Exam 2
Chem 311
Evans
Fall 2009

Name:

1-12: 2 pts each

1. Consider the following unbalanced redox equation:

$$Pb\ (s) + PbO_2\ (s) + 2\ HSO_4^-\ (aq) \rightarrow 2\ PbSO_4\ (s)$$

Which species is being oxidized?

A. HSO_4^-
B. Pb(s)
C. PbO_2(s)
D. $PbSO_4$(s)
E. There is not enough information to tell.

2. Which of the following statements best describes the movement of electrons in an electrochemical cell?

A. Electrons flow from the cathode to the anode through an external wire.
B. Electrons flow from the anode to the cathode through an external wire.
C. Electrons flow from the anode to the cathode through the salt bridge.
D. Electrons flow from the salt bridge to the cathode.
E. Electrons flow from the salt bridge to the anode.

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3. Which statement best describes what is happening at a zinc anode of a battery whose half reaction is

   A. Solid zinc loses two electrons to the solution and changes to the zinc ion. The electrons go into solution and the zinc ion travels through an external wire.
   B. Solid zinc loses two electrons to the salt bridge and changes to the zinc ion. The zinc ion goes into solution, but the electrons travel through the salt bridge to the cathode.
   C. Solid zinc loses two electrons to the cathode and changes to the zinc ion. The zinc ion goes into solution, but the electrons travel through an external wire.
   D. Solid zinc loses two electrons to the cathode and changes to the zinc ion. The electrons and the zinc ion travel through an external wire.
   E. Solid zinc loses two electrons to other zinc atoms and changes to the zinc ion. The zinc ion goes into solution.

4. Consider an electrochemical cell in which a reaction is proceeding spontaneously. If you were to apply a voltage greater than E_{cell} to that cell, which of the following changes could occur?

   A. Change in the direction of the flow of anions through the salt bridge from one half cell to the other half cell.
   B. Change in the direction of the flow of cations through the salt bridge from one half cell to the other half cell.
   C. Change in the direction of the flow of electrons through the external wire from one half cell to the other half cell.
   D. A and B
   E. A, B, and C

5. The half-cell potential of Ag/AgCl reference electrode provides a source of constant potential because

   A. the $[Ag^+]$ of the filling solution is 0.010 M
   B. the filling solution consists of a saturated KCl solution
   C. the Ag/AgCl half-reaction contains only solids
   D. junction potential is negligible
   E. it is a one electron transfer

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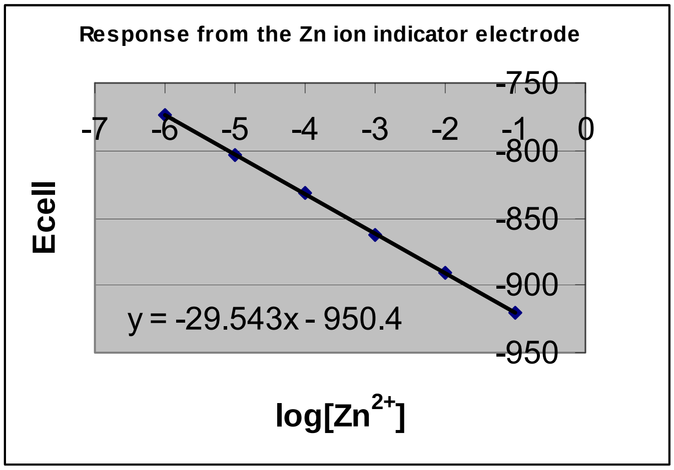
6. The following standard curve was obtained from a Zn indicator electrode that was constructed using a Ag/AgCl reference electrode. Measurement of an unknown solution of zinc acetate, $Zn(Ac)_2$, a soluble salt, produced a cell voltage of -876 mV. Using the data below, determine the $[Zn^{2+}]$ of the zinc acetate solution. The $[Zn^{2+}]$ is in units of M.



