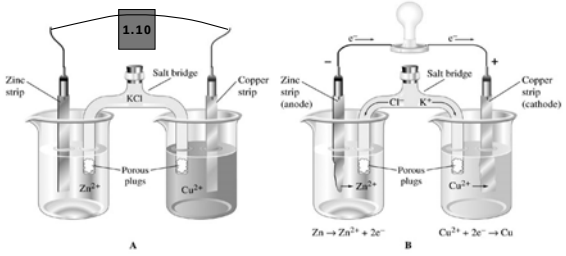
- A redox reaction can be separated into its ½-reactions and allowed to react in separate chambers that are connected by a wire and a salt bridge.
- Electrons are "pushed" along the wire from the ½-cell where oxidation occurs to the reduction ½-cell.
- Charge balance is maintained for the ½-cells by a salt bridge.
- The oxidation ½-cell is called the ANODE.
- The reduction ½-cell is called the CATHODE.

Galvanic cells can contain a salt bridge as in (a) or a porous-disk connection as in (b).



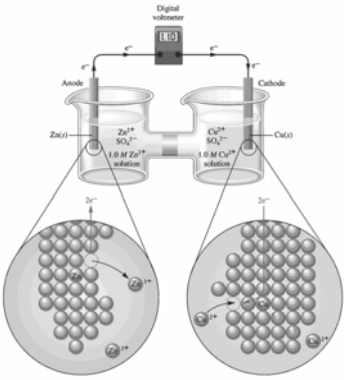
Voltaic / Galvanic Cell

- The following electrochemical cell produces energy by the reaction of Cu^{2+} ions with Zn metal.
- A cell that produces energy when a spontaneous reaction occurs is called a voltaic or galvanic cell.



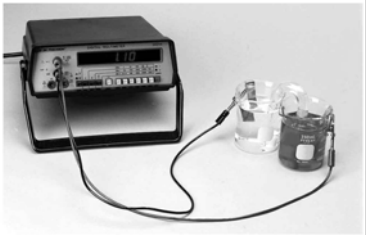
Zn/Cu cell (cont.)

- Write the reaction for each ½-cell.
- Write the overall reaction.
- Write the cell notation.



Zn/Cu cell (cont.)

- Calculate the standard cell potential ($\mathcal{E}°$) for the Zn/Cu cell.



$$E^o_{cell} = E^o_{red} + E^o_{oxid}$$

Book's Method :

$$E°_{cell} = E°_{red,CATHODE(reduction)} - E°_{red,ANODE(oxidation)}$$

Electrical Potential

- Electromotive force (emf) is the driving or pushing of electrons from the anode to the cathode.
- Electrons always flow from the electrode with the lower reduction potential to the electrode with the higher reduction potential.
- Cell potential ($\mathcal{E}^\circ$) is related to electrical work (Joules) as charge (coulombs) flows in a circuit:

  Volt (V) = Joule (J) / coulomb (C)
- A coulomb is the amount of charge that passes a single point in an electrical circuit when one ampere of current flows for 1 second.

  1 Coulomb = 1 Ampere • second

  1 Coulomb = charge of 6.24 x 10^{18} electrons

  charge of 1 electron = 1.602 x 10^{-19} C

Electrical Potential

- Galvanic cells must always have a positive cell potential.
- Which of the following redox pairs will function at the ANODE in each of the following pairs? Also calculate the cell potential.
  - **Cd^{2+} / Cd and Sn^{4+} / Sn^{2+}**
  - **Zn^{2+} / Zn and Al^{3+} / Al**
  - **Br_2 / Br^- and MnO_4^- / Mn^{2+}**

Standard Potentials

- Standard potentials are measured for Standard Thermodynamic conditions:
  T = 298 K
  [X] = 1 *M* P_X = 1 atm
- All standard reduction potentials are measured relative to the Standard Hydrogen Electrode (**SHE**).
- SHE is composed of a solution that is 1.0 *M* H^+ and an enclosed atmosphere with P_{H2} = 1.0 atm
- SHE is assigned a standard reduction potential of zero.

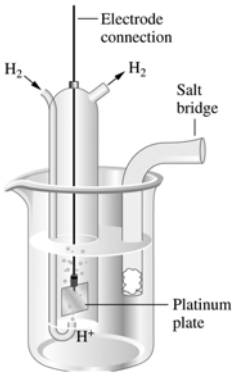
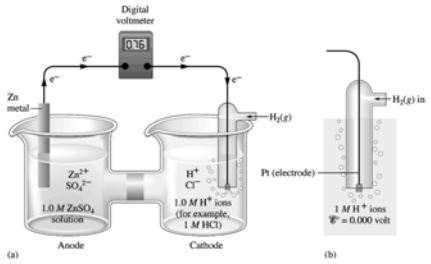


Figure a: A galvanic cell involving the reactions:
$Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation - at the anode)
$2\ H^+ + 2\ e^- \rightarrow H_2$ (reduction - at the cathode)
and has a potential of 0.76 V.

