March 3, 2002

CH 342 S02, Project 1

due Monday, March 11, 2002

# Introduction

The company Metaries, Ltd. (manufacturers of metal batteries) has developed a metal alloy A that is to be used as the anode in a rechargable battery. A solid Ti core will be surrounded by an aqueous salt of the A alloy. The cathode will collect the precipitating $A^+$(aq) cation while the Ti oxidizes (to a salt), leading to the overall reaction $2A^+$(aq) + Ti(s) $\rightarrow$ 2A(s) + $Ti^{2+}$(aq).

Experiments have established that battery voltage decreases as the $A^+$(aq) cation is consumed. Also, if the $A^+$(aq) cation concentration in the battery falls below 5% of its initial value, the battery cannot be recharged. The engineers testing the battery are unfortunately unable to provide the much desired specific relationship between battery voltage and concentration of $A^+$(aq).

# Objective

As the physical chemist of the design team, your goal is to establish from first principles the minimum voltage when the battery must be recharged. The objectives are to define the specific relationship between $E$ and the concentration of $A^+$(aq) and, from this equation, to establish the voltage of the battery when the concentration of $A^+$(aq) is 95% of its initial value.

# Information

The principle formulation to solve this problem is the Nernst equation

$$E = E^{\ominus} - \frac{RT}{\gamma F} \ln(Q)$$

where $E$ is the battery voltage (V), $E^{\ominus}$ the standard state battery voltage (V), $R$ is the gas constant (8.314 J/mol K), $\gamma$ the moles of electrons transferred per mole of reactant consumed (2 in this case), $F$ is the Faraday constant (96485 C/mol), and $Q$ the (dimensionless) reaction quotient for the system. The value of $E^{\ominus}$ is found by subtracting the half cell reduction potentials of Ti(s) from that for A(s). Metaries, Ltd. has reported that A has a standard half cell reduction potential $E^{\ominus}$ of 0.33 V (the value for Ti(s) can be found in a standard reference text). The reaction quotient $Q$ for the chemical reaction is written as

$$Q = \left(\frac{\gamma_T}{\gamma_A^2}\right)\left(\frac{b_T\, b^{\ominus}}{b_A^2}\right)$$

where $\gamma_i$ is the activity coefficient for $Ti^{2+}$(aq) ($i = T$) or $A^+$(aq) ($i = A$) and $b_i$ are the corresponding cation solution molalities. Clearly, the battery voltage depends on ion concentrations. How does it depend on the extent of reaction?

The moles of either cation $n_i$ can be written based on initial moles $n_i^o$ the extent of reaction of $A^+$(aq) as

$$n_A = n_A^o - \varepsilon$$
$$n_T = n_T^o + \frac{\varepsilon}{2} = \frac{\varepsilon}{2}$$

A more useful expression for both cases above is obtained by substituting the fractional amount of $A^+$(aq) reacted (converted to solid A), $f_r = (n_A^o - n_A)/n_A^o$. Also, assuming the mass of the water in the battery stays constant, moles are proportional to molality ($n_i \propto b_i$). These considerations lead to the expressions

$$b_A = (1 - f_r) b_A^o$$

$$b_T = f_r \, b_A^o$$

where $b_A^o$ is the initial molality of $A^+$(aq) in the battery and $f_r$ is the amount reacted (from 0% initially to 100% at complete reaction). The battery cannot be recharged with $f_r$ is greater than 95%.

The above expressions lead to the equation

$$E = E^{\ominus} - \frac{RT}{2F} \ln\left(\frac{\gamma_T}{\gamma_A^2}\right) - \frac{RT}{2F} \ln\left(\frac{f_r b^{\ominus}}{2\,(1 - f_r)^2\, b_A^o}\right)$$

The battery voltage $E$ is a complex function of $f_r$ and $b_A^o$ (initial concentration of $A^+$(aq)). The most appropriate way to present results of such complexity is graphically.

## Project Statement

The project report shall be three pages. It should start with a cover (title) page as shown below. The cover page will not be numbered.

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The Recycle Voltage for a Metal Battery

(Your Name)

March 11, 2002

Submitted by request for Project 1 in CH 342, S02

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The second page shall be a plot of battery voltage $E$ versus fractional extent of reaction $f_r$. The graph will show three curves for initial concentrations of $A^+$(aq) at 1 molality, 0.1 molality, and

0.01 molality respectively. The range of $E$ will be from 1.70 V to 2.10 V, and the range of $f_r$ from 0 to 1. The plot will also show a vertical (dashed) line at a value of $f_r = 0.95$, signifying the point where the battery must be recharged.

The third page of the report shall be a table of the initial concentration of $A^+$(aq) and recycle voltage.

## Assumptions

Assume ideal solution behavior in the battery, and report all values at 25 $^{o}$C.

## Grading

The project report will be graded at 100 points according to the following scale:

| | | |
|---|---|---|
| Report Format | 10% | (partial credit given) |
| Correct Plot | 50% | (**no** partial credit given) |
| Plot Quality | 30% | (partial credit given) |
| Correct Results | 10% | (**no** partial credit given) |

A correct plot is one that follows the requested format and shows the three curves of the correct shape and in the correct locations. The quality of the plot includes issues of its size, labels, titles, and readability. Correct results are those that agree with the answer key.

## Extra Credit (10 points)

The activity coefficients of the two cations have been determined to depend on concentration according to the expressions

$$\gamma_A = 1 + a\, b_A^2$$

$$\gamma_T = 1 + t\, b_T^2$$

where $a$ and $t$ are adjustable variables.

The extra credit shall be done on two pages that are attached to the end of the required report. On the first extra credit page (worth 5 points), show the expression for $E$ as a function of $f_r$, $a$, $t$, and $b_A^o$ for the non-ideal system. This must be reported as the output from a symbolic math program and cannot be done by hand.

On the second extra credit page, show a plot of three curves, all at $b_A^o$ of 1 molal. The first curve shall be from the ideal system, the second shall be for $a = 1$ and $t = 0.1$, and the third shall be for $a = 0.1$ and $t = 1$. Use the same scales as those for the required plot.