A) 0.0030 M
B) 0.00030 M
C) 0.020 M
D) 0.00020 M
E) -3 M

7. The analytical response of a pH meter is a function of what is occurring

A. at the anode
B. at the cathode
C. in the bulk solution
D. at the glass membrane
E) none of the above

8. The most accurate expression for the Ksp of $Ca(OH)_2$ is

A. $[Ca^{2+}][OH^-]^2$
B. $\mathcal{A}_{Ca2+}\mathcal{A}_{OH-}$
C. $[Ca^{2+}][OH^-]$
D. $\mathcal{A}_{Ca2+}\mathcal{A}_{OH-}{}^{2}$
E. $\mathcal{A}_{Ca2+}\mathcal{A}_{OH-}{}^{1/2}$

Name:

9. A Jones Reductor is a bed of zinc in a column used to
    A. prereduce an analyte without adding excess reductant that would interfere with the subsequent redox titration.
    B. prereduce an analyte without adding excess oxidant that would interfere with the subsequent redox titration.
    C. preoxidize an analyte without adding excess oxidant that would interfere with the subsequent redox titration.
    D. preoxidize an analyte without adding excess reductant that would interfere with the subsequent redox titration.
    E. prereduce the triiodide ion without adding excess reductant that would interfere with the subsequent redox titration.

10. In iodometric titrations it is common practice to add the starch indicator
    A. immediately after reaching the endpoint.
    B. immediately before reaching the endpoint.
    C. at the beginning of the titration.
    D. directly to the titrant.
    E. midway through the titration.

11. The Y^{4-} species of the EDTA system binds to most metal ions in the following stoichiometry.
    A. 1:2 M^{n+}/Y_4^-
    B. 2:1 M^{n+}/Y_4^-
    C. 1:1 M^{n+}/Y_4^-
    D. 3:1 M^{n+}/Y_4^-
    E. 2:1 M^{n+}/Y_4^- and 1:1 M^{n+}/Y_4^-

12. A pair of EDTA titrations can be used to measure water hardness (Mg^{2+} and Ca^{2+} concentration). One of the titration is performed at pH 10 and the other at pH 12. Which statement is true?

    A. At pH 10 both Mg^{2+} and Ca^{2+} bind to the EDTA titrant.
    B. At pH 12 the Mg^{2+} precipitates out as magnesium hydroxide.
    C. The difference between the two endpoints can be used to calculate the $[Mg^{2+}]$.
    D. These titrations would not work at pH 4, because the Kf ' for Mg and Ca are too low at this pH.
    E. All of the above.

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Short answer

1. Predict whether or not a reaction occurs. If a reaction occurs, predict the products and write a balanced reaction. Assume 0.10 M concentrations of all soluble species (2 pts each)

a) $2Fe^{3+} + Cu(s) \rightarrow 2Fe^{2+} + Cu^{2+}$
$E^0(Fe^{3+}/Fe^{2+}) = 0.771$ V
$E^0(Cu^{2+/}Cu) = 0.339$ V
$E^0(Cu^{2+}/Cu^{+}) = 0.161 << 0.518 = E0(Cu^{+}/Cu) =$, so it will go all the way to Cu^{2+}
E^0 is positive, favorable

b) $Ce^{3+} + Fe^{3+} \rightarrow$ NR
$E^0(Fe^{3+}/Fe^{2+}) = 0.771$ V
$E^0(Ce^{4+/}Ce^{3+}) = 1.72$ V
E0 is very negative, NR

c) $MnO_4^- + Cu(s) \rightarrow$
$2MnO_4^-$ + 16H+ + 5Cu(s) ➔ 2Mn2+ + 8H2O + 5Cu2+

$MnO_4^- + 8H^+ + 5e^-$ ➔ $Mn^{2+} + 8H_2O$ $E^0 = 1.507$ V
$Cu^{2+} + 2e^-$ ➔ Cu(s) $E^0 = 0.339$ V
E^0 is positive, favorable

d) $Zn^{2+} + Fe^{2+} \rightarrow$ NR
$E^0(Fe^{3+}/Fe^{2+}) = 0.771$ V
$E^0(Zn^{2+/}Zn) = -0.762$ V
E^0 is very negative, NR

e) $Pb^{2+} + Zn(s) \rightarrow Zn^{2+} + Pb(s)$
$E^0(Pb^{2+}/Pb) = -0.126$ V
$E^0(Zn^{2+/}Zn) = -0.762$ V
E^0 is positive, favorable

