MSE 112
Mid-Term EXAM, SPRING 2019

NAME: SOLUTIONS

The use of books or notes during the Exam is NOT permitted.

ALL WORK IS TO BE DONE IN THIS BOOKLET. YOU MAY USE THE BACKS OF PAGES

All voltages are measured with respect to SHE.

Logs are in base 10.

1 Joule = 1 volt•coulomb = 0.239 calorie
R=gas constant = 1.9872 cal/(mole°K)
F= Faraday's Constant ≈ 96,500 coulombs/equivalent
Temperature = 25°C = 298K

Problem	*Point Value*
1	10
2	45
3	20
4	25

$X + ne^- \rightarrow Y$

$$\Delta\phi_e = \Delta\phi_e^\circ - \frac{RT}{nF} \ln \{[Y]/[X]\} = (\text{at } 25^\circ C)\ \Delta\phi_e^\circ - (0.059V/n) \log_{10} \{[Y]/[X]\}$$

$pH = -\log_{10} [H^+]$

$H^+ + OH^- \rightarrow H_2O$ K_W at 25°C = 10^{-14}

$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr + 7H_2O$	$\Delta\phi_e^\circ = 1.330V$ vs SHE
$Au^{+3} + 3e^- \rightarrow Au$	$\Delta\phi_e^\circ = 1.300V$ vs SHE
$1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\Delta\phi_e^\circ = 1.229$ vs SHE
$Pt^{+2} + 2e^- \rightarrow Pt$	$\Delta\phi_e^\circ = 1.118V$ vs SHE
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$\Delta\phi_e^\circ = 0.401V$ vs SHE
$Cu^{++} + 2e^- \rightarrow Cu$	$\Delta\phi_e^\circ = 0.337V$ vs SHE
$2H^+ + 2e^- \rightarrow H_2$	$\Delta\phi_e^\circ = 0.0V$ vs SHE
$H_2O + e^- \rightarrow 1/2\ H_2 + (OH^-)$	$\Delta\phi_e^\circ = -0.828V$ vs SHE
$Fe^{++} + 2e^- \rightarrow Fe$	$\Delta\phi_e^\circ = -0.447V$ vs SHE
$Cr^{+++} + 3e^- \rightarrow Cr$	$\Delta\phi_e^\circ = -0.740V$ vs SHE

$$i_{ox} = (zF/N_o)N_M{}'N_B d_{MB}{}^2(8\pi kT/m)^{1/2}\exp(-\Delta G^{\pm}/RT)\exp(zF\beta{}^M\Delta{}^S\phi/RT).$$

$$i_{red} = zF(C_{M^{+z}})N_B d_{MB}{}^2(8\pi kT/m)^{1/2}\exp\{-(\Delta G^{\pm} + \Delta G_O)/RT\}\exp\{-zF(1-\beta){}^M\Delta{}^S\phi/RT\}$$

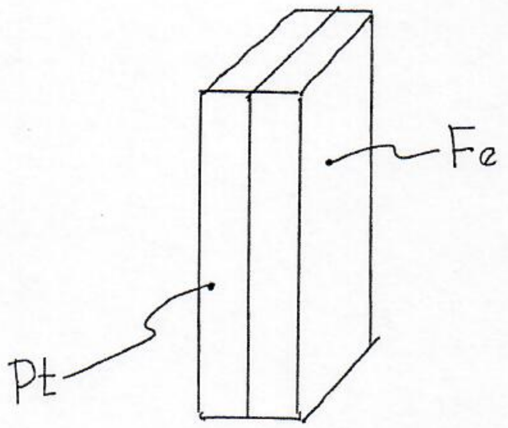
$$i_o = \{zFd^2(8\pi RT/m)^{1/2}\exp(-[\Delta G_o + \Delta G^{\pm}]/RT)\exp(z[1-\beta]F\,\Delta\phi_e^\circ/RT)\}[H+](P_{H2}]^{1/2}/[H^+])^{1-\beta}$$

$$i_o = D(R_aR_bR_c\ldots)\{(P_iP_jP_k\ldots)/(R_aR_bR_c\ldots)\}^{\beta} = D\,(P_iP_jP_k\ldots)(R_aR_bR_c\ldots)^{1-\beta}$$

$$i_o = D[H^+]([P_{H2}]^{1/2}/[H^+])^{1-\beta} = D\,P_{H2}{}^{(1-\beta)/2}\,[H^+]^{\beta}$$

