CHEM465/865, 2006-3, Oct. 22, Dr. M. Eikerling, C9034, x4463

Exercise Series 4

Due date: Nov. 1, 2006

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1. **Specific adsorption.**
   (a) The following table shows Gibbs free energies of adsorption for a series of anions at a Hg electrode.

Electrode	ΔG^0_{ad} **/ eV**
Ag/Br$^-$	**-0.751**
Ag/Cl$^-$	**-0.651**
Ag/F$^-$	**-0.104**

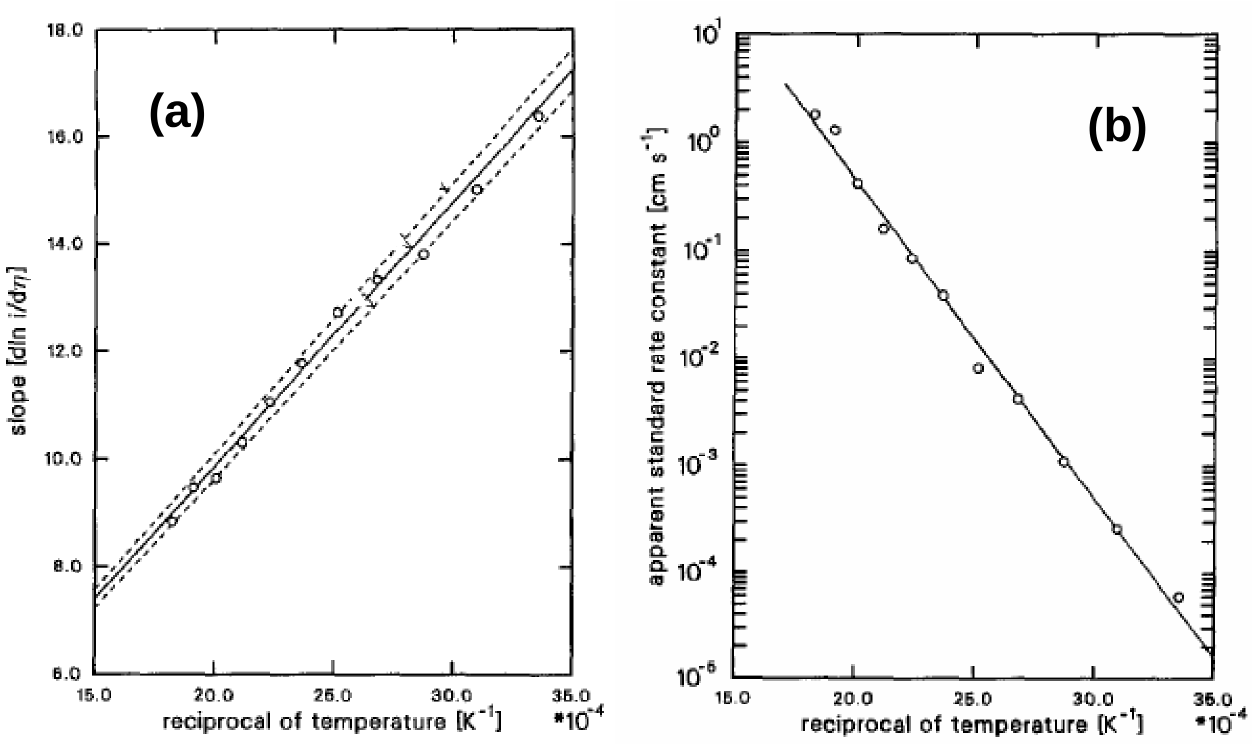
   Explain why the adsorption energies vary in this particular order.
   Why is Ag/I$^-$ no listed?

   (b) For the **Langmuir isotherm**, the relation

$$I = Q_0 \frac{\mathrm{d}\theta}{\mathrm{d}t} = Q_0 v_s \left(-\frac{zF}{RT}\right)\theta\left(1-\theta\right)$$

   between current and surface coverage was discussed in lecture and tutorials. Derive the corresponding relation for the **Frumkin isotherm**.

2. Consider the kinetics of the Fe2+/Fe3+ reaction on a gold electrode in a pressurized aqueous solution of perchloric acid.