Name:

Do problem 1 or 2! (22 pts)

1. Some people have an allergic reaction to the food preservative sulfite (SO_3^{2-}). Sulfite in a wine was measured by the following procedure. A standard solution was prepared by mixing 0.8043 g KIO_3 (FW 214.00 g/mol) and 5 g KI and diluting with de-ionized water to the 100.00 mL mark. 5.00 mL of this standard solution was added to 50.00 mL of wine. Acidification of the solution quantitatively converted the IO_3^- to I_3^-. Some of the I_3^- generated reacted with the SO_3^{2-} to generate SO_4^{2-}, leaving excess I_3^- in solution. Titration of the excess I_3^- required 12.86 mL of 0.04818 M $Na_2S_2O_3$ to reach a starch end point. Determine the concentration of the sulfite in the wine in mg/L.

   You can find all necessary reactions within Chapter 16 and Appendix H.

Total mmol I_3^- = ((0.8043g/214)/20)*(3 mmol I_3^-/1 mmol IO_3^-)*1000 = 0.564 mmol I_3^-
(1/20 or 5.00 mL/100.0 mL) is the dilution factor.
3 is the stoichiometry between I_3^- and IO_3^-.

Excess mmol I_3^- = 12.86*0.04818*(1 mol I_3^-/2 mol S_2O_3) = 0.310 mmol I_3^-

mmol I_3^- reacted with SO_3^{2-} = mmol SO_3^{2-} = 0.254 mmol

$SO_4^{2-} + 2H^+ + 2e \rightarrow SO_3^{2-} + H_2O$
$I_3^- + 2e \rightarrow 3I^-$
1:1 stoichiometry between I_3^- and SO_3^{2-}

(0.254 mmol)*(32.065 +3*15.9994mg/mmol)/0.050 L = 407 mg/L

2. A 0.2265 g vitamin C (Ascorbic acid, $C_6H_8O_6$, 176.12 g/mol) tablet was dissolved in 10 mL of 1.0 M HCl, quantitatively transferred to a 100.00 mL volumetric flask and diluted to the mark with 1.0 M HCl. A 25.00 mL aliquot of this solution is analyzed by redox titration using 0.02839 M Ce^{4+} in 1.0 M HCl as the titrant. The titration was followed potentiometrically vs. the Ag/AgCl reference electrode. The endpoint was reached in 20.04 mL. Calculate the weight percent of ascorbic acid in the tablet. Calculate E_{cell} at 5.01 mL. Calculate the Ecell at the equivalence point.

$D + 2H^+ + 2e \Rightarrow A + H_2O$ $E^0 = 0.390$ V

$Ce^{4+} + e \Rightarrow Ce^{3+}$ $E^0 = 1.47$

$2Ce^{4+} + A + H_2O \Rightarrow 2Ce^{3+} + D + 2H^+$

Wt % = (20.04)*(.02839 mmol/mL)*(1mmol A/2 mmol Ce^{4+})*(100/25)*(176.12 mg/mmol)*(1/226.5)*100 = 88.48 %

Ecell @ 5.01 mL added
$= (0.390-(.05916/2)\log((20.04-5.01)/(5.01(1.0)^2)) -0.197 = 0.178$ V

Ecell @ Ve

$3E_+ = 2(0.390) + 1.47$
$E_+ = 0.75$
$E = 0.75 - 0.197 = 0.55$ V

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Do Problem 3 or 4! (22 pts)

3. Using Appendix H calculate the E^0 for the reduction of PuO_2^{2+} to Pu(s).

$PuO_2^{2+} + 4H^+ + 2e^- \Rightarrow Pu^{4+} + 2H_2O$ $E^0 = 1.000$ V
$Pu^{4+} + e \Rightarrow Pu^{3+}$ $E^0 = 1.006$ V
$Pu^{3+} + 3e^- \Rightarrow Pu(s)$ $E^0 = -1.978$ V