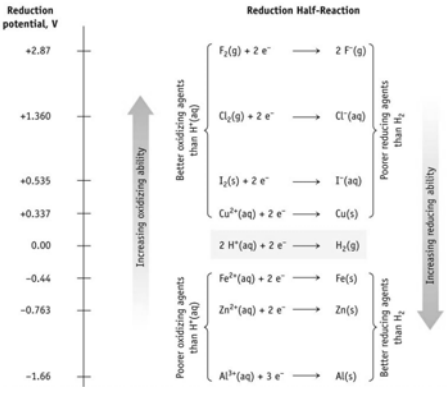


What is the reduction potential for Zinc?

Electrochemical Cell with Cu and SHE

- Cu has a standard reduction potential of + 0.34 V.
- Will copper be oxidized or reduced in a cell with SHE?
- Diagram a standard cell that could be used to find the standard reduction potential of copper. Use SHE as one electrode in the cell.

Relative Oxidizing and Reducing Power



Relative Oxidizing and Reducing Power

- Which of the following is most easily oxidized?
  Al **Sn** **Cd**
- Which of the following is most easily reduced?
  Mg^{2+} **Na^{+}** **V^{3+}**
- Which of the following is the best reducing agent?
  Zn **Zn^{2+}** **V^{2+}**
- Which of the following is the best oxidizing agent?
  H^{+} **Ni^{2+}** **Fe^{2+}**

Relative Oxidizing and Reducing Power

- Which of the following can reduce Al^{3+}?
  K *or* **Fe**
- Which of the following can oxidize Al?
  Mg^{2+} *or* **Zn^{2+}**
- Which of the following can reduce H^{+}?
  F^{-} *or* **Ni**
- Which of the following can oxidize H_2?
  Sn^{4+} *or* **Zn^{2+}**

Relationship of Free Energy and Cell Potential

- The free energy change for a reaction relares to the maximum amount of work that can be done by a chemical system:

$$\Delta G = w_{\max}$$

- Electrical work is related to cell potential and the number of electrons transferred in a chemical process:

$$w_{\max} = -nFE$$

- Combining these two equations, we can relate free energy change and cell potential:

$$\Delta G = -nFE$$

Where n = # electrons transferred (as determined from the balanced reaction), and F = Faraday constant:

$$F = 96{,}485 \frac{J}{V \bullet mol(electron)} = 96{,}485 \frac{C}{mol(electron)}$$

Standard Free energy and Cell Potential

- Under standard thermodynamic conditions:

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

Standard Cell Potentials & K

$$E^\circ = \frac{RT}{nF} \ln K$$

$$E^\circ = \frac{0.0257}{n} \ln K$$

Standard and Non-Standard Cell Potentials

$$E^o_{cell} = E^o_{red} + E^o_{oxid}$$

$$E_{cell} = E_{red} + E_{oxid}$$

Book's Method :

$$E_{cell} = E_{red,CATHODE} - E_{red,ANODE}$$

Nernst Equation

- Under non-standard conditions of pressure or concentration (at 298 K):

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

- Because R,T, and F are all constant (T=298 K), we often use the following form of the Nernst equation:

$$E = E^\circ - \frac{0.0257}{n} \ln Q$$

Electrochemical Cell Diagrams

Diagram a functional voltaic cell with the following couple under standard conditions:

{Fe^{+2} / Fe} {$OCl^-_{(aq)}$ / $Cl^-_{(aq)}$ (in basic solution)}

Be sure to include all of the following in the diagram:

- Label cathode and anode
- Appropriate metal electrodes
- Concentrations of important SPECIES in each cell.
- BALANCED half reaction occurring in each cell.
- All components required to have an operating circuit.

Fe^{2+} / OCl^- Cell diagram (cont.)

- Write the balanced overall reaction for the cell.
- Calculate $\mathcal{E}°$ for the cell.
- Calculate $\Delta G°$ for the reaction.
- Calculate K for the reaction.
- Calculate $\mathcal{E}_{cell}$ (at 298 K) if:

$[Fe^{2+}]$ = 0.10 *M*

$[OCl^-]$ = 0.25 *M*

$[Cl^-]$ = 0.50 *M*

pH = 12.00

Electrochemical Cell Diagram

Diagram a functional voltaic cell with the following couple under standard conditions:

{Cu^{+2} / Cu} {$MnO_4^-{}_{(aq)}$ / $Mn^{2+}_{(aq)}$ (in acidic solution)}

Be sure to include all of the following in the diagram:

- Label cathode and anode
- Appropriate metal electrodes
- Concentrations of important SPECIES in each cell.
- BALANCED half reaction occurring in each cell.
- All components required to have an operating circuit.