$$i_{corr} = (\partial i/\partial\phi)|_{CORR}/(b_{ox} + b_{red})$$

1. When a sheet of platinum is intimately connected (i.e., metallurgically bonded) to a sheet of iron an electrostatic potential difference is developed between the two metals, ${}^{Pt}\Delta^{Fe}\phi = \phi^{Pt} - \phi^{Fe}$. Similarly, when a sheet of platinum is immersed into an aqueous solution of air-saturated 1M HCl, an electrostatic potential difference is developed between the platinum and the aqueous solution, ${}^{Pt}\Delta^{S}\phi = \phi^{Pt} - \phi^{S}$. Briefly explain why it is possible with the aid of a DC power supply to change the value of ${}^{Pt}\Delta^{S}\phi$ but it is not possible to change the value of ${}^{Pt}\Delta^{Fe}\phi$ (e.g., by employing a DC power supply).



The value of ${}^{Pt}\Delta^{Fe}\phi$ can not be changed because the
mobile charge carriers in Pt and in Fe are the same: electrons,
and the Pt-Fe interface is completely permeable to electrons.
Consequently, changes to ${}^{Pt}\Delta^{Fe}\phi$ will be negated by electron
flow across the Pt-Fe interface.

The mobile charge carriers in the aqueous solution are anions and cations,
in contrast to platinum, in which the mobile charge carriers are Pt's free
electrons. As a result of the different mobile charge carriers of the
two phases, it is possible to change the concentration of excess charge
on either side of the interface without causing charge flow across the
interface.

In order to change the value of ${}^{Pt}\Delta^{S}\phi$ it is necessary to change the
concentration of excess charge on either side of the interface

2. An automobile bumper of carbon steel (Fe-0.06 wt. percent C) is to be electroplated with a thin surface coating of chromium (i.e., chromium will be electrodeposited onto the steel). The electroplating is conducted inside a large steel tank that is protected against corrosion by an inert plastic coating. In this problem you are asked to select the optimum composition of the plating bath.

   In all cases the bath contains 1M Cr^{+3}. You are asked to select the pH of the solution and to determine if it is necessary to deoxygenate the solution (i.e., to reduce the solution's dissolved oxygen concentration from 0.2 atm (= air-saturated) to 0 atm). In making your decision you need to consider the following:

   1. It is of utmost importance that the steel's surface remains bare (i.e., no solid corrosion product) when it is immersed in the plating bath (otherwise the electrodeposited Cr coating will be of poor quality).
   2. There are three possible values of pH of commercially available plating baths: 0, 4 or 7. Thus, you must select a pH of either 0, 4 or 7.
   3. A platinum counter electrode is used for electroplating chromium onto the steel. When electroplating is not being conducted the platinum counter electrode remains immersed in the plating bath. It is important that the platinum not be significantly corroded. Specifically, the concentration of platinum ions in the solution immediately adjacent to the platinum electrode must not exceed $5x10^{-5}$ M.
   4. During pauses in the electroplating operation it is essential that toxic hexavalent chromium (e.g., $Cr_2O_7^{=}$) not be generated and that Cr^{+3} remains stable in the plating bath.
   5. From cost considerations it is desirable (but not essential) that the bath not be deoxygenated.

   Identify the optimum bath chemistry (i.e, select the pH of 0, 4, or 7; select the dissolved oxygen concentration of either 0 or 0.2 atm).

⑤ (1.) and (2.) ⇒ pH must be either 4 or 0 in order to prevent formation of surface oxide / hydroxide

(3.) For deoxygenated:

(i) pH = 0

$$\Rightarrow \Delta\phi_e(H) = 0$$

$$\therefore \Delta\phi_e(Pt) = 1.118V - \frac{.0592V}{2} \log \frac{\cancel{[Pt]}}{[Pt^{++}]}$$

∴ $[Pt^{++}]$ in solution adjacent to Pt is:

$$0V = 1.118V + \frac{.0592V}{2} \log [Pt^{++}]$$

$$\log [Pt^{++}] = -37.77 \Rightarrow [Pt^{++}] = 1.70 \times 10^{-38} M$$

⑤

(ii) pH = 4

$\Rightarrow \Delta\phi_e(H) = -0.2368\, V_{SHE}$

$\therefore$ $[Pt^{++}]$ in solution adjacent to Pt is

⑤ $-0.2368\, V_{SHE} = 1.118\, V + \frac{.0592\, V}{2} \log [Pt^{++}]$

$\Rightarrow \log [Pt^{++}] = -45.77$

$\therefore$ both pH = 0 and pH = 4 are sufficiently non-corrosive toward Pt when deoxygenated.

