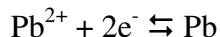


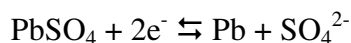
**Electrochemistry Exam 3 March 2014, 13:30 – 15:30**

*Question 1 (10 points)*

- (a) Given that the standard equilibrium potentials for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and the  $\text{Fe}^{2+}/\text{Fe}$  redox couples are 0.77 and -0.44 V vs. NHE, calculate the standard equilibrium for the  $\text{Fe}^{3+}/\text{Fe}$  redox couple.
- (b) Write the Nernst equations for the

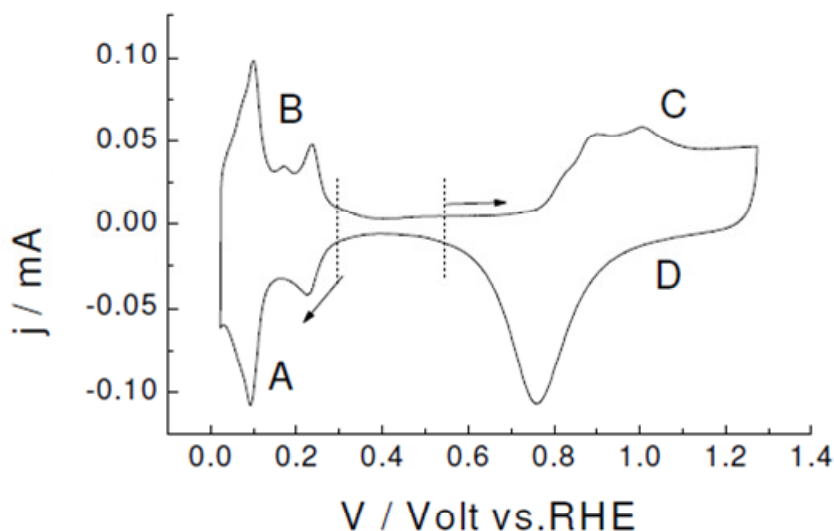


and the



redox couples, and from their respective standard equilibrium potentials, -0.13 V and -0.36 V, calculate the solubility product of the lead sulfate salt.

*Question 2 (10 points)*



The figure shows the “blank voltammetry” of a platinum electrode in sulfuric acid. Explain how:

- (a) you would determine the real surface area of the platinum electrode (in  $\text{cm}^2$ )
- (b) you would determine quantitatively the double layer capacity (in  $\mu\text{F cm}^{-2}$ ).

*Question 3 (10 points)*

The potential of zero charge of a platinum electrode has been estimated to be close to 0.1 V vs. RHE. Suggest two methods to estimate the potential of zero charge of a platinum electrode. By referring to the blank voltammetry in the figure above, explain why this potential of zero charge is difficult to determine accurately.

*Question 4 (10 points)*

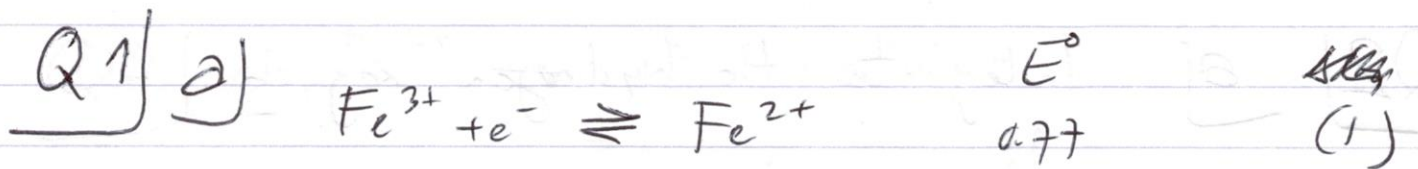
The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple is studied at a spherical platinum micro-electrode in a sulfuric acid solution which is not stirred. The initial concentrations of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are 25 and 50 mM, resp. The diameter of the platinum micro-electrode is 28  $\mu\text{m}$ . The measured anodic limiting current is 0.61  $\mu\text{A}$ .

- (a) Calculate the diffusion coefficient of  $\text{Fe}^{2+}$ .
- (b) If the ratio  $D[\text{Fe}^{3+}]/D[\text{Fe}^{2+}]$  is equal to 0.91, what is the cathodic limiting current?

*Question 5 (10 points)*

Rosca and Koper (Phys.Chem.Chem.Phys. 2006) studied the oxidation of ammonia to  $\text{N}_2$  on a Pt(100) electrode in 0.1 M NaOH. From their Tafel plot of the  $\ln[\text{oxidation current}]$  vs. potential, they estimated a Tafel slope of 30 mV/dec.

