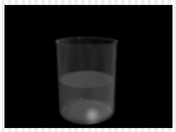
Chapter 17

Electrochemistry



Redox Reactions

- Electrochemistry is the study of batteries and interconversion of chemical and electrical energy.
- Based on redox (oxidation-reduction) reactions in which one element gains electrons and another loses electrons.
  - These two processes MUST happen together.
- Have to assign oxidation numbers to determine (see Chapter 4).

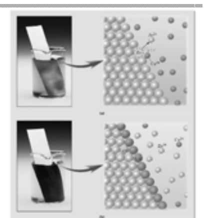
Oxidation Numbers

- Elements in their natural states are 0.
- Elements in binary ionic compounds are the same as their charges.
- H: usually +1, except with alkali metals (LiH, NaH, etc.)
- O: usually -2, except in peroxides (H_2O_2, K_2O_2)
- The non-oxygen element in a polyatomic ion has to be determined from the other oxidation numbers.

Redox Reactions

- Oxidation: loss of electrons
- Reduction: gain of electrons
  - LEO the lion goes GER
- The substance oxidized is also called the reducing agent (it caused the other substance to be reduced). And vice versa.
- $Cu(s) + AgNO_3 \rightarrow Ag(s) + Cu(NO_3)_2$

$Cu(s) + Zn(NO_3)_2(aq)$



Redox Reactions

- $CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$
- $Na(s) + HCl(aq) \rightarrow NaCl(aq) + H_2(g)$
- For each reaction:
  - What is oxidized, reduced?
  - What is the oxidizing agent? Reducing agent?
- Combustion, decomposition, combustion, and single-replacement reactions are usually redox.

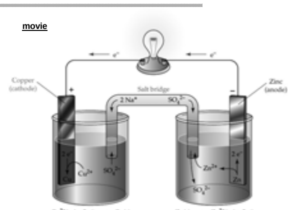
Balancing Redox Reactions

- $Cr^{3+}(aq) + Be(s) \rightarrow Cr(s) + Be^{2+}(aq)$
- To balance (notice the charges), we break it up into two **half reactions**, the oxidation half and reduction half.
- We have to balance electrons.
- Oxidation: $Be(s) \rightarrow Be^{2+}(aq) + 2e^-$
- Reduction: $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$
- $2Cr^{3+}(aq) + 3Be(s) \rightarrow 2Cr(s) + 3Be^{2+}(aq)$

Galvanic Cells

Electron motion in a cell

Figure 17.2 **movie**



Galvanic Cells

- **O**xidation reaction: occurs at the **a**node (mass decreases over time) - both vowels
- **R**eduction reaction: occurs at the **c**athode (mass increases over time) - both consonants
- Electrons are transferred across a wire (through a voltmeter)
  - Voltage is the cell potential, E (or Electromotive Force, EMF)
- Salt bridge - soluble salt solution used to neutralize ions in each solution; cations travel toward cathode, anions toward anode

Batteries

- Galvanic cells are describing the batteries we use in everyday life.
- Batteries die when 1) the anode is completely consumed, 2) the cathode solution is consumed, or 3) the salt bridge runs out of ions.
- Bigger batteries only last longer, they don't have more volts. Volts are determined by the chemicals used.
- Worked example 17.1, Problem 17.1

Short-hand Notation

- $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
- $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$
- Anode | anode ion || cathode ion | cathode
- This is always written in order of the oxidation half reaction, then the reduction half reaction.
- Not all half reactions use a solid metal electrode.
- Worked Example 17.2, Problem 17.3

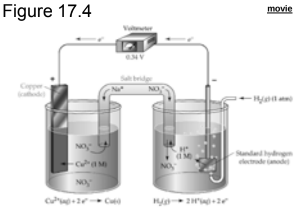
Inert Electrodes

- If the electrode needed is a soluble ionic compound or a gas, we can use Graphite or Platinum as the electrode.
- These substances allow electrons to transfer but don't take place in the reaction.

Galvanic Cells - Pt electrode

- Figure 17.4

movie



Standard Cell Potential, E°

- Gases at 1 atm
- Solutions at 1 M
- Temperature at 298 K (25°C)
- Standard potential for any galvanic cell is the sum of the half-cell potentials.
  - $E^o_{cell} = E^o_{ox} + E^o_{red}$
- $H_2(g) \mid H^+(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$
- Write the half reactions.

Reduction Potentials

- We can use the table of Reduction Potentials of half reactions to determine the cell potential of a galvanic cell.
- Table 17.1: All potentials are listed at **reduction** potentials.
- How do we determine **oxidation** potentials?