For Air-saturated:

$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$\Delta\phi_e(oxy) = 1.229 - \frac{.0592}{2} \log \frac{[H_2O]}{P_{O_2}^{1/2} [H^+]^2} = 1.229 + \frac{.0592}{4} \log(0.2) - .0592\, pH$

$\Delta\phi_e(oxy) = 1.219 - 0.0592\, pH$

(i) pH = 0

$\Delta\phi_e(oxy) = 1.219\, V$

$\therefore$ $[Pt^{++}]$ in solution adjacent to Pt is

$1.219 = 1.118\, V + \frac{.0592\, V}{2} \log [Pt^{++}]$

⑤ $\therefore \log [Pt^{++}] = 3.4 \rightarrow [Pt^{++}] = 2.5 \times 10^3\, M$

$\Rightarrow$ solution is too corrosive toward Pt

(ii) pH = 4

$\Delta\phi_e(oxy) = 0.982\, V$

$\therefore$ $[Pt^{++}]$ in solution adjacent to Pt is

$0.982\, V = 1.118\, V + \frac{.0592\, V}{2} \log [Pt^{++}]$

⑤ $\therefore \log [Pt^{++}] = -4.598 \Rightarrow [Pt^{++}] = 2.5 \times 10^{-5}\, M$

$\therefore$ for air-saturated conditions, pH = 0 is too corrosive to Pt and pH = 4 is sufficiently non-corrosive.

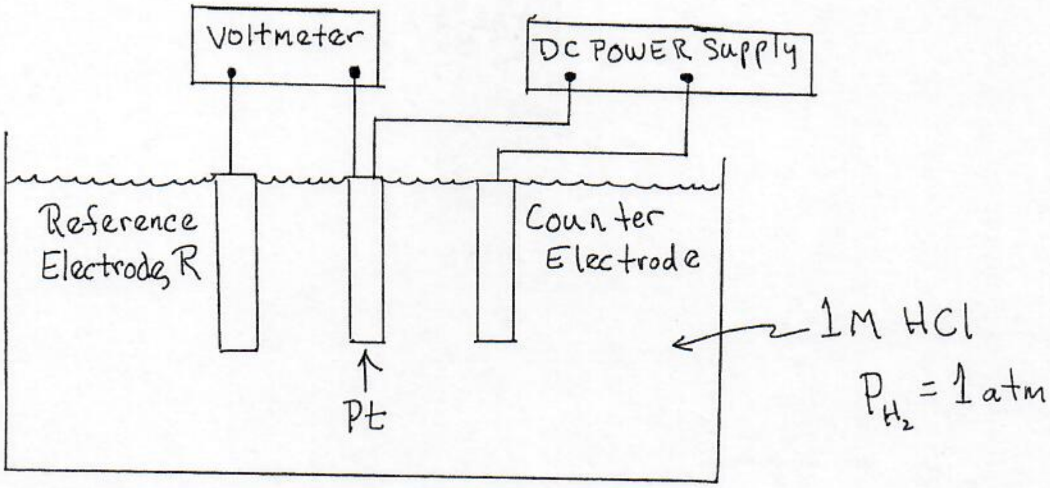
(4.) $Cr_2O_7^{=} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$

$\therefore \Delta\phi_e(Cr^{+6}/Cr^{+3}) = 1.330\, V - \frac{.0592\, V}{6} \log \frac{[Cr^{+3}]^2 [H_2O]^7}{[Cr_2O_7^{=}][H^+]^{14}}$

$[Cr^{+3}] = 1M$

$\therefore \Delta\phi_e(Cr^{+6}/Cr^{+3}) = 1.330\, V + \frac{.0592}{6} \log [Cr_2O_7^{=}][H^+]^{14}$