$PuO_2^{2+} + 4H^+ + 6e^- \Rightarrow Pu(s) + 2H_2O$ $E^0 = ?$

$\Delta G1 + \Delta G2 + \Delta G3 = \Delta Grxn$

$2F(1.000) + 1F(1.006) + 3F(-1.978) = 6FE^0$

$E^0 = 2(1.000+1.006-3(1.978)/6 = -0.488$ V

OR

$PuO_2^{2+} + e \Rightarrow PuO_2^+$ $E^0 = 0.966$ V
$PuO_2^+ + e \rightarrow PuO_2(s)$ $E^0 = 1.585$ V
$PuO_2(s) + 4H^+ + 4e^- \Rightarrow Pu(s) + 2H_2O$ $E^0 = -1.369$ V

$PuO_2^{2+} + 4H^+ + 6e^- \Rightarrow Pu(s) + 2H_2O$ $E^0 = ?$

$\Delta G1 + \Delta G2 + \Delta G3 = \Delta Grxn$

$1F(0.966) + 1F(1.585) + 4F(-1.369) = 6FE^0$

$E^0 = (0.966+1.585-4(1.369)/6 = -0.488$ V

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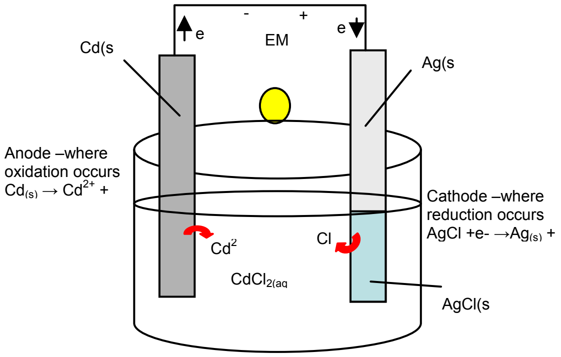
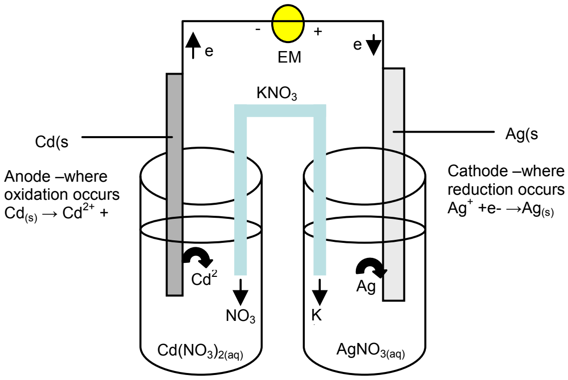
4. Both of the cells shown below work. Electrons flow through the wires from the negative terminal to the positive terminal, producing a positive voltage on the voltmeter. The first one does not require the anode and cathode to be separated. The second on requires the anode and cathode to be compartmentalized and linked through a salt bridge. Explain the different requirements of the design of theses cells. What would happen if the second cell was configured the same as the first? What would happen if the salt bridge was removed from the second cell and why?



$Cd_{(s)} + 2AgCl_{(s)} \leftrightarrow Cd^{2+} + 2Ag_{(s)} + 2Cl^{-}$



$Cd_{(s)} + 2Ag^{+} \rightarrow Cd^{2+} + 2Ag_{(s)}$

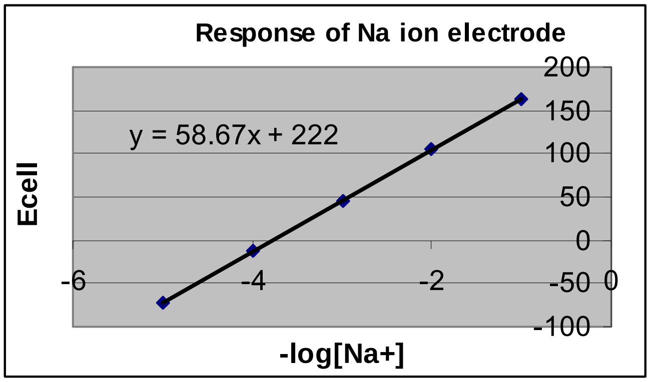
The reactants of the first cell are both solids (the anode and cathode) and are not in direct contact. The only way the reaction can occur is through the transfer of electrons through the wire. Therefore both the anode and cathode can be present in the same solution. In the second cell one of the reactants is an ion in solution. If both electrodes were present in the same solution, the Ag^{+} could migrate to the surface of the Cd electrode and the electron transfer could take place directly without going through the external circuit.

