Chapter 20 – Electrochemistry

Kahoot!

1. The oxidation state of N in NH_4^+ is ___. +1, 0, -1, -3
2. The oxidation state of Mn in MnO_4^- is ___. -1, +2, +4, +7
3. The reducing agent in Zn + Cu^{2+} -> Zn^{2+} + Cu is ___. Zn, Cu^{2+}, Zn^{2+}, Cu
4. The oxidizing agent in Zn + Cu^{2+} -> Zn^{2+} + Cu is ___. Zn, Cu^{2+}, Zn^{2+}, Cu
5. To balance MnO_4^- -> Mn^{2+}, ___ electrons need to be added to ___ side. 5; product, 2; product, 2; reactant, 5; reactant
6. The purpose of the salt bridge is to ___. Provide H+ ions needed to balance charges, maintain neutrality by allowing the flow of ions, serve as the site for oxidation to occur, serve as the site for reduction to occur.
7. Reduction occurs at the ___. anode, cathode, electrode, electrolytic cell
8. Oxidation occurs at the ___. anode, cathode, electrode, electrolytic cell
9. Which is the strongest oxidizing agent? F_2, Cl_2, Br_2, I_2
10. Which is the strongest reducing agent? Zn, Al, Na, Li
11. If Cl_2 -> $2Cl^-$ has E = +1.36V, and I_2 -> $2I^-$ has E = +0.54V then ___. Cl_2 will reduce I^- to I_2, Cl_2 will oxidze I^- to I_2, I_2 will reduce Cl^- to Cl_2, I_2 will oxidze Cl^- to Cl_2
12. If the value of Ecell is positive then the reaction is ___. at equilibrium, spontaneous, nonspontaneous, very fast
13. A ___ cell uses an external energy source to produce a redox reaction. galvanic, voltaic, electrolytic, anionic
14. The Nernst equation is most useful when ___ are nonstandard. Oxidizing agents, reducing agents, ion concentrations, temperatures

Whiteboard Examples:

Balancing Redox Example I:
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

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

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

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

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

-- 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

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

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

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

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

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

-- 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-

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

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

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

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

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

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

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

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

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

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

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

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

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

Voltaic 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.

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

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

$$\cancel{6OH^-_{(aq)}} + 3Cd_{(s)} + 4H_2O + \cancel{6e^-} + 2MnO^-_{(aq)} \rightarrow 3Cd(OH)_{2(s)} + \cancel{6e^-} + 2MnO_{2(s)} + 2\cancel{8}OH^-_{(aq)}$$

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

E_{cell} 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.

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

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

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

Gibbs Example: Calculate the E_{cell} for the following reaction and determine if the reaction is spontaneous.

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

$$E^\circ_{cell} = -\frac{\Delta G^o_{rxn}}{nF} = -\frac{-34.5kJ \times \frac{1000J}{kJ} \times \frac{1C\bullet V}{1J}}{1\,mol\ e^- \times 9.65\times10^4\ C/_{mol}} = \boxed{0.358\,V}$$

this system is spontaneous

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

$$E^\circ_{cell} = -\frac{\Delta G^o_{rxn}}{nF} = -\frac{2.9kJ \times \frac{1000J}{kJ} \times \frac{1C\bullet V}{1J}}{1\,mol\ e^- \times 9.65\times10^4\ C/_{mol}} = \boxed{-0.0301\,V}$$

this system is nonspontaneous

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

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

$[Fe^{3+}] = [Cr^{2+}] = 1.50x10^{-3}$M, $[Fe^{2+}] = [Cr^{3+}] = 2.5x10^{-4}$M

Using Appendix E in your book

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

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

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

$$E_{cell} = 1.18V - \frac{0.0592}{1}\log\frac{[2.5\times10^{-4}]^2}{[1.50\times10^{-3}]^2} = 0.938\,V$$