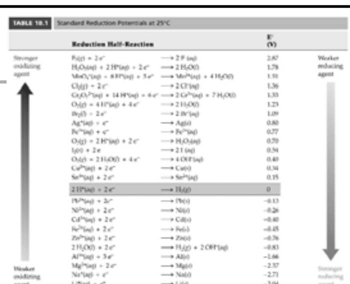


TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\rightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\rightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-(aq)$	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	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\rightarrow Li(s)$	-3.04	Stronger reducing agent

Cell Potentials

- Once you find the potentials for the half reactions, you add the values together to get the overall cell potential.
- E° is in Volts (V = J/C or C = J/V or J = CV)
- All cell potentials are compared to hydrogen (**SHE: standard hydrogen electrode**)
- $H_2(g) \rightarrow 2H^+ + 2e^-$ $\quad E^o_{red} = 0$ V
- Standard reduction potentials (E^o_{red}) are compared to SHE.

Cell Potentials

- Positive E^o_{cell} means the reaction is product-favored (and spontaneous).
  - The reaction will go forward until the battery dies.
  - A negative E^o_{cell} means the reaction won't really happen.
- Therefore, we want two half reactions that yield the most positive E^o_{cell} value.
- **$E^o_{cell} = E^o_{red} + E^o_{ox}$**

Cell Potentials

- $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ $E^o_{red} = 2.87$ V
- This is the most positive E^o_{red} value. Makes sense: F is the most electronegative element and really wants to gain an electron (be reduced, or act as oxidizing agent).

Cell Potentials

- $Li^+(aq) + e^- \rightarrow Li(s)$ $E^o_{red} = -3.04$ V
- This is the most negative E^o_{red} value. Does this make sense?
- Li is going to lose an electron and be oxidized. This makes it a good reducing agent.

Oxidizing/Reducing Agents

Cell Potentials

- Based on their E^o_{red} values, determine the best oxidizing agent, best reducing agent, worst oxidizing agent, and worst reducing agent.
- $Au^{3+} + e^- \rightarrow Au(s)$ $E^o_{red} = 1.50$ V
- $Br_2(l) + e^- \rightarrow 2Br^-(aq)$ $E^o_{red} = 1.07$ V
- $Pb^{2+} + e^- \rightarrow Pb(s)$ $E^o_{red} = -0.13$ V
- $Ni^{2+} + e^- \rightarrow Ni(s)$ $E^o_{red} = -0.25$ V

TABLE 18.1 Standard Reduction Potentials at 25°C

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	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	-2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	-2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	-3.04	Stronger reducing agent

Cell Potentials

- Ni(s) is the easiest to oxidize, best reducing agent.
- Au^{3+} is the easiest to reduce, best oxidizing agent.
- Au(s) is the hardest to oxidize, worst reducing agent.
- Ni^{2+} is the hardest to reduce, worst oxidizing agent.

Cell Potentials in Reactions

- What will E^o_{cell} be if we react Ni(s) with Au^{3+}?
- E^o_{ox} Ni(s) = +0.25V, E^o_{red} Au^{3+} = 1.50 V
- E^o_{cell} = +0.25 V + 1.50 V = 1.75 V

- What will E^o_{cell} be if Pb^{2+} reacts with Br^-?
- E^o_{cell} = -1.07 V + -0.13 V = -1.20 V
- Not a spontaneous reaction.

Cell Potentials of Reactions

- What combination of 2 reactions will yield the most positive E^o_{cell}?
  - Au^{3+} + Ni(s)
- Worked Example 17.4, 17.5; Problems 17.7 - 17.9

Example: $Cl_2(g) + Zn(s)$

- What combination of 2 reactions will yield the most positive E^o_{cell}?
- $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^o_{red} = 1.36$ V
- $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^o_{red} = -0.76$ V
- The first reaction is a stronger oxidizing agent than the second reaction. Therefore it wants to be the reduction ½ reaction and the second reaction wants to be the oxidation ½ reaction.
- $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^o_{ox} = +0.76$ V
- The E^o_{ox} reaction is flipped so the sign is flipped!
  - (Zn^{2+} is a weak oxidizing agent, Zn is a strong reducing agent!)

E^o_{cell}, K, and ΔG^o

- **$\Delta G^o = - nFE^o$**
  - n = number of electrons transferred (from the overall balanced cell reaction)
  - F = Faraday's constant: 96,500 J/V·mol e^-
  - E = cell potential of the reaction
- $\Delta G = \Delta G^o + RT \ln K$ (not standard state)
- $-nFE = -nFE^o + RT \ln K$
- **$E = E^o_{cell} - (RT/nF) \ln K$**

Cell Potential Equations

- $E = E^o_{cell} - (2.303\ RT) / nF \log Q$ (correction between ln and log)
- **$E = E^o_{cell} - (0.0592\ V) / n \log Q$ (at 25°C)**
  - This only applies if all solutions **aren't** 1 molar. Then it is non-standard.
- **$E^o_{cell} = (RT / nF) (\ln K)$ (At equilibrium)**
  - R = 8.314 J/mol·K
- If we know one of these values (K, Q, or E^o_{cell}), we can find the other two.

