

MSE 112  
Mid-Term EXAM, SPRING 2014

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.

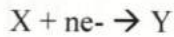
Logs are in base 10.

1 Joule = 1 volt•coulomb = 0.239 calorie

R=gas constant = 1.9872 cal/(mole°K)

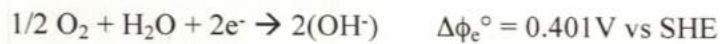
F= Faraday's Constant  $\approx$  96,500 coulombs/equivalent

<u>Problem</u>	<u>Point Value</u>
1	30
2	20
3	50



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

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



$$i_{\text{ox}} = (zF/N_0) N_M N_B d_{MB}^2 (8\pi kT/m)^{1/2} \exp(-\Delta G^\ddagger/RT) \exp(zF\beta^M \Delta S_\phi/RT)$$

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

$$i_o = \{zFd^2(8\pi RT/m)^{1/2} \exp(-[\Delta G^\ddagger + \Delta G^\ddagger]/RT) \exp(z[1-\beta]F \Delta\phi_e^\circ/RT)\} [\text{H}^+] (P_{\text{H}_2})^{1/2} / [\text{H}^+]^{1-\beta}$$

$$i_o = D(R_a R_b R_c \dots) \{(P_i P_j P_k \dots) / (R_a R_b R_c \dots)\}^\beta = D (P_i P_j P_k \dots) (R_a R_b R_c \dots)^{1-\beta}$$

$$i_o = D[\text{H}^+] (P_{\text{H}_2})^{1/2} / [\text{H}^+]^{1-\beta} = D P_{\text{H}_2}^{(1-\beta)/2} [\text{H}^+]^\beta$$

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

1. Equal surface areas of palladium (Pd) and thallium (Tl) are immersed in  $\text{N}_{2(\text{g})}$ -saturated 1M NaCl (pH = 7). After immersion, the Pd and Tl are electrically connected by a metal wire (outside of the aqueous solution). The standard free energies of formation of  $\text{Pd}^{++}$  and  $\text{Tl}^{+3}$  are given by the following reactions



At steady-state specify exactly as possible the corrosion potential of the galvanic couple (i.e., if possible state the numerical value of the corrosion potential. If it is not possible to state the exact value, then state the range of possible values by specifying the minimum and maximum possible values.)

$$\text{Pd: } -42,206 \text{ cal/mole} \times \frac{1 \text{ Joule}}{0.239 \text{ cal}} = 176,594 \frac{\text{Joule}}{\text{mole}}$$

$$\text{Tl: } -49,807 \text{ cal/mole} \times \frac{1 \text{ Joule}}{0.239 \text{ cal}} = 208,440 \frac{\text{Joule}}{\text{mole}}$$

$$\Delta \phi_e^\circ = -\frac{\Delta G^\circ}{nF}$$

$$\textcircled{4} \quad \text{Pd: } \Delta \phi_e^\circ = \frac{176,594 \text{ J/M}}{2 \frac{\text{equiv}}{\text{M}} \cdot 96,500 \frac{\text{coul}}{\text{equiv}}} = 0.915 \text{ V}$$

$$\textcircled{4} \quad \text{Tl: } \Delta \phi_e^\circ = \frac{208,440 \text{ J/M}}{3 \frac{\text{equiv}}{\text{M}} \cdot 96,500 \frac{\text{coul}}{\text{equiv}}} = 0.720 \text{ V}$$

$$\Delta \phi_e^\circ(\text{H}) = +0.059 \text{ V} \log [\text{H}^+] = -0.413 \text{ V}$$

$\therefore$  Concentration of  $\text{Pd}^{++}$  for which Pd is in equilibrium with H is:

$$\textcircled{8} \quad -0.413 \text{ V} = 0.915 \text{ V} + \frac{0.0592 \text{ V}}{2} \log [\text{Pd}^{++}]$$

$$\Rightarrow \log [\text{Pd}^{++}] = -44.865 \text{ or } [\text{Pd}^{++}] = 1.365 \times 10^{-45} \text{ M}$$

$\therefore$  Concentration of  $\text{Tl}^{+3}$  for which Tl is in equilibrium with H is:

$$\textcircled{8} \quad -0.413 \text{ V} = 0.720 \text{ V} + \frac{0.0592 \text{ V}}{3} \log [\text{Tl}^{+3}]$$

$$\therefore \log [\text{Tl}^{+3}] = -57.42$$

$\textcircled{6} \Rightarrow$  Both Pd and Tl act as H-electrodes  
 $\Rightarrow \Delta \phi_{\text{corr}}^{\text{Pd}} = \Delta \phi_{\text{corr}}^{\text{Tl}} = \Delta \phi_e^\circ(\text{H}) = -0.413 \text{ V vs SHE}$

