UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATIONS, DECEMBER 2001

CHE 553H1 - ELECTROCHEMISTRY

Examiner - F.R. Foulkes

Time allowed: 2.5 hours

Be sure to PRINT your name on every page!

General Instructions:

1. All calculations are to be made on the special pages provided, which are to be handed in.
2. One question and solution per page. No marks will be assigned for material on other pages.
3. Use the back of the same page, if necessary.
4. Write all final answers in the rectangular boxes provided.
5. Marks will be deducted for answers not reported with a reasonable number of significant figures, and for failure to report answers in the units requested.
6. Programmable calculators are not permitted.

Physical Constants, Conversion Factors, and Data

$R = 8.314\ J\ mol^{-1}\ K^{-1}$	$e_o = 1.602192\times10^{-19}\ C$	$N_A = 6.02217\times10^{23}\ mol^{-1}$
1 equiv = 1 mol of electrons	$F = 96487\ C\ equiv^{-1}$	$k = R/N_A$
$k = 1.38062\times10^{-23}\ J\ K^{-1}$	$0°C = 273.15\ K$	1 funt = 96 solotnik
$1\ atm = 1.01325\times10^{5}\ Pa$	$1\ bar = 10^{5}\ Pa$	$\varepsilon_o = 8.8544\times10^{-12}\ F\ m^{-1}$

The marks assigned for each question are listed at the end of the paper.

1. Calomel (mercurous chloride, Hg_2Cl_2) is used in the manufacture of calomel reference electrodes, which are widely used in electrochemical research. Calomel is a sparingly soluble salt which, when dissolved, dissociates into mercurous dions, Hg_2^{++}, and Cl^- ions. At 25°C, the solubility product $K_{SP}^{(m)}$ of Hg_2Cl_2 is 1.454×10^{-18}. What is the molal solubility of calomel in aqueous 0.10 molar NaCl solution at 25°C? For the concentrations involved in this problem, you may assume that molal concentrations are essentially the same as molar concentrations. Use the following (next page) form of the Davies equation to take account of activity coefficient corrections.

$$\log_{10}\gamma_{\pm} = \frac{-0.51159\,|z_+ \times z_-|\sqrt{I^{(c)}}}{1+\sqrt{I^{(c)}}} + 0.10\,|z_+ \times z_-|\,I^{(c)}$$

2. The equivalent conductivities at 25°C of 0.100 M HCl and of 0.100 M NaCl are 390.4 $cm^2\,S\,eq^{-1}$ and 106.8 $cm^2\,S\,eq^{-1}$, respectively.

(a) Assuming that γ_{Cl^-} is the same in each solution, calculate $|E_{cell}|$ at 25°C for the cell

$$Ag\,|\,AgCl_{(s)}\,|\,0.10\ M\ HCl_{(aq)}\ \vdots\ 0.10\ M\ NaCl_{(aq)}\,|\,AgCl_{(s)}\,|\,Ag$$

Any minor differences between molal concentration and molar concentration may be neglected in solutions at these dilutions. Hint: Mr. Henderson is your friend, but not his wife, Mrs. Planck-Henderson!

(b) Which of the electrodes will be the positive terminal? Don't guess! The mark will be subtracted for an incorrect answer.

3. A porous lead plate and a porous lead dioxide are immersed into a beaker containing two moles of H_2SO_4 dissolved in 2.00 kg of water and allowed to reach equilibrium at 25°C. The two plates then are electrically connected through an external circuit containing a variable resistor. The cell is allowed to discharge at 25°C and one bar pressure through the resistor until no more current flows. During the discharge, the resistor is continously adjusted so that the cell terminal voltage is maintained at 1.25 V. The discharge requires 48 hours. The cell reaction is

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(liq)} \qquad \Delta H^{\circ}_{298.15} = -462.06\ kJ\ mol^{-1}$$

(a) What is the *cathode* reaction in this cell?
(b) What is the activity of the water in the initial cell electrolyte?
(c) What is the molal activity of the sulfuric acid in the initial cell electrolyte?
(d) What is the initial cell equilibrium voltage before the discharge begins?
(e) What is the value of the equilibrium constant at 25°C for the cell reaction?
(f) When the cell has completely run down, what is the molal concentration of H_2SO_4 remaining in the electrolyte?
(g) Excluding the energy dissipated in the resistor (which could be utilized as electrical work), how much heat is released during the discharge?
(h) What is the percentage energy conversion efficiency for this cell?
(i) What is the theoretical maximum energy conversion efficiency for this cell?
(j) What is ΔS° for the overall cell reaction at 25°C?
(k) What is the average power output of the cell?
(l) What is the average value of the resistance of the external resistor?

Data: $E^{\circ}_{cat} = 1.6913$ V; $E^{\circ}_{an} = -0.3588$ V; The stoichiometric mean molal ionic activity coefficient of 1.00 molal H_2SO_4 at 25°C is 0.1316. The molal osmotic coefficient (ϕ) for 1.00 molal H_2SO_4 at 25°C has a value of 0.721. The molar mass of H_2O is 18.015 $g\,mol^{-1}$.

4. The anodic reaction in which reactants *A* and *B* react to form product *H* proceeds by the mechanism shown at the right. This reaction is carried out at 25°C at an inert planar platinum anode of effective area 0.250 cm^2 in conjunction with a saturated calomel reference electrode, the latter being located inside a luggin capillary. Because of poor placement of the luggin capillary there is a constant electrical resistance of 0.60 ohms in the electrolyte solution between the tip of the capillary and the anode surface. When the process is carried out at an operating potential very close to its open circuit potential, the total anodic overvoltage (including the solution IR-drop) is 950 μV at an anodic current of 10.00 μA. What will the total anodic overvoltage be if a current of 100.0 mA is passed through this electrode, assuming that no concentration polarization is present? Report your answer in *millivolts*.

$$A \rightleftharpoons C + D$$
$$B \rightleftharpoons E$$
$$C + D \xrightarrow{RDS} E + e^-$$
$$2(E \rightleftharpoons F + e^-)$$
$$2F \rightleftharpoons G$$
$$G \rightleftharpoons 2H + e^-$$

Question	1	2(a)	2(b)	3(a)	3(b)	3(c)	3(d)	3(e)	3(f)	3(g)	3(h)	3(i)	3(j)	3(k)	3(l)	4
Marks	6	6	1	1	1	1	2	1	1	1	1	1	1	1	2	8

Total marks = 35