Exam 2
Chem 311
Fall 2002

You must do (1 or 2), (3 or 4), (5 or 6), (7 or 8), and one other problem!!!
All problems are worth 20 points

1) A 100.0 ml solution containing 0.0100 M $(NH_4)_2Ce(NO_3)_6$, 2.00 mM $Cl_2(aq)$ and 1 F HCl is mixed with 50.00 ml of a solution containing 1.00 mM $(NH_4)_2Ce(NO_3)_5$, 0.100 M KCl, and 1 F HCl.

Write a complete redox reaction describing this mixture. Answer the following questions according to the way in which you have chosen to write the reaction!!!!

Calculate the ΔG°, E, and ΔG for the reaction.

When a new equilibrium position is established, will the concentration of $[Ce^{4+}]$ be less than or greater than $6.667*10^{-3}$ M. Justify your answer.

$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$ $\quad E^0 = 1.47$ V

$Cl_2(aq) + 2e^- \leftrightarrow 2Cl^-$ $\quad E^0 = 1.396$ V

$2Ce^{4+} + Cl^- \leftrightarrow Cl_2(aq) + Ce^{3+}$

$E = E^0 - 0.05916/2 \log([Cl_2][Ce^{3+}]^2/[Cl^-]^2[Ce^{4+}]^2)$

$E^0 = 1.47 - 1.3604 = 0.074$ V

$\Delta G^0 = -nFE^0 = -2(9.6485*10^4)(0.074) = -14000\text{ J} = 14\text{ kJ}$

the two solution were mixed and the initial concentrations prior to reaching equilibrium must be calculated.

$[Cl_2] = (2.00\text{ mM})(100.0\text{ ml})/(150.00\text{ ml}) = 1.333$ mM
$[Ce^{3+}] = 1.00\text{ mM}(50.00\text{ ml})/150.0\text{ ml}) = 0.3333$ mM
$[Cl^-] = 100\text{ mM}(50.00\text{ ml})/(150.0\text{ ml}) = 33.33$ mM
$[Ce^{4+}] = 0.0100(100\text{ ml})/(150.0\text{ ml}) = 6.667$ mM

$E = 0.074 - 0.05916/2 \log([1.333][0.3333]^2/[33.33]^2[6.667]^2) = 0.148$ V

$\Delta G = -nFE = -2(9.6485*10^4)(0.148) = -28000\text{ J} = -28\text{kJ}$

ΔG is negative and therefore the equilibrium position will shift toward the formation of products. Therefore, the concentration of Ce^{4+} will decrease and necessarily be less than 6.667 mM.

2) Using information from Appendix H calculate E^0 for the reduction of UO_2^+ to $U_{(s)}$. Calculate the equilibrium constant for this reaction.

$$UO_2^+ \leftrightarrow U_{(s)}$$

Add together the following half reactions

(1)	$UO^{2+} + 4H^+ + e- \leftrightarrow U^{4+} + 2H_2O$	$E^0_1 = 0.39$ V
(2)	$U^{4+} + e- \leftrightarrow U^{3+}$	$E^0_2 = -0.577$ V
(3)	$U^{3+} + 3e- \leftrightarrow U_{(s)}$	$E^0_3 = -1.642$ V
(4)	$UO^{2+} + 4H^+ + 5e- \leftrightarrow U_{(s)} + 2H_2O$	

$$\Delta G_4 = \Delta G_1 + \Delta G_2 + \Delta G_3$$
$$-n_4FE^0_4 = -n_1FE^0_1 + -n_2FE^0_2 + -n_3FE^0_3$$

$$\begin{aligned} E^0_4 &= (-n_1E^0_1 - n_2E^0_2 - n_3E^0_3)/n_4 \\ &= \{-(1)(0.39) - (1)(-0.577) - (3)(-1.642)\}/ 5 \\ &= -1.02 \text{ V} \end{aligned}$$

$$K = 10^{nE0/0.05619} = 10^{5(-1.02)/(0.05916)} = 10^{-86.2} = 6*10^{-87}$$

3) A lead ion electrode measured a potential of -33.9 mV when immersed in a 50.00 ml of water from a polluted stream. Upon the addition of 500 µl of a 0.105 mM solution of $Pb(NO_3)_2$ the potential changed to -11.2 mV. Write an expression for the response of this ion-selective electrode. Calculate the concentration of Pb^{2+} in the stream. According to this measurement, what can you say about the CO_3^{2-} concentration in the stream (quantitatively)?

