Electrochemistry

Chapter 17

Electrochemistry

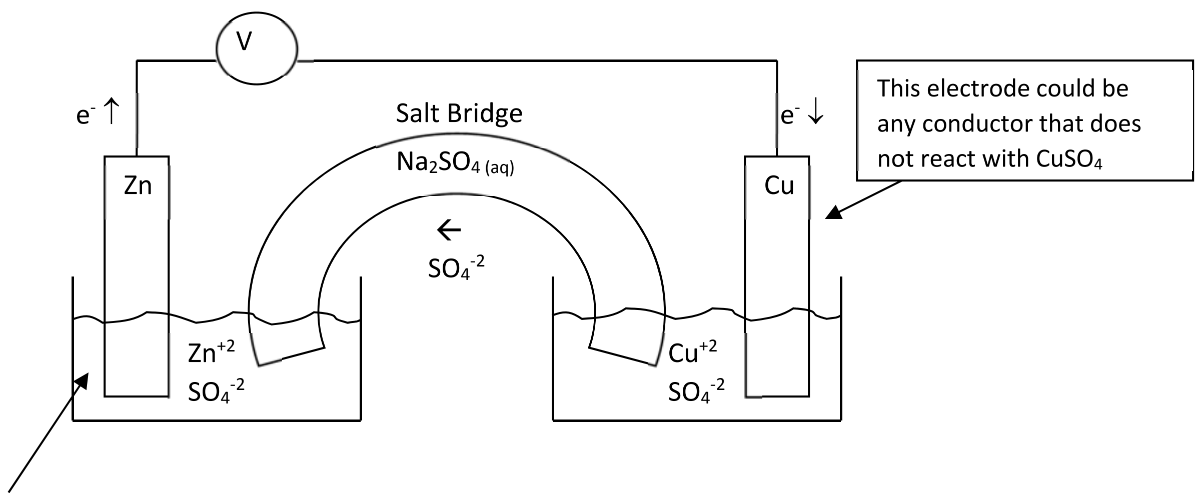
- the study of the interchange of electrical and chemical energy
- you can use a chemical reaction to produce an electric current
- you can use an electric current to produce a chemical change

Review

- <u>oxidation</u>- the loss of electrons (reducing agent)
- <u>reduction</u>- the gain of electrons (oxidizing agent)
- <u>half-reaction</u>- an equation showing either the oxidation or reduction half of a redox reaction

Galvanic Cell (Luigi Galvani, 1737-1798)

- a device in which chemical energy is changed into electrical energy
- makes use of a <u>spontaneous</u> redox reaction
- oxidation and reduction must occur in separate chambers



$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

or

$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$

Oxidation ½ Cell $\mathbf{Zn \rightarrow Zn^{+2} + 2e^-}$

- Zn goes into solution as Zn^{+2} (this electrode loses mass
- <u>electrons</u> flow <u>out</u> of this electrode
- the electrode where <u>oxidation</u> occurs is called the <u>anode</u>

Reduction ½ Cell $\mathbf{Cu^{+2} + 2e^- \rightarrow Cu}$

- electrons flow into this electrode
- the positive copper ions are attracted to it and reduced out of solution as Cu
- this electrode gains mass
- the electrode where reduction occurs is called the cathode

Anode – oxidation occurs here
- loses mass

Cathode – reduction occurs here
- gains mass

(AnOx, Red Fat Cat)

Salt Bridge

- the anion common to both cells and the bridge flows through it
- it flows from the reduction ½ cell to the oxidation ½ cell
- this keeps the solutions in both ½ cells neutral

Cell Potential

- this is the force "pulling the electrons from the oxidizing ½ cell to the reducing ½ cell
- this is measured in volts by a voltmeter (Alessandro Volta)

Standard Reduction Potential ($\mathbf{E^0}$)

- the potential for a reduction ½ reaction under standard conditions (1M concentration)
- measured against the potential for the reduction of Hydrogen
  - o $2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0.00$
  - o compared to itself, it's difference is "0 volts"
- for an oxidation ½ reaction
  - o find the reduction ½ reaction for that substance
  - o reverse the reaction and change the sign on the E^0
- the potential of a chemical cell is the sum of the potentials for the oxidation and reduction ½ reactions that are occurring.