Calculations

- Write the half reactions and balanced net reaction.
- Find the E^o_{red} values, find E^o_{ox} values
- Calculate ΔG^o
  - $\Delta G^o = -nFE^o$
- Calculate K
  - $E^o = (RT/nF) \ln K$

Calculations

- Calculate ΔG^o for the Ni(s) + Au^{3+} reaction.
  - E^o_{cell} = 1.75 V, 6 mol e^- transferred
  - $\Delta G^o = -(6 \text{ mol } e^-)(96{,}500 \text{ J/V·mol } e^-)(1.75 \text{ V})$ = **-1.01×10^4 kJ**
- Calculate K for this cell at 25°C:
- Ni(s) | Ni^{2+}(aq) || Br^-(aq) | Pt(s)

Cell Potentials Summary

- Large values of K; product-favored reaction
  - ΔG^o is negative, E^o_{cell} is positive
- Small values of K; reactant-favored reaction
  - ΔG^o is positive, E^o_{cell} is negative

The Nernst Equation

- **$E = E^o_{cell} - (RT/nF) \ln Q$**
- At equilibrium, E = 0 and Q = K
- **$E^o_{cell} = RT/nF \ln K$**
- Calculate the cell potential if $[Pb(NO_3)_2]$ = 0.88 M and $[Ag(NO_3)]$ = 0.14 M
- Write the half-reactions for this cell. Write the short-hand notation of this reaction and draw the galvanic cell.
- Examples 17.6 - 17.7, Problem 17.10 - 17.11

Pb and Ag Galvanic Cell

- $2Ag^+(aq) + Pb(s) \rightarrow 2Ag(s) + Pb^{2+}(aq)$
- E^o_{cell} = 0.13 V + 0.80 V = 0.93 V
- $Q = (0.88\ M) / (0.14\ M)^2 = 44.9$
- $E = E^o - (RT/nF) \ln Q$
- Worked Example 17.9; Problems 17.13, 17.14

Corrosion

- The oxidative deterioration of a metal (i.e., solid metal converted to ions).
- Rust formation is the corrosion of iron.
- Metals can be plated with non-reactive metals (chromium, tin, or zinc are common)

sample electrolytic cell

Electrolysis

Electroplating movie

- Electrolytic Cell: Electrical energy from an external source (outlet or a battery) is used to force a redox reaction to go in the nonspontaneous direction.
- Molten salt: $2NaCl(l) \rightarrow 2Na(s) + Cl_2(g)$
- E_{cell} = - 4 V
- This reaction naturally wants to run in reverse direction. We need more than 4 volts to drive this reaction forward. Salts don't normally decompose into elements.

Electrolysis of Water

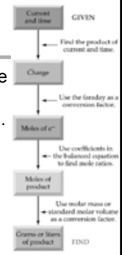
- Water doesn't naturally decompose into hydrogen and oxygen.
- $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ $E_{cell} = -1.23$ V

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode: $4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$

Electrolysis of Water Movie

Electrolysis Calcs.

- Used to find mass or volume of product produced by passing current through cell.
- Current: measured in Amps (A = C/s).
- Change time to seconds.
- Convert to moles (use F)

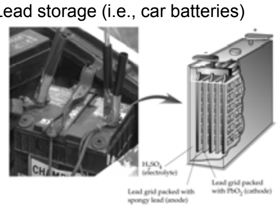


Electrolysis Calculations

- How many grams of copper can be collected in 1.00 hour by a current of 1.62 A from a $CuSO_4$ solution?
- Current (C/s) x time (s) = C
- C x (1 mol e^- / 96,500 C) = mol e^-
- mol e^- x (mol solid / mol e^-) = mol solid
- mol solid x (molar mass) = mass solid
- Worked Examples 17.10, 17.11; Problems 17.22, 17.23

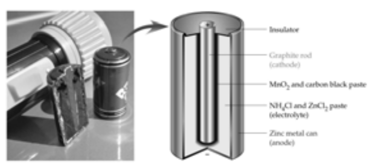
Batteries

- Lead storage (i.e., car batteries)

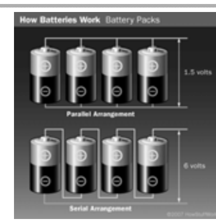


Household batteries

- Dry-cell (or Laclanche) batteries



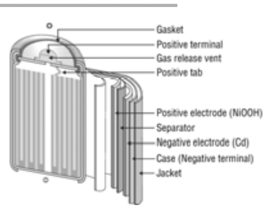
9V battery – sum of 1.5 Volts



Ni-Cad Batteries - rechargeable

Positive electrode: NiOOH

Negative electrode: Cd



Lithium Batteries

- Lithium Ion:

Positive electrode:
Lithium cobalt oxide

Negative electrode:
Carbon