Chapter 20 - Electrochemistry

• 20.1 Oxidation States & Oxidation-Reduction Reactions

- oxidation number is the charge an atom will take in order to get to its nearest octet/noble gas
    -- metals will loose electrons
    -- nonmetals will gain them
    -- metalloids can do either
- H tends toward +1 and O tends toward -2 although both can have other oxidation states/numbers as well
- see Sections 4.4 and 8.5 if you need to review
- for redox reaction we have a reducing and an oxidizing agent
    -- reducing agent gets oxidized which means it looses the electrons
    -- oxidizing agent gets reduced so it will take the electrons from the reducing agent

• 20.2 Balancing Redox Equations

- Example 1 - Balance the following redox reaction given the solution is acidic:

$$Br_{2(l)} + SO_{2(g)} \rightarrow Br^-_{(aq)} + SO^{2-}_{4(aq)}$$

-- step 1 - separate the eqn into the ox'n and red'n half-rxns

$$Br_{2(l)} \rightarrow Br^-_{(aq)}$$

$$SO_{2(g)} \rightarrow SO^{2-}_{4(aq)}$$

-- step 2 - balance the non-O and H atoms

$$Br_{2(l)} \rightarrow 2Br^-_{(aq)}$$

$$SO_{2(g)} \rightarrow SO^{2-}_{4(aq)}$$

-- step 3 - determine the ON of the non-O and H atoms and balance charge with e-

$$2e^- + \underbrace{Br_{2(l)}}_{ON=0} \rightarrow \underbrace{2Br^-_{(aq)}}_{ON=-1}$$

$$\underbrace{SO_{2(g)}}_{ON=+4} \rightarrow \underbrace{SO^{2-}_{4(aq)}}_{ON=+6} + 2e^-$$

-- step 4 - balance charge for each half-rxn using H^+

$$2e^- + Br_{2(l)} \rightarrow 2Br^-_{(aq)}$$

$$SO_{2(g)} \rightarrow SO^{2-}_{4(aq)} + 2e^- + 4H^+$$

-- step 5 - mass balance O and H with water

$$2e^- + Br_{2(l)} \rightarrow 2Br^-_{(aq)}$$

$$2H_2O + SO_{2(g)} \rightarrow SO^{2-}_{4(aq)} + 2e^- + 4H^+$$

-- step 6 - use a constant to make sure electrons cancel and add the two equations

$$2e^- + Br_{2(l)} \rightarrow 2Br^-_{(aq)}$$

$$2H_2O + SO_{2(g)} \rightarrow SO^{2-}_{4(aq)} + 2e^- + 4H^+$$

$$\cancel{2e^-} + Br_{2(l)} + 2H_2O + SO_{2(g)} \rightarrow 2Br^-_{(aq)} + SO^{2-}_{4(aq)} + \cancel{2e^-} + 4H^+$$

$$Br_{2(l)} + 2H_2O + SO_{2(g)} \rightarrow 2Br^-_{(aq)} + SO^{2-}_{4(aq)} + 4H^+$$

-- you can check and make sure your equation is correct by looking to make sure both sides of the equation are balanced both by charge and number of atoms

- Example 2 - Balance the following reaction in basic solution:

$$ZrO(OH)_{2(s)} + SO_{3(aq)}^{2-} \rightarrow Zr_{(s)} + SO_{4(aq)}^{2-}$$

-- step 1 - separate the eqn into the ox'n and red'n half-rxns

$$ZrO(OH)_{2(s)} \rightarrow Zr_{(s)}$$

$$SO_{3(aq)}^{2-} \rightarrow SO_{4(aq)}^{2-}$$

-- step 2 - balance the non-O and H atoms - NA

-- step 3 - determine the ON of the non-O and H atoms and balance charge with e-

$$4e^- + \underbrace{ZrO(OH)_{2(s)}}_{ON=+4} \rightarrow \underbrace{Zr_{(s)}}_{ON=0}$$

$$\underbrace{SO_{3(aq)}^{2-}}_{ON=+4} \rightarrow \underbrace{SO_{4(aq)}^{2-}}_{ON=+6} + 2e^-$$