[from L.A. Curtiss, J. Electrochem. Soc. 138, 2033 (1991).]

a) It can be assumed that the reaction proceeds via an outer-sphere mechanism. Explain what this mechanism implies.
b) At 25°C the rate constant is $k^0 = 10^{-5}$ **cm s**$^{-1}$. Calculate the corresponding standard exchange current density.
c) Part (a) of the figure above shows the slope of the Tafel-plots, $\mathrm{d}\ln(j)/\mathrm{d}\eta$ for the anodic branch of the reaction as a function of inverse temperature, $1/T$. Is the linear dependence in-line with the expectation of the Butler-Volmer equation? Determine the transfer coefficient α from these data [using the expression for $\ln(j)$ given in the lecture and the fit indicated by the solid line]. What does this result tell you about the symmetry of the reaction? Does the value of α favor the cathodic or anodic branch?
d) Part (b) of the figure shows an Arrhenius plot of the standard rate constant k^0 (as a function of inverse temperature, $1/T$). Determine the Gibbs free energy of activation, $\Delta G^{\dagger,0}$, and the preexponential factor, A. [Note: In the lecture I have sometimes used the symbol k_0 for the rate constant. Both symbols mean the same.].
e) As you know, the best means of accelerating a chemical reaction is increasing the temperature. Now we know all fundamental parameters needed to discuss and evaluate various factors that affect the rate of the electrochemical processes considered in this example. Let's consider a reference case with $T = 25°\mathrm{C}$, $c^{\mathrm{b}}_{\mathrm{red/ox}} = 1\ \mathrm{mM}$ (neglect mass transport losses between bulk and surface, i.e. $c^{\mathrm{b}}_{\mathrm{red/ox}} = c^{\mathrm{s}}_{\mathrm{red/ox}}$) and $\eta = 100\ \mathrm{mV}$. Calculate the current density corresponding to this reference case from the BV equation. Consider one after another the following modifications relative to the reference case:
   (i) an increase in reactant concentrations by a factor 10;
   (ii) an increase in T from $25°C$ to $100°C$
   (iii) an increase in overpotential from $100\ \mathrm{mV}$ to $400\ \mathrm{mV}$.
   Which effect is the most significant one?

3. In an acidic fuel cell, hydrogen is oxidized at the anode and oxygen is reduced at the cathode. At 60˚C, the kinetic parameters for the hydrogen oxidation reaction (HOR) $j_A^0 = 2 \text{ mA cm}^{-2}$ and $\alpha_A = 0.5$. Here the values for the exchange current densities refer to real catalyst surface. In a fuel cell, however, by using porous electrodes and small catalyst particles, each cm^2 of the outer fuel cell electrode area contains in fact about 200 cm^2 of real catalyst surface. This means that the so-called heterogeneity factor or real to apparent surface area ratio is $\xi = 200 \text{ cm}^2 / 1 \text{ cm}^2$. This factor has to be taken into account in calculating the actual current density.

a) For the anodic reaction, calculate the charge transfer resistance R_{CT}^A (including the heterogeneity factor).

b) Assume that for the cathode reaction the kinetic parameters (j_C^0, $1-\alpha_C$) are not known initially. A measurement at $T = 60°C$ has, however, resulted in the following values (again per real surface area):

η / mV	100	150	200	250	300
j / μA cm^{-2}	0.053	0.205	0.75	2.72	10.5

Plot these data in the appropriate form (using the understanding that oxygen reduction is a sluggish reaction) and determine j_C^0, and $1-\alpha_C$. Calculate R_{CT}^C and k_C^0 (assuming standard pressures and concentrations).

c) What are the losses in cell potentials due to overpotentials at anode and cathode if a current density of $j = 0.5 \text{ A cm}^{-2}$ is drawn from the cell [take into account the heterogeneity factors]?

d) The proton transport from the anode to the cathode is not free of losses since the mobility of protons is finite. A typical specific resistivity for proton transport in the solid polymer electrolyte is $R_{PEM} = 7 \ \Omega \text{ cm}$, whereas a typical thickness of the membrane would be $L_{PEM} = 50 \ \mu\text{m}$. Calculate the voltage loss in the membrane, η_{PEM}, at the current density of c).

e) Calculate the measured cell voltage of the fuel cell, E, at the current density specified in c), i.e. add up all overvoltage losses calculated in c) and d), add 0.2 V due to unspecified contributions (unconsidered components and processes), and subtract the sum from the open circuit voltage of the cell, $E_{cell}^{eq} = 1.21 \text{ V}$. Which component causes the major portion of the losses? Why (i.e. which parameter is responsible)?

f) Calculate the voltage efficiency of the cell, defined by $\varepsilon_V = E / E_{cell}^{eq}$.