Cu^{2+} / MnO_4^- Cell diagram (continued)

- Write the balanced overall reaction for the cell.
- Calculate $\mathcal{E}°$ for the cell.
- Calculate $\Delta G°$ for the reaction.
- Calculate K for the reaction.
- Calculate $\mathcal{E}_{cell}$ (at 298 K) if:

$[Cu^{2+}]$ = 2.0 *M*

$[MnO_4^-]$ = 0.10 M

$[Mn^{2+}]$ = 0.50 M

$[H^+]$ = 1.0 M

The Nernst Equation and non-standard half-cells

- Calculate the E_{red} for a $Ni^{2+}/Ni_{(s)}$ ½-cell when $[Ni^{2+}]$ = 0.001 *M*.
- Calculate the E_{red} for a $Ni^{2+}/Ni_{(s)}$ ½-cell when $[Ni^{2+}]$ = 5.0 *M*.
- Calculate the E_{oxid} for a Sn^{4+}/ Sn^{2+} ½-cell when $[Sn^{4+}]$ = 0.50 *M* & $[Sn^{2+}]$ = 0.00025 *M*.

Concentration Cells

Equilibrium Constant & Cell potentials

- Based on cell potentials, calculate K for the following reactions at 25˚C:

Equilibrium Constant & Cell potentials

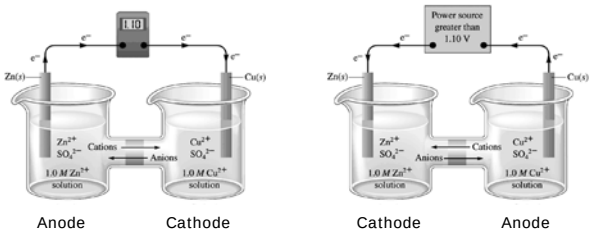
- Based on cell potentials for the following ½-reactions, calculate the K_{sp} value for AgBr at 25˚C.
- Compare this to the listed value in the book.

Electrolysis

- Electrolysis is the use of an applied electrical current to bring about chemical change.
- A voltaic (or galvanic) cell produces electrical energy as a spontaneous reaction occurs.
- An electrolytic cell uses electrical energy to drive the non-spontaneous chemical process.

Galvanic and Electrolytic Cell Comparison

Figure (A): A standard galvanic cell based on the spontaneous reaction
Figure (B): A standard electrolytic cell. A power source forces the opposite reaction



Formation of $CuBr_2$

- Elemental bromine reacts with metal copper in a highly product favored reaction:
- Based on the ½-cell potentials, estimate a value of K for this reaction.

Electrolysis of $CuBr_2$

- $CuBr_2$ does not spontaneously decompose to $Cu_{(s)}$ and $Br_{2(l)}$. Consider the reaction:
- If we wish to drive this reaction, we must change the conditions to make this process favorable.
- We can apply an external voltage from a power source.
- The voltage we apply must be greater in magnitude than the cell potential for the spontaneous reaction, and applied in the reverse polarity.

Electrolysis of $CuBr_2$ (continued)

- What minimum voltage must be applied to electrolyze copper (II) bromide?
- Consider a diagram of the electrolytic cell:
- Note that the electrolytic cell need not be separated into individual compartments.

Electrolysis of H_2O

- Consider the electrolysis of water under neutral conditions with a strong electrolyte like KCl in solution (to increase the conductivity of the water). View quicktime movie.
- Diagram the electrolytic cell.
- Write both ½-reactions.
- Determine the minimum potential needed to electrolyze the water.

Electrolysis of H_2O (continued)

- If we try to electrolyze other compounds in water, we must consider whether the electrolysis of water or of the ion in solution is more favorable at that electrode.

Electrolysis of KBr

- To determine if KBr can be electrolyzed to $K_{(s)}$ and $Br_{2(l)}$ in aqueous solution, we must consider all potential reactions at the cathode and anode.
- CATHODE:
- ANODE:

Electrolysis of KBr (continued)

- Based on the cathode and anode reactions that are most favorable, write the overall reactions for the electrolysis of a KBr solution.
- Calculate the minimum applied voltage to drive this reaction.

Electrolysis of KBr (continued)

- In order to separate KBr into its elements, molten KBr must be electrolyzed. Because of the high temperature required, special equipment is needed.
- Consider a diagram of the electrolysis of molten KBr:
- Estimate the minimum applied voltage to drive the reaction.