Let $x = [Pb^{2+}]$ in unknown

Then the $[Pb^{2+}]$ in the spiked sample =

$$(50\ ml*x + (1.05*10^{-4}\ mM)(0.500\ ml))/50.500\ ml$$

unknown sample

$$-33.9 = const + 59.16/2 \ \log x$$

spiked sample

$$-11.2 = const + 59.16/2 \ \log \{(50\ ml*x + (1.05*10^{-4}\ mM)(0.500\ ml))/50.500\ ml\}$$

solve simultaneously

$$-0.767 = \log \{50.50\ x/(50.00x + 5.25*10^{-5})\}$$

$$10^{-0.767} = 50.50\ x/(50.00x + 5.25*10^{-5})$$

$$10^{-0.767} *(50.00x + 5.25*10^{-5}) = 50.50\ x$$

$$x = 2.14*10^{-7}\ M = 214\ nM$$

$$Pb^{2+} + CO_3^{2-} \leftrightarrow PbCO_{3(s)} \qquad Ksp = [CO_3^{2-}][Pb^{2+}] = 7.4*10^{-14}$$

$$[CO_3^{2-}]_{max} = 7.4*10^{-14}/2.14*10^{-7} = 3.46*10^{-7}\ M$$

4) The filling solution in the Pb^{2+} ion-selective electrode that was used to acquire the data in problem 3 is $3.00*10^{-6}$ M . How might you go about preparing this filling solution. Give a recipe for making a filling solution that has the $[Pb^{2+}]$ buffered to a concentration of $3.00*10^{-6}$ M.

$$Pb^{2+} + 2C_2O_4^{2-} \leftrightarrow Pb(C_2O_4)_2^{2-}$$

$$K = [Pb(C_2O_4)_2^{2-}] / [Pb^{2+}] [C_2O_4^{2-}]^2 = 10^{6.54}$$

$$K [Pb^{2+}] = 10^{6.54} * 3.00*10^{-6} = [Pb(C_2O_4)_2^{2-}] / [C_2O_4^{2-}]^2 = 10.40$$

Recipe: Make up a filling solution that is 0.100 M $Pb(C_2O_4)_2^{2-}$ and 0.0980 M $C_2O_4^{2-}$. The $[Pb^{2+}]$ of this solution will be $3.00*10^{-6}$ M.

5) 25.00 ml of a polluted water sample was analyzed for Sn^{2+} by redox titration with $Mn(EDTA)^-$, and the endpoint of the titration can be found potentiometrically vs the Ag/AgCl reference electrode. The concentration of the titrant was 1.27 mM, and it took 12.52 ml to reach the end point. Calculate the concentration of Sn^{2+} in the water sample. Calculate the cell voltage at the equivalence point. (25 points)

$Sn^{4+} + 2e- \leftrightarrow Sn^{2+}$ $\qquad E^0 = 0.139$ V

$Mn(EDTA)^- + e- \leftrightarrow Mn(EDTA)^{2-}$ $\qquad E^0 = 0.825$ V

$2Mn(EDTA)^- + Sn^{2+} \leftrightarrow 2Mn(EDTA)^{2-} + Sn^{4+}$

$[Sn^{2+}] = \{(1.27 \text{ mM})(12.52 \text{ ml})*(1\text{mmol } Sn^{2+} / 2 \text{ mmol MnEDTA})\}/ (25.00 \text{ ml})$
$= 0.318$ mM

$E_+ = 0.139 – 0.05916/2 \log \{[Sn^{2+}]/[Sn^{4+}]\}$

$E_+ = 0.825 – 0.05916 \log \{[Mn(EDTA)^{2-}]/[Mn(EDTA)^-]\}$

$2E_+ = 2(0.139) – 0.05916 \log \{[Sn^{2+}]/[Sn^{4+}]\}$

$3E_+ = 2(0.139) – 0.05916 \log\{[Sn^{2+}]/[Sn^{4+}]\} + 0.825 – 0.05916 \log\{[Mn(EDTA)^{2-}]/[Mn(EDTA)^-]\}$

$3E_+ = 2(0.139) + 0.825 – 0.05916 \log\{[Sn^{2+}][Mn(EDTA)^{2-}]/[Sn^{4+}] [Mn(EDTA)^-]\}$

$3E_+ = 2(0.139) + 0.825$

$E_+ = 0.368$ V

$Ecell = 0.368 – E^0_{\text{sat AgCl}} = 0.368 – 0.197 = 0.171$ V

6) The chemical oxygen demand (COD) of the intake water from a water treatment plant was determined by redox titration (see Box 16-1 on pg 362). A 25.00 ml aliquot of the intake water was placed into a 50.00 ml volumetric, and diluted to the mark with water that has been de-ionized and filtered to remove organics. 10.00 ml of this solution was refluxed for 2 hr with 20.00 ml of a 5.01 mM solution of dichromate in 1 M H_2SO_4 containing a Ag catalyst. The unreacted $Cr_2O_7^{2-}$ was then titrated with 51.8 mM Fe^{2+} in 1 M H_2SO_4, taking 7.52 ml to reach the end point. Calculate the COD (in moles per L) of the intake water in terms of equivalent moles of oxygen consumed in the oxidation of the organics in the water (see Box 16-1 on pg 362).