-- step 4 - balance charge for each half-rxn using OH^-

$$4e^- + ZrO(OH)_{2(s)} \rightarrow Zr_{(s)} + 4OH^-$$

$$2OH^- + SO_{3(aq)}^{2-} \rightarrow SO_{4(aq)}^{2-} + 2e^-$$

-- step 5 - mass balance O and H with water

$$H_2O + 4e^- + ZrO(OH)_{2(s)} \rightarrow Zr_{(s)} + 4OH^-$$

$$2OH^- + SO_{3(aq)}^{2-} \rightarrow SO_{4(aq)}^{2-} + 2e^- + H_2O$$

-- step 6 - use a constant to make sure electrons cancel and add the two equations

$$H_2O + 4e^- + ZrO(OH)_{2(s)} \rightarrow Zr_{(s)} + 4OH^-$$

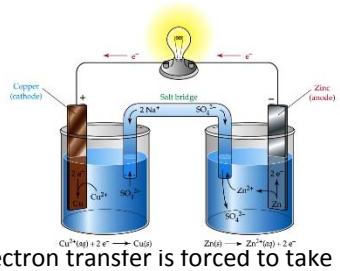
$$2 \bullet \left(2OH^- + SO_{3(aq)}^{2-} \rightarrow SO_{4(aq)}^{2-} + 2e^- + H_2O\right)$$

$$\cancel{H_2O} + \cancel{4e^-} + ZrO(OH)_{2(s)} + \cancel{4OH^-} + 2SO_{3(aq)}^{2-} \rightarrow Zr_{(s)} + \cancel{4OH^-} + 2SO_{4(aq)}^{2-} + \cancel{4e^-} + \cancel{2}H_2O$$

$$ZrO(OH)_{2(s)} + +2SO_{3(aq)}^{2-} \rightarrow Zr_{(s)} + 2SO_{4(aq)}^{2-} + H_2O$$

• 20.3 Voltaic Cells

- electrochemistry: branch of chemistry that examines the connection btwn chemical and electrical energy
- galvanic or voltaic cell



-- defn: a device in which electron transfer is forced to take place thru an external pathway rather than directly btwn reactants

-- components:

--- electrodes: metal wires or plates connected by a conducting wire

--- salt bridge: U-shaped tube filled with an inert salt gel (completes the circuit) and allows e-'s to flow between the 2 cells

--- cathode & anode

-- rxn in this figure: $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Cu_{(s)} + Zn_{(aq)}^{2+}$

-- anode

--- half cell where oxidation takes place

--- in this case: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

--- Zn is the reducing agent

-- cathode

--- half cell where reduction takes place

--- in this case: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

--- Cu^{2+} is the oxidizing reagent

-- electrons flow from the anode to the cathode

--- this should make sense since our anode produces e-'s which can then be used to reduce a species at our cathode

--- also, since our anode is negative and our cathode is positive it is logical the negative e-'s want to flow to the positive cathode

- Example: A voltaic cell with a basic electrolyte is based on the oxidation of $Cd_{(s)}$ to $Cd(OH)_{2(s)}$ and the reduction of MnO_4^- to $MnO_{2\,(s)}$. Write the half-rxns, the balaced cell reaction and draw a diagram of the cell.

$$anode: \quad 3\left(2OH^-_{(aq)} + Cd_{(s)} \rightarrow Cd(OH)_{2(s)} + 2e^-\right)$$

$$cathode: 2\left(2H_2O + 3e^- + MnO^-_{(aq)} \rightarrow MnO_{2(s)} + 4OH^-_{(aq)}\right)$$

