Reading: Moore chapter 19, sections 15.6-15.12
Questions for Review and Thought: 36, 40, 42, 44, 50, 54, 60, 64, 70

Key Concepts and Skills:
• definition of ampere, battery, concentration cell, coulomb, electrolysis, Nernst equation, primary battery, secondary battery
• Calculate $\Delta G°$ and K_{eq} from the value of $E°_{cell}$. Use the Nernst equation to calculate E_{cell} from the concentrations of redox reactants and products and vice-versa. Calculate the quantity of product formed at an electrode given the current passing through the cell and the time during which the current flows.

Lecture Topics:
I. Relationship between cell voltage, $E°_{cell}$ and Gibbs Free Energy, $\Delta G°$
Note: "Free" energy is energy available to do work and is related to the cell voltage (potential energy difference between the electrodes)
Work = Force x distance
Electrical work = charge x potential energy difference
J oules = coulombs x Joules/coulomb   remember: 1V = 1J/C

Useful ➔ charge on one mole of electrons: **9.64 x 10^4 coulombs/mol e$^-$ = F**
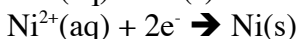**F** is the Faraday constant

Thus, electrical work = quantity of charge transferred x $E°_{cell}$ = n **F** $E°_{cell}$
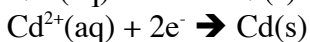Where n is the number of moles of electrons transferred, and n **F** is the total charge transferred.
Electrical work = **$\Delta G°$= -n F $E°_{cell}$**
Note: $\Delta G°$ is always negative for product-favored processes (since $E°_{cell}$ >0)

Example: Calculate $\Delta G°$ for the following reaction:
$Ni^{2+}(aq) + Cd(s)$ ➔ $Ni(s) + Cd^{2+}(aq)$
$Ni^{2+}(aq) + 2e^-$ ➔ $Ni(s)$ $E°_{red}$= -0.25V better oxidant, thus cathode
$Cd^{2+}(aq) + 2e^-$ ➔ $Cd(s)$ $E°_{red}$= -0.40 V
Note that 2 moles of electrons are transferred in this process! $E°_{cell}$= 0.15V
$\Delta G°$= -n F $E°_{cell}$ = -(2 mol e$^-$) (9.64x10^{4}C/mol)(0.15 J/C) = -28,950 J/mol = -28.95 kJ/mol

•Since we know $\Delta G°$= -RT ln K_{eq} and $\Delta G°$= -n F $E°_{cell}$
equating gives   -RT ln K_{eq}=-n F $E°_{cell}$
Nernst Equation: **$E°_{cell}$= RT/n F ln K_{eq}**
Since R=8.314 J/molK; F=9.64 x 10^4 coulombs/mol e$^-$; T=25°C=298K

At 25°C, this is: **$E°_{cell}$= 0.0257V/n ln K_{eq}**
Or   **$E°_{cell}$= 0.0592V/n log K_{eq}**

Example: Determine K_{eq} at 25°C for
$Hg^{2+}(aq) + 2I^-(aq)$ ➔ $Hg(l) + I_2(s)$

$Hg^{2+} + 2e^- \rightarrow Hg(l)$ $E°_{red} = 0.855V$ better oxidant, thus cathode
$I_2 + 2 e^- \rightarrow 2 I^- (aq)$ $E°_{red} = 0.535 V$
$E°_{cell} = E°_{ox} + E°_{red} = 0.855V + (-0.535V) = 0.32 V$
2 electrons transferred in the process, thus
$$E°_{cell} * n/0.052V = log K_{eq}$$
$$K_{eq} = 6.3 \times 10^{10}$$
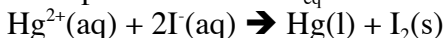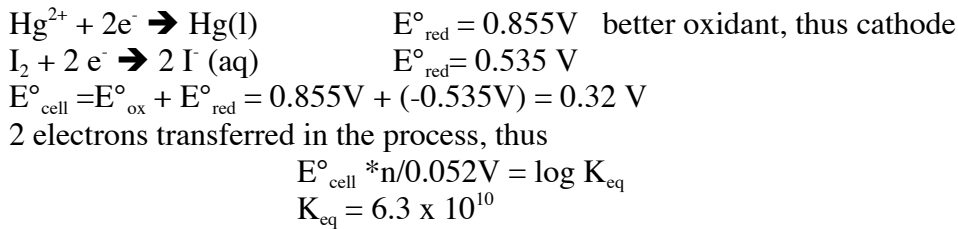
II. Concentration Effects on Cell Voltage

Since $E°_{cell}$ indicates **standard conditions**, i.e., gases at 1 bar; solutes at 1M concentration, what is the value of E_{cell} under non-standard conditions?