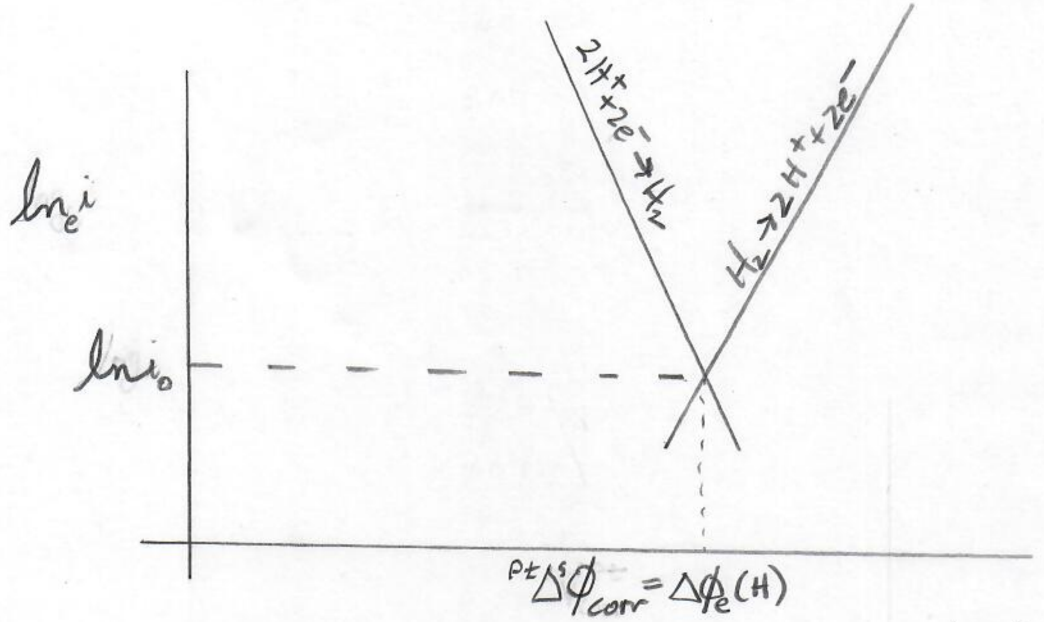
3. Assuming ideal solution behavior a Standard Hydrogen Electrode can be created by immersing a platinum electrode into an aqueous solution of 1M HCl that is saturated with 1 atm of $H_2(g)$. The value of β for the charge transfer reaction associated with the SHE is 0.500. The objective is to measure the numerical value of the exchange current density, i_o, of the H/H^+ redox couple of the SHE.
The apparatus for determining i_o is illustrated in the following sketch. R is a theoretically ideal reference electrode.



The DC power supply sets a particular value of cell voltage. At each value of cell voltage the potential of the platinum electrode is measured with respect to the reference electrode, R; that value of potential is then subtracted from the corrosion potential of platinum. The difference is listed in the left-hand column of the following Table. The second column lists i_{ex}, which is the current density that flows through the external circuit that connects the platinum and counter electrodes to the DC power supply (i_{ex} is obtained by measuring the cell current and dividing by the surface area of the platinum electrode).

${}^{Pt}\Delta^{S}\phi - {}^{Pt}\Delta^{S}\phi_{corr}$ (mV)	i_{ex} (amp/cm^2)
-50	-0.0583
-20	-0.0205
-10	-0.0101
-5	-0.005
-2	-0.002
-1	-0.001
1	0.001
2	0.002
5	0.005
10	0.0101
20	0.0205
50	0.0583

Use the information provided to calculate the exchange current density of the SHE, $i_{o(SHE)}$.



In this problem, i_{corr} on the Platinum electrode = $i_o(H)$

$$\therefore i_o(H) = \left.\frac{\partial i_{ex}}{\partial\left({}^{Pt}\Delta^{s}\phi_{corr}\right)}\right|_{{}^{Pt}\Delta^{s}\phi_{corr}=0} \left(\frac{1}{b_{ox}+b_{red}}\right)$$

$$b_{ox} = \frac{Z\beta F}{RT} = \frac{\left(1\,\frac{equiv}{mole}\right)\left(\frac{1}{2}\right) 96{,}500\,\frac{coul}{equiv}}{1.9872\,\frac{cal}{mole\,K}\;298K\;\frac{1\,volt\cdot Coul}{0.239\,cal}}$$