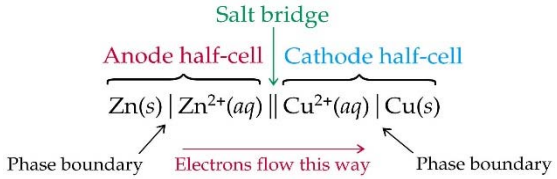
$$\cancel{6OH^-_{(aq)}} + 3Cd_{(s)} + 4H_2O + \cancel{6e^-} + 2MnO^-_{(aq)} \rightarrow 3Cd(OH)_{2(s)} + \cancel{6e^-} + 2MnO_{2(s)} + 2\cancel{OH^-_{(aq)}}$$

$$3Cd_{(s)} + 4H_2O + 2MnO^-_{(aq)} \rightarrow 3Cd(OH)_{2(s)} + 2MnO_{2(s)} + 2OH^-_{(aq)}$$

Shorthand Notation for Voltaic Cells

- we always write the cell such that it demonstrates the flow of e-'s

-- represent the anode first and then the cathode



- we also often use a plantinum electrode to complete either the cathode/anode

-- anode: $Pt_{(s)} \left| Sn^{2+}_{(aq)}, Sn^{4+}_{(aq)} \right\| Ag^+_{(aq)} \left| Ag_{(s)} \right|$

-- cathode: $Pb_{(s)} \left| Pb^{2+}_{(aq)} \right\| Br_{2(l)} \left| Br^-_{(aq)} \right| Pt_{(s)}$

• 20.4 Cell Potential Under Standard Conditions

- electromotive force or cell potential (E_{cell}): voltage btwn electrodes of a voltaic cell

-- defn: is the driving force that pushes electrons from the anode to the cathode

-- it has units of volts

-- this force related to the amount of work the cell is capable of

-- SI unit for electrical charge is a coulomb, C (e.g. 1 e- = 1.602×10^{-19}C)

- total charge, C = nF where is C is the total charge, n is the number of e- moles and F is the Faraday constant, 9.65×10^4 C/mol

- standard potential (E°): the emf of a half-rxn written in its reduction form where all the species are in their standard states with their concentrations or partial pressures being 1M or 1 bar.

- standard cell potential, $E^o_{cell} = E^o_{cathode} - E^o_{anode}$ or $E^o_{cell} = E^o_{ox} + E^o_{red}$

-- standard potentials are always written as reduction half-rxns so we change the sign of the oxidation

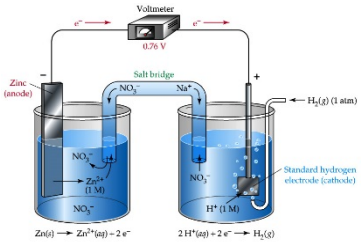
potential and reverse the order of the half-rxn

-- standard hydrogen electrode (S. H. E.)

--- all standard potentials are referenced to the hydrogen half-rxn

--- ox'n: $H_{2(g)} \rightarrow 2H^+ + 2e^- \quad E^o = 0.00V$

--- red'n: $2H^+ + 2e^- \rightarrow H_{2(g)} \quad E^o = 0.00V$



-- oxidation/reduction strength - measured against S. H. E.

--- strong oxidizing agents more willing take e⁻'s e.g. F

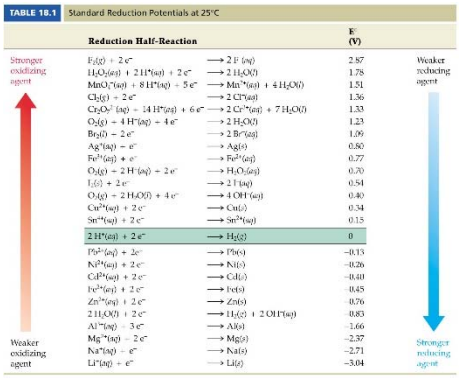
---- they are EN and have higher EA

---- standard cell potential is positive

--- strong reducing agents are more willing to loose e⁻'s e.g. Li^+

---- they are less EN

---- standard cell potential is negative



-- Example: Given the information below determine the voltage and write the balanced equation of the following voltaic cell.