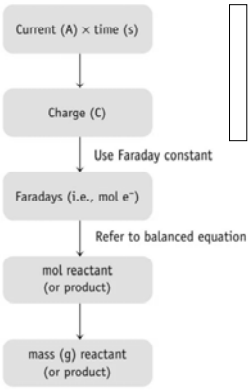
Electrolysis & Current

- Electrolytic processes are important in the production of a number of important industrial chemicals: aluminum metal, copper metal, chlorine gas, sodium hydroxide, and many others.
- To determine the mass that is formed when an electrolytic process takes place, we must know the current applied and the time it is applied.
- Current (ampere) is the flow of charge.

1 ampere (A) = 1 coulomb (C) / second (s)

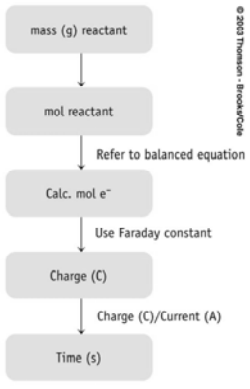
Electrolysis and counting electrons

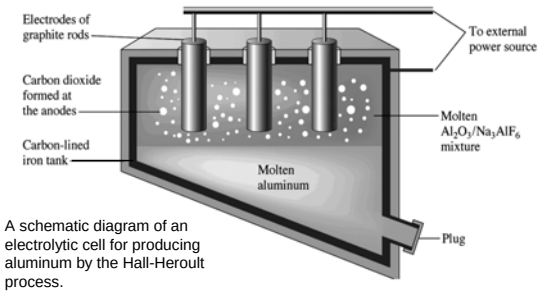
- What mass of zinc can be plated by the application of 10.0 A for 30 minutes?



Electrolysis and counting electrons

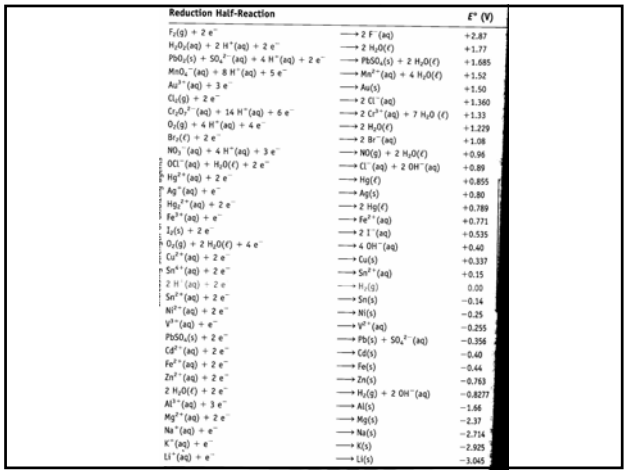
- What time is required to plate 500 mg of gold onto a ring by applying a current of 5.0 A to a solution of $AuCl_3$?





A schematic diagram of an electrolytic cell for producing aluminum by the Hall-Heroult process.

Aluminum is produced commercially by the process illustrated above. What current must be applied to produce 1000. kg of aluminum in 2.0 hours?



Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2\ e^-$	$\longrightarrow 2\ F^-(aq)$	+2.87
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^-$	$\longrightarrow 2\ H_2O(\ell)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	$\longrightarrow PbSO_4(s) + 2\ H_2O(\ell)$	+1.685
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$	$\longrightarrow Mn^{2+}(aq) + 4\ H_2O(\ell)$	+1.52
$Au^{3+}(aq) + 3\ e^-$	$\longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2\ e^-$	$\longrightarrow 2\ Cl^-(aq)$	+1.360
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^-$	$\longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O\ (\ell)$	+1.33
$O_2(g) + 4\ H^+(aq) + 4\ e^-$	$\longrightarrow 2\ H_2O(\ell)$	+1.229
$Br_2(\ell) + 2\ e^-$	$\longrightarrow 2\ Br^-(aq)$	+1.08
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^-$	$\longrightarrow NO(g) + 2\ H_2O(\ell)$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2\ e^-$	$\longrightarrow Cl^-(aq) + 2\ OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2\ e^-$	$\longrightarrow Hg(\ell)$	+0.855
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2\ e^-$	$\longrightarrow 2\ Hg(\ell)$	+0.789
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2\ e^-$	$\longrightarrow 2\ I^-(aq)$	+0.535
$O_2(g) + 2\ H_2O(\ell) + 4\ e^-$	$\longrightarrow 4\ OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2\ e^-$	$\longrightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2\ e^-$	$\longrightarrow Sn^{2+}(aq)$	+0.15
$2\ H^+(aq) + 2\ e^-$	$\longrightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2\ e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\ e^-$	$\longrightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\longrightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2\ e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2\ e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\ e^-$	$\longrightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2\ e^-$	$\longrightarrow Zn(s)$	−0.763
$2\ H_2O(\ell) + 2\ e^-$	$\longrightarrow H_2(g) + 2\ OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3\ e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\ e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.045