Ex. $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$ E^0

Oxidation: $Zn \rightarrow Zn^{+2} + 2e^-$ 0.76V

Reduction: $Cu^{+2} + 2e^- \rightarrow Cu$ 0.34V

$E^0_{cell} = 1.10V$

- the number of electrons lost must equal the number of electrons gained

Ex. $Fe^{+3} + Cu \rightarrow Cu^{+2} + Fe^{+2}$

Ox $Cu^0 \rightarrow Cu^{+2} + 2e^-$

Red $Fe^{+3} + 1e^- \rightarrow Fe^{+2}$ (must be multiplied by 2)

so

Ox $Cu^0 \rightarrow Cu^{+2} + 2e^-$ -0.34V

Red $2Fe^{+3} + 2e^- \rightarrow 2Fe^{+2}$ +0.77V (DO NOT multiply E^0)

$E^0_{cell} = +0.43V$

- to be spontaneous a cell reaction must have a positive E^0 ($+E^0$ = spontaneous)

If you are given two half reactions, how can you tell what will be oxidized and what will be reduced?

- remember E^0 must be positive if a reaction is going to occur

Ex. given: $Ag^+ + e^- \rightarrow Ag$ $E^0 = 0.80v$

$2Fe^{+3} + 2e^- \rightarrow 2Fe^{+2}$ $0.77V$

What reaction will occur? (To get a positive E^0, leave Ag alone and reverse Fe^{+3})

Red: $Ag^+ + e^- \rightarrow Ag$ $E^0 = 0.80v$

Ox: $Fe^{+2} \rightarrow Fe^{+3} + e^-$ $-0.77V$

$E^0_{cell} = +0.03V$

So: $Fe^{+2} + Ag^+ \rightarrow Fe^{+3} + Ag$

Faraday ($\mathfrak{I}$)

- is the charge on one mole of electrons
- is 96,500 coluombs
  - coulomb = the quantity of electricity transferred by a current of 1 ampere in 1 second
- The cell potential (E) is related to the free energy difference (ΔG) for a chemical reaction
  - $\Delta G = -n\mathfrak{I}E$ ***found on the equation sheets

ex 17.3 Using table 17.1 (Standard Electrode Potentials), calculate ΔG^0 for the reaction

$Fe + Cu^{+2} \rightarrow Cu + Fe^{+2}$

Is the reaction spontaneous?

Dependence of E on Solution Concentration

- when you calculate E^0, all solutions must be in standard state (1M)
- if ther are other than 1M, the E_{cell} will not be equal to E^0_{cell}
- if a change in concentration favors the forward reaction, E increases
- if a change in concentration favors the reverse reaction, E decreases

Ex. 17.5 For the reaction

$$2Al(s) + 3Mn^{+2}_{(aq)} \rightarrow 2Al^{+3}_{(aq)} + 3Mn_{(s)},\ E^0 = 0.48V$$

Predict whether E_{cell} is larger or smaller than E^0 when

A) $[Al^{+3}] = 2.0M$
$[Mn^{+2}] = 1.0M$

B) $[Al^{+3}] = 1.0M$
$[Mn^{+2}] = 3.0M$

Nernst equation (Hermann Nernst 1864-1941)

- this equation is used to calculate E for a cell at nonstandard conditions
- it relates E_{cell} to E^0_{cell}

$$E = E^0 - \frac{.0592}{n}\log Q$$

****Found on equation sheets**

where n = the number of moles of electrons transferred
Q = the reaction quotient ($[P]^{coeff} / [R]^{coeff}$)

Ex. for the cell
$2Al_{(s)} + 3Mn^{+2}_{(aq)} \rightarrow 2Al^{+3}_{(aq)} + 3Mn_{(s)}$,
if $[Al^{+3}] = 1.5M$ $[Mn^{+2}] = 0.5M$ Calculate E

For any cell:

- E or E^0 = the maximum potential before any current has flowed
- as the cell discharges and []'s change, R $\rightarrow$ P
  less more
- the cell will discharge until the reaction reaches equilibrium
- at equilibrium, E=0 (and ΔG=0)
- at this point the battery is DEAD!!

Electrolysis

- this is using an electric current to make a nonspontaneous redox reaction occur
- this type of cell is called an “Electrolytic Cell”
- the amount of chemical change that occurs depends on the amount of current and how long that current flows.
- current is measured in amperes
    - 1amp = 1coulomb/second

Ex. What mass of copper is plated out when a current of 10.0 amps passes through a solution containing $Cu^{+2}_{(aq)}$ for 30.0 minutes?

1. converting amps and time to coulombs:

2. converting coulombs to $\mathfrak{I}$ to mole e^-

3. Using moles to calculate moles of Cu formed

4. mol Cu $\rightarrow$ gCu

Ex. 17.9 How long must a current of 5.00A be applied to a solution of Ag^+ to produce 10.5g of silver metal?