If the salt bridge were removed from the second cell, no current would flow because there would be a build up of positive charge in the anode compartment and a build up of negative charge in the cathode compartment, which is highly unfavorable (large energy barrier).

Do problem 5 or 6! (22pts) Name:

5. A sodium ion electrode is used to measure the sodium concentration of seawater. A series of standard Na^+ solutions were prepared. Each were buffered to a pH of 8.0 with a buffer system that does not interfere with the measurement of Na^+ and each contained only trace levels of K^+. Measurement of these standards produced the following data. (25 pts)

[Na+] (M)	log[Na^+]	Ecell (mV)
1.00E-1	-1	163.33
1.00E-2	-2	104.66
1.00E-3	-3	45.99
1.00E-4	-4	-12.68
1.00E-5	-5	-71.35



A plot of the log[Na^+] vs Ecell, gives a slope of 58.67 mV and an intercept of 222 mV. A sample of seawater is diluted by a factor of 10 with the pH 8.0 buffer and measured with the sodium ion electrode, giving a voltage of 34.3 mV.

Part A) Calculate the [Na^+] concentration of the seawater assuming that the response to the K^+ and H^+ in the seawater is negligible.

{(34.3-222)/58.67}*10(dilution factor) *(1000 mmol/mol)= 6.32 mM

Part B) The pH of the undiluted seawater was measured to be 5.50 using a pH meter. Given that the selectivity factor of the sodium ion electrode is $k_{Na+/H+} = 36$, do you expect the low pH of the seawater to effect the measurement of the [Na^+] from Part A. Explain your answer.

The pH of the seawater is irrelevant because it was diluted by a factor of 10 with a buffer to set the pH to 8.0 before measuring. The H^+ concentration at pH 8 causes a negligible error in the measurement.

Part C) Diluting all solutions with a concentrated buffer solution minimized the interference from H^+, while keeping the ionic strength constant. The constant ionic strength enables the Nernst Eq. to be expressed in terms of concentration. It also increases that accuracy of the measurements because the junction potential at the salt bridge remains relatively constant from sample to sample.

6. 20.00 mL of a 0.200 M $Fe(NO_3)_2$ solution in 1 M HNO_3 and 20.00 mL of a 0.200 M $AgNO_3$ solution in 1 M HNO_3 is mixed in a large beaker.

A. Write down a balanced reaction describing what occurs when these solutions are mixed and calculate an Ecell describing the initial conditions.

$Fe^{3+} + e- \Rightarrow Fe^{2+}$ $E^0 = 0.746$ V

$Ag^+ + e \Rightarrow Ag(s)$ $E^0 = 0.7993$ V

$Ag^+ + Fe^{2+} = Ag(s) + Fe^{3+}$

Initial concentrations
$[Ag^+] = 0.100$ M
$[Fe^{2+}] = 0.100$ M

$E = (0.7993-0.746) - 0.05916\log(0/(.1)^2) = 0.053$ V

B. Calculate the cell voltage once half the Ag^+ reacts.

Concentration if ½ Ag^+ reacts
$[Ag^+] = 0.050$ M
$[Fe^{2+}] = 0.050$M
$[Fe^{3+}] = 0.050$ M

$E = (0.7993-0.746) - 0.05916\log(0.05/(0.05)^2) = -0.024$ V

C. Will this point (the depletion of half the Ag^+ referred to in Part B) ever be reached? Explain.

Equilibrium is reached when the cell voltage goes to zero. Part B gave a negative value for the cell voltage. This suggests that equilibrium will be reached before half of the Ag^+ reacts.