•As reactant concentrations decrease in a cell, the cell voltage drops and finally reaches zero when the reactants and products are at equilibrium (at this point there is no **net** transfer of electrons, although a dynamic equilibrium is still operative)
•Use the Nernst equation to relate the real-time voltage of a Voltaic cell to the concentration of reactants or products:

Remember: $\Delta G = \Delta G° + RTlnQ$
Where Q is the reaction quotient and has the same form as K_{eq}
$\Delta G = -n F E_{cell}$
$\Delta G° = -n F E°_{cell}$ under **standard conditions**
Thus $\Delta G = -n F E°_{cell} + RTlnQ = -n F E_{cell}$
And $E_{cell} = E°_{cell} - RT/nF \ lnQ$
As above, more conveniently: $E_{cell} = E°_{cell} - 0.0592V/n \ logQ$ @ 25°C
This equation is used to calculate the voltage in an electrochemical cell under non-standard conditions.
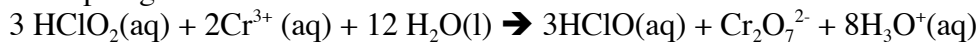
Example: given
$3 HClO_2(aq) + 2Cr^{3+} (aq) + 12 H_2O(l) \rightarrow 3HClO(aq) + Cr_2O_7^{2-} + 8H_3O^+(aq)$
$E°_{cell} = 0.31V$; $E_{cell} = 0.15V$; $[Cr_2O_7^{2-}]=0.8M$; $[HClO_2]=0.15M$; $[HClO]=0.2M$, pH=0
Calculate $[Cr^{3+}]$.
Note: $Q=[H_3O^+]^8[Cr_2O_7^{2-}][HClO]^3/[HClO_2]^3[Cr^{3+}]^2$ $pH=-log[H_3O^+]$
$[Cr^{3+}]=1\times10^{-8}M$

Application: Concentration cells and pH meters

A concentration cell is a cell in which the voltage is generated because of a difference in concentration.
Consider two beakers with the same metal and electrolyte solutions, but different concentrations of electrolyte. We predict that charge (electrons) will flow in a direction to offset the concentration difference between the two beakers
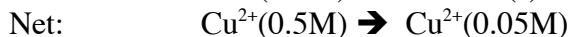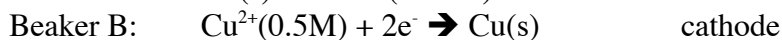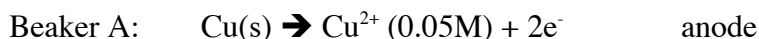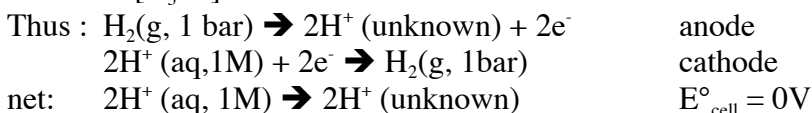
Beaker A: $Cu(s) \rightarrow Cu^{2+} (0.05M) + 2e^-$ anode
Beaker B: $Cu^{2+}(0.5M) + 2e^- \rightarrow Cu(s)$ cathode
Net: $Cu^{2+}(0.5M) \rightarrow Cu^{2+}(0.05M)$
$E°_{cell} =0 V$ since under standard conditions there is no concentration difference, with all solutes at 1M.