$$Ag_{(aq)} + e^- \rightarrow Ag_{(s)} \qquad E^o = 0.80\,V$$

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \qquad E^o = -0.76\,V$$

Answer: If the cell is voltaic, it must be spontaneous so E > 0. Therefore, we must be oxidizing Zn – so we need to reverse the equation to oxidation for zinc and reverse the sign of the emf.

$$2\left(Ag_{(aq)} + e^- \rightarrow Ag_{(s)}\right) \qquad E^o = 0.80\,V$$

$$\underline{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E^o = -(-0.76\,V)}$$

$$2Ag_{(aq)} + Zn_{(s)} \rightarrow 2Ag_{(s)} + Zn^{2+}_{(aq)} \qquad E^o = 1.56V$$

• 20.5 Free Energy & Redox Reactions

- free energy: $\Delta G = -nFE_{cell}$

-- ΔG is called the Gibbs free-energy change and tells us whether a process is spontaneous (will happen without help)

-- negative because the cell is performing work on its surroundings

--- when ΔG < 0 the system is spontaneous

--- when ΔG > 0 the system is nonspontaneous

-- therefore if ΔG < 0 and E_{cell} > 0 we have a spontaneous reaction

-- conversion: 1 C*volt = 1 J

-- Ex. Calculate the E_{cell} for the following reaction and determine if the reaction is spontaneous.

a.) $2Cu^+ \rightarrow Cu^{2+} + Cu_{(s)} \quad \Delta G^o_{rxn} = -34.5kJ$

$$E^{\circ}_{cell} = -\frac{\Delta G^{o}_{rxn}}{nF} = -\frac{-34.5kJ \times \frac{1000J}{kJ} \times \frac{1C \cdot V}{1J}}{1\,mol\ e^{-} \times 9.65 \times 10^{4}\ {}^{C}/_{mol}} = \boxed{0.358\,V}$$

this system is spontaneous

b.) $Ag_{(s)} + Fe^{3+} \rightarrow Ag^{+} + Fe^{2+} \quad \Delta G^{o}_{rxn} = 2.9kJ$

$$E^{\circ}_{cell} = -\frac{\Delta G^{o}_{rxn}}{nF} = -\frac{2.9kJ \times \frac{1000J}{kJ} \times \frac{1C \cdot V}{1J}}{1\,mol\ e^{-} \times 9.65 \times 10^{4}\ {}^{C}/_{mol}} = \boxed{-0.0301\,V}$$

this system is nonspontaneous

- electrolytic cell: requires an external source to cause the flow of e-'s

-- electrolytic cells are non-spontaneous, $\Delta G > 0$ $E < 0$

-- voltaic cells are always spontaneous, $\Delta G < 0$ $E > 0$

• 20.6 Cell Potential Under Nonstandard Conditions

- Nernst Eqn:

for aA + bB $\rightarrow$ cC + dD

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

- Example: Calculate the E_{cell} at 298K for the cell based on the following:

$$Fe^{3+}_{(aq)} + Cr^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Cr^{3+}_{(aq)}$$

$[Fe^{3+}] = [Cr^{2+}] = 1.50 \times 10^{-3}M$, $[Fe^{2+}] = [Cr^{3+}] = 2.5 \times 10^{-4}M$

Using Appendix E in your book

$Cr^{3+} + e^{-} \rightarrow Cr^{2+} \quad E^{o} = -0.41V$

$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad E^{o} = 0.770V$

$$Fe^{3+}_{(aq)} + Cr^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Cr^{3+}_{(aq)} \qquad E^{o} = 0.770 + 0.41 = 1.18V$$

$$E_{cell} = 1.18V - \frac{0.0592}{1} \log \frac{[2.5 \times 10^{-4}]^{2}}{[1.50 \times 10^{-3}]^{2}} = 0.938\,V$$

• 20.7 – 20.9 – Skip!