$Cr_2O_7^{2-} + 14H^+ + 6e- \leftrightarrow 2Cr^{3+} + 7\ H_2O$

$Fe^{3+} + e- \leftrightarrow Fe^{2+}$

________________________________ -

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \leftrightarrow 2Cr^{3+} + 7\ H_2O + 6\ Fe^{3+}$

Total mol $Cr_2O_7^{2-}$ added = (20.00 ml)($5.01*10^{-3}$) = 0.1002 mmol $Cr_2O_7^{2-}$

Excess mol $Cr_2O_7^{2-}$ that reacted with Fe^{2+} = (7.52 ml)($51.8*10^{-3}$)(1mol /6mol Fe^{2+}) = 0.0649 mmol $Cr_2O_7^{2-}$

Mol $Cr_2O_7^{2-}$ that oxidized organics = (0.1002 - 0.0649) = 0.03528 mmol

Equiv mol of O_2 that oxidizes organics = 0.03528 mmol *(1.5 mmol O_2/1mmol $Cr_2O_7^{2-}$) = 0.05292 mmol O_2

Dilution factor (0.05292)*(50.00 ml)/(10.00 ml) = 0.2646 mmol

[organics in sample] = 0.2646 mmol/25 ml = 10.6 mM of equiv O_2

7)

The sulfite concentration of a Nutter Butter can be determined by coulometric titration. A piece Nutter Butter cookie was ground up to obtain a fine homogenized powder. About 100 ml of 1.0 M NaOH was added to 5.325 g of the powder to dissolve the sulfite salts. The solution was passed through a filter to remove the insolubles and titrated with I_2(aq). The titrant was generated coulometrically at a constant current of 3.25 mA. The endpoint was reached in 112 s. Calculate the SO_3^{2-} content of a cookie. The average mass of a Nutter Butter is 13.5 g. Express the answer in µg SO_3^{2-} per cookie.

$I_2 + 2e^- \leftrightarrow 2I^-$ $\qquad E^0 = 0.620$ V

$SO_4^{2-} + H_2O + 2e^- \leftrightarrow SO_3^{2-} + 2OH^-$ $\qquad E^0 = -0.936$ V

$I_2 + SO_3^{2-} + 2OH^- \leftrightarrow 2I^- + SO_4^{2-} + H_2O$

$(3.25*10^{-3}\text{ A})(112\text{ s}) *(1/9.6485*10^4\text{ C}) *(1\text{ mol }SO_3^{2-}/2\text{ mol e-})*(80.064\text{ g /mol }SO_3^{2-})*(10^6\ \mu\text{g}/1\text{ g}) * (13.5\text{ g}/5.325\text{ g})$

$= 383$ mg SO_3^{2-} per cookie

8)

This problem refers to problem 17-27 (the problem that shows the data from a standard addition experiment determining [Cu^{2+}] in tap water).

This problem was solved in the notes for chapter 17. However, the solution in the notes is wrong because your professor forgot to take into account the current of the blank sample.

In a stripping experiment the current is directly proportional to the concentration of the analyte prior to deposition on the surface of the electrode.

$$i = m[Cu^{2+}] + b$$

where m is the sensitivity (μA L/mol) and b is the current for the "blank" sample.
Judging from the data illustrated in the figure and expressed in tabular form below, choose the answer the best represents the [Cu^{2+}] of the tap water. **Justify your answer.**

sample	**current**
blank	0.40
tap water	0.98
100 ppm added	1.13
200 ppm added	1.33
300 ppm added	1.53
400 ppm added	1.75
500 ppm added	1.95

a) 110 ppm
b) 150 ppm
c) 280 ppm
d) 560 ppm
e) 1500 ppm

$$I = m[Cu^{2+}] + b$$

$$0.98 = m[Cu^{2+}]_{t.w} + 0.40$$

$$- \quad 1.53 = m\,\{[Cu^{2+}]_{t.w} + 300\} + 0.40$$

$$-0.55 = -300m$$
$$m = 0.0018333$$

plug back in

$[Cu^{2+}]_{t.w} = (0.98 - 0.40)/\ 0.0018333 = 316$ ppm, answer c) is the best answer!!!!!