- (a) Suggest a mechanism that can explain this Tafel slope.
- (b) Which technique is the most suitable to follow *in situ* the formation of  $\text{N}_2$  during the measurement?



$$\Delta G_{\text{Fe}^{3+}/\text{Fe}} = \Delta G_{\text{Fe}^{3+}/\text{Fe}^{2+}} + \Delta G_{\text{Fe}^{2+}/\text{Fe}}$$

$$3 \times E^\circ_{\text{Fe}^{3+}/\text{Fe}} = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} + 2 \times E^\circ_{\text{Fe}^{2+}/\text{Fe}}$$

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.04 \text{ V}_{\text{NHE}}$$

b)  $E^\circ_{\text{Pb}^{2+}/\text{Pb}} = E^\circ_{\text{Pb}^{2+}/\text{Pb}} + \frac{RT}{2F} \ln [\text{Pb}^{2+}]$

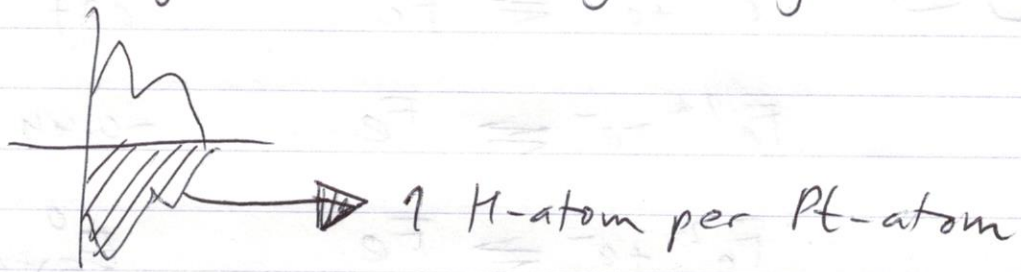
$$E^\circ_{\text{PbSO}_4/\text{Pb,SO}_4^{2-}} = E^\circ_{\text{PbSO}_4/\text{Pb,SO}_4^{2-}} + \frac{RT}{2F} \ln \frac{1}{[\text{SO}_4^{2-}]}$$

$$K_s = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

$$E^\circ_{\text{Pb}^{2+}/\text{Pb}} + \frac{RT}{2F} \ln K_s = E^\circ_{\text{PbSO}_4/\text{Pb,SO}_4^{2-}}$$

$$K_s = 1.66 \times 10^{-8}$$

Q2] a) Integrate the hydrogen region



$$Q = F N_{\text{surf}}^{\text{atom}}$$

$$A = \frac{N_{\text{surf}}^{\text{atom}}}{N_{\text{atom}}(1 \text{ cm}^2 \text{ Pt})}$$

b)

$$C_d = \frac{\text{current}}{\text{sweep rate}} \frac{1}{A} \quad \text{between } 0.3 \text{ and } 0.55 \text{ V}_{\text{RHE}}$$

or Impedance spectroscopy  
in the double layer region  
between 0.3 and 0.55 V<sub>RHE</sub>

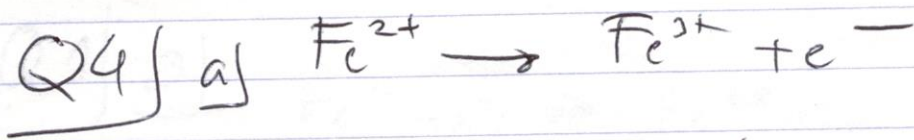
Q3]

1. From the work function of Pt

$$E_{\text{pzc}}^{\text{Pt}} = \Phi_{\text{Pt}}/e_0 - \Phi_{\text{NHE}}/e_0$$

2. Measure  $C_d(E)$  at low electrolyte concentration and determine minimum

0.1 V is in the hydrogen region so  $E_{\text{pzc}}$  is not in the double layer region  
→ difficult to determine



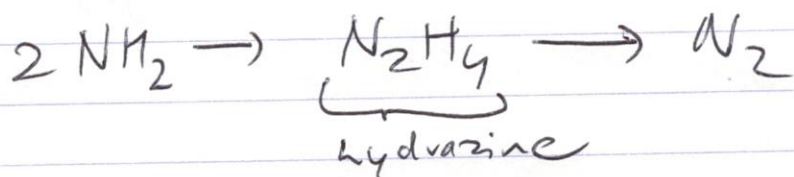
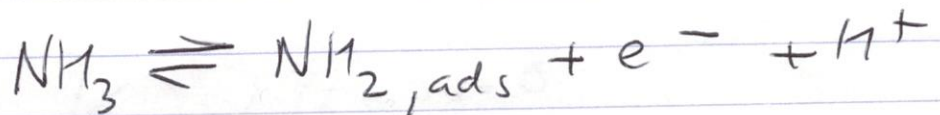
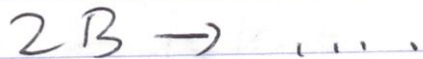
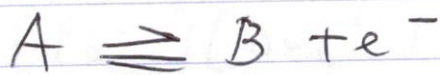
$$i_{an}^L = A F \frac{D_{\text{Fe}^{2+}}}{\delta_{\text{Fe}^{2+}}} C_{\text{Fe}^{2+}} = 0.61 \mu\text{A}$$

$\swarrow$        $\swarrow$        $\swarrow$        $\swarrow$   
 $4\pi r^2$      $96485 \text{ C mol}^{-1}$      $228 \mu\text{m}$      $50 \text{ mM}$   
 $\uparrow$        $14 \mu\text{m}$

$D =$  ~~value~~  
 $7.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

b)  $j_{cath}^L = - j_{an}^L \times 0.91 \cdot \frac{25}{50}$   
 $= -0.28 \mu\text{A}$

Q5 a) 20 mV/dec suggests



b) online mass spectrometry is able to see  $\text{N}_2$