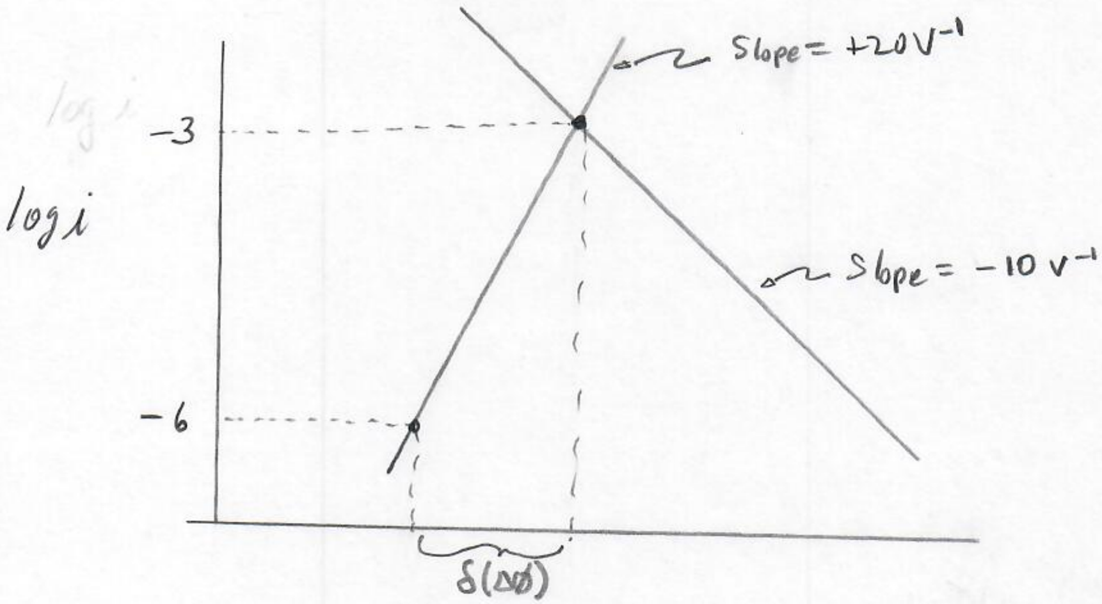
⑩ $\left\{\; \therefore b_{ox} = 19.47\,V^{-1} \right.$ and $b_{red} = 19.47\,V^{-1}$

⑩ $$\therefore i_o(H) = \left(\frac{0.001\,A/cm^2}{0.001\,V}\right)\left(\frac{1}{19.47+19.47}\,V\right)$$

$$\therefore i_o(H) = 25.7\,\frac{mA}{cm^2}$$

4. A cast iron pipe transports waste of a chemical refining plant to a waste storage facility. The waste is an oxygen-free, aqueous solution of pH 4. Measurements indicate that the pipe's corrosion rate is 1×10^{-3} A/cm^2. To extend the lifetime of the pipe it is necessary to lower its corrosion rate. It is decided to cathodically polarize the pipe in order to lower its corrosion rate to 1×10^{-6} A/cm^2. To that end laboratory tests are performed in which samples of the cast iron pipe are anodically and cathodically polarized in the waste and the slopes of the polarization curves are measured as:
slope of anodic polarization curve = $\partial \mathrm{Log}_{10} i / \partial \eta_{corr} = +20\mathrm{V}^{-1}$; and
slope of cathodic polarization curve = $\partial \mathrm{Log}_{10} i / \partial \eta_{corr} = -10\mathrm{V}^{-1}$.

Use the information provided to calculate the value of the applied current density, $i_{applied}$, that is required to lower the oxidation rate of the pipe to 1×10^{-6} A/cm^2.



For the kinetics of oxidation:

$$20\mathrm{V}^{-1} = \frac{-3-(-6)}{\delta(\Delta\phi)}$$

⑩

$$\Rightarrow \delta(\Delta\phi) = 0.150\,\mathrm{V} =$$ amount that potential must be lowered below $\Delta\phi_{corr}$

For the kinetics of reduction:

$$-10\mathrm{V}^{-1} = \frac{\log i_{red} - (-3)}{-0.150\,\mathrm{V}}$$

$$\Rightarrow \log i_{red} = -1.5$$

$$\therefore i_{red} = 31.6\,\mathrm{mA/cm^2}$$

⑮

$$i_{ex} = i_{red} - i_{ox} = 31.6\frac{\mathrm{mA}}{\mathrm{cm^2}} - 1\times10^{-6}\frac{\mathrm{A}}{\mathrm{cm^2}} \simeq 31.6\frac{\mathrm{mA}}{\mathrm{cm^2}}$$