$E_{cell}= E°_{cell} - 0.0592/n \log Q = -0.0592/2$ mol e⁻ $* \log 0.05M/0.5M = 0.0296$ V
Thus, this is a spontaneous process, and current will flow in an electrochemical cell constructed from the two beakers. The [Cu^{2+}] in beaker A will increase and the [Cu^{2+}] in beaker B will decrease till both beakers have equal concentrations, when Q=0, $E_{cell}=E°_{cell}=0$.

pH meters are concentration cells!
Standard hydrogen Electrode (1M H_3O^+) coupled to another hydrogen electrode of unknown [H_3O^+]< 1M
Thus : H_2(g, 1 bar) ➔ $2H^+$ (unknown) + 2e⁻   anode
        $2H^+$ (aq,1M) + 2e⁻ ➔ H_2(g, 1bar)   cathode
net: $2H^+$ (aq, 1M) ➔ $2H^+$ (unknown) $E°_{cell} = 0V$

$E_{cell}= E°_{cell} - .0592/2$ mol e⁻ $*\log [H^+]^2_{(unknown)} / [1M]^2 = -0.0592/2 \log [H_3O]^2$
$\mathbf{E_{cell}/ .0592\ V = pH}$ since pH=-log[H_3O^+] and log[H_3O^+]^2 = 2log[H_3O^+]
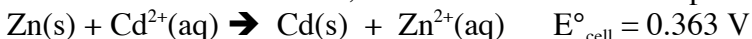
III. **Counting electrons**

Given the measured current running through a galvanic cell, find the mass of solids deposited at the electrodes.
Recall: Charge = current x time;   1 ampere of current = 1 coulomb/second
For current I (in amperes),
        the number of moles of e⁻ = I t / 96,485 C/mol = I t / F

Example: for the following cell, a current of 1.45 Amps is observed to flow for 2.6 h. how much Zn metal is lost, how much Cd metal is deposited on the respective electrodes?
$Zn(s) + Cd^{2+}(aq)$ ➔ $Cd(s) + Zn^{2+}(aq)$ $E°_{cell} = 0.363$ V
$Zn(s)$ ➔ Zn^{2+} (aq) + 2e⁻   2 moles of electrons released for each mole Zn consumed
Cd^{2+} (aq) + 2 e⁻ ➔ $Cd(s)$ 2 moles of electrons consumed for each mole of Cd formed

I t / 96,485 C/mol = # moles e⁻ = (1.45 C/s)(9360s)/ 96485C/mol = 0.1404 mol e⁻
 0.1404 mol e⁻ * 1 mol Zn / 2 mol e⁻ = .0703 mol Zn consumed
Zn (65.3 g/mol) * 0.0703 mol Zn = 4.59 g Zn lost
0.1404 mol e⁻ * 1 mol Cd / 2 mol e⁻ = .0703 mol Cd formed
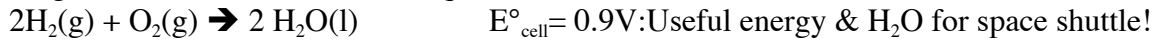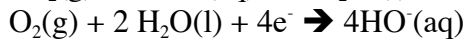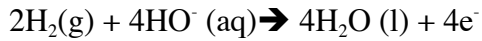Cd(112.48 g/mol) * 0703 mol Cd = 7.9 g Cd formed.

IV. Applications of Electrochemistry

Batteries - Voltaic Cells
Primary Batteries – electrochemical reactions cannot be easily reversed: Alkaline batteries are an example: $Zn(s) +2MnO_2(s) + H_2O(aq)$ ➔ $ZnO(aq) + 2MnO(OH)(s)$
Secondary Batteries- are rechargeable by reversing the electron flow. Anode and cathode reactions are reversed and reactants are regenerated. Nickel-Cadmium batteries are an example: $Cd(s) + 2NiO(OH)(s) +2H_2O(l)$ ➔ $Cd(OH)_2$ (s) + $2Ni(OH)_2(s)$

A Fuel cell is an electrochemical cell that converts the chemical energy of fuels directly into electrons. In a typical fuel cell, a contiuous flow of hydrogen is oxidized to H_2O and a continuous flow of oxygen is reduced to H_2O in basic conditions:

$2H_2(g) + 4HO^-(aq) \rightarrow 4H_2O(l) + 4e^-$

$O_2(g) + 2 H_2O(l) + 4e^- \rightarrow 4HO^-(aq)$

$2H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$ $E°_{cell} = 0.9V$:Useful energy & H_2O for space shuttle!
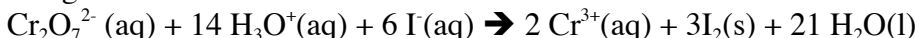
In **Electrolysis**, electrons forced into an electrochemical cell from a source of electric current can cause reactant-favored processes to form products. This method is useful in the production and purification of metals. Consider molten NaCl:

$2Na^+ + 2Cl^- \rightarrow 2Na(l) + Cl_2(g)$ $E°_{cell} = -1.35$ V; if you supply 2V <u>against</u> the electrodes, you can force the reduction of Na^+ and the oxidation of Cl^-. What is produced during the electrolysis of brine (NaCl, aq)?

Additional problems

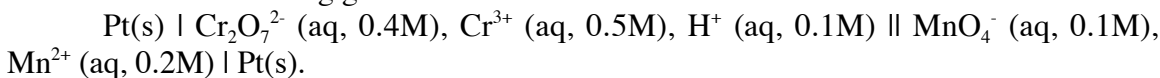1. A galvanic cell is constructed in which the overall reaction is
$Cr_2O_7^{2-}$ (aq) + 14 H_3O^+(aq) + 6 I^-(aq) ➔ 2 Cr^{3+}(aq) + 3I_2(s) + 21 H_2O(l)
    (a) calculate $E°_{cell}$ for this cell
    (b) At pH 0, with $[Cr_2O_7^{2-}]$ = 1.5M and $[I^-]$=0.40M, the cell voltage is found to equal
        0.87 V. Calculate $[Cr^{3+}]$ in the cell.

2. What mass of platinum would be plated on an electrode from the electrolysis of a $Pt(NO_3)_2$ solution with a current of 0.500A for 55 min?

3. Consider the following galvanic cell:
        Pt(s) | $Cr_2O_7^{2-}$ (aq, 0.4M), Cr^{3+} (aq, 0.5M), H^+ (aq, 0.1M) || MnO_4^- (aq, 0.1M),
Mn^{2+} (aq, 0.2M) | Pt(s).

    (a) Write the half-reaction for the process occurring at the anode, the half reaction for
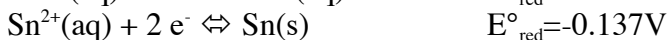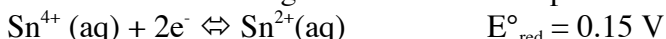   the process occurring at the cathode, and the overall reaction for the cell.
    (b) What is $E°_{cell}$ and K_{eq} for the overall cell reaction at 298K?
    (c) When the switch is initially closed, what is E_{cell} at 298K? Show all work.

4. A concentration cell contains Pb electrodes in equal volume solutions of Pb^{2+} of 0.432M and 0.000149M concentration. Draw the cell and label all of the components. Write the spontaneous half-reaction at each electrode and the overall cell process. What will be the cell potential when the cell is first connected? What will happen to the cell potential as current is allowed to flow? What will be the final concentration of Pb^{2+} in each compartment?

5. A galvanic cell contains two hydrogen gas electrodes. One is in a 1M H^+ solution and is the cathode; the other is in a solution of unknown pH. The cell potential is 0.0251V. What is the unknown pH?

6. Given the following standard reduction potentials:
Sn^{4+} (aq) + 2e^- ⇔ Sn^{2+}(aq) $E°_{red}$ = 0.15 V
Sn^{2+}(aq) + 2 e^- ⇔ Sn(s) $E°_{red}$=-0.137V
What is the standard reduction potential for the <u>half-reaction</u>: Sn^{4+}(aq) + 4e^- ⇔ Sn(s) ?
Be careful! This is not obtained from the algebraic sum of the two potentials listed above!
Convert each $E°_{red}$ first to $\Delta G°$, sum the $\Delta G°$ values, and then convert back to E°, taking care to note always the number of electrons involved for each process. Remember: reduction potential $E°_{red}$ is energy per unit charge (J/C), not energy!