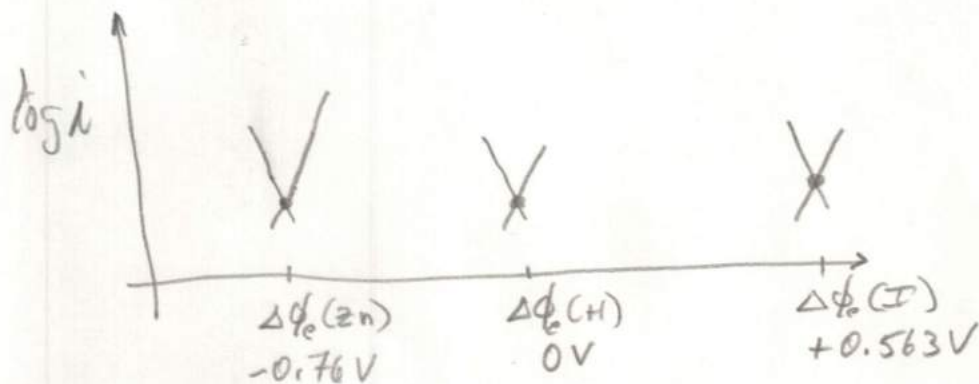
2. A zinc-iodine battery consists of electrodes of zinc and platinum immersed in aqueous 1M HI (pH=0) that is saturated with  $I_{2(g)}$  and contains 1M of  $ZnI_2$ . What is the theoretical maximum possible value of the battery's cell potential (i.e., the maximum possible difference in potential between the Zn electrode and the platinum electrode)? Explain why the battery's measured cell voltage is most likely smaller than the theoretical maximum value.

$$\textcircled{1} \rightarrow \Delta\phi_e(\text{Zn}) = -0.760 + \frac{0.0592}{2} \log[Zn^{2+}] = -0.760V$$

$$\textcircled{1} \rightarrow \Delta\phi_e(\text{H}) = 0V$$

$$\Delta\phi_e(\text{I}) = 0.535V - \frac{0.0592V}{2} \log \frac{P_{I_2}}{[I^-]^2} = 0.535V + 0.0592 \log 3$$

$$\textcircled{2} \rightarrow \Delta\phi_e(\text{I}) = +0.5632V$$



$$\textcircled{8} \rightarrow \therefore V_{\text{cell}}^{\text{theor}} \Big]_{\text{MAX}} = 0.5632V - (-0.760V) = 1.323V$$

$$V_{\text{cell}}^{\text{theor}} \Big]_{\text{min}} = 0.563V - 0V = 0.563V$$

$\textcircled{8} \rightarrow$  It's likely that  $-0.76V < \Delta\phi_{\text{corr}}^{\text{Zn}} < 0V$

$\Rightarrow$  It is likely that  $V_{\text{cell}}$  is less than  $+1.323V$   
(and greater than  $+0.563V$ )

3. The corrosion rate and corrosion potential of nickel are  $10 \text{ mA/cm}^2$  and  $-0.224 \text{ V}$ , respectively, in an air-saturated aqueous electrolyte of  $\text{pH}=4$ . When the aqueous solution is saturated with nitrogen gas the corrosion rate of nickel is lowered to  $17.3 \times 10^{-6} \text{ A/cm}^2$  and its corrosion potential is  $-0.500 \text{ V}$ . In the nitrogen-saturated solution, the slope of the reduction reaction (i.e.,  $\partial \log i_{\text{red}} / \partial \Delta \phi$ ) on the surface of nickel is  $-(1/0.118) \text{ V}^{-1}$ . The rate determining step of the reduction of hydrogen ions is:  $\text{H}^+ + \text{e}^- \rightarrow \text{H}$ .

The steady-state corrosion rate must be further lowered to  $5 \times 10^{-6} \text{ A/cm}^2$ . Specify the exact change you would make to the chemistry of the aqueous solution in order to lower the corrosion rate of nickel to  $5 \times 10^{-6} \text{ A/cm}^2$ .

Air sat'd:  $i_{\text{corr}} = 10 \frac{\text{mA}}{\text{cm}^2}$   $\Delta \phi_{\text{corr}} = -0.224 \text{ V}$   
 $\text{N}_2$ -sat'd:  $i_{\text{corr}} = 17.3 \times 10^{-6} \text{ A/cm}^2$   $\Delta \phi_{\text{corr}} = -0.500 \text{ V}$   
 $\therefore$  reduction rxn:  $\text{pH}=4$   $\frac{\partial \log i_{\text{red}}}{\partial \Delta \phi} = -\frac{1}{0.118 \text{ V}}$

(10)  $\rightarrow \therefore \frac{\partial \log i_{\text{ox}}}{\partial \Delta \phi} = \frac{\log 10^{-2} - \log 17.3 \times 10^{-6}}{-0.224 - (-0.500)} = \frac{-2 - 1.238 + 6}{0.276} = \frac{2.762}{0.276} = 10 \text{ V}^{-1}$

$\Delta \phi_e(\text{H}) = 0 \text{ V} - \frac{0.0592}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2} = 0.0592 \log [\text{H}^+] = -0.2368 \text{ V}$

Kinetics of  $\text{H}^+$  reduction  $\Rightarrow \log \frac{17.3 \times 10^{-6}}{i_0} = \frac{-1}{0.118 \text{ V}} [-0.500 - (-0.2368)]$

$1.238 - 6 - \log i_0 = 2.2305 \text{ V}^{-1}$

(10)  $\rightarrow \therefore \log i_0 = -6.9925$  and  $i_0 = 1.0175 \times 10^{-7} \frac{\text{A}}{\text{cm}^2}$

$i_0 = D [\text{H}^+]^{\beta} P_{\text{H}_2}^{\frac{1-\beta}{2}} = D [\text{H}^+]^{\beta}$

$i_{\text{red}} = i_0 \exp \left( -\frac{zF(1-\beta)}{RT} \eta_e \right)$

$\therefore \frac{\partial \log i_{\text{red}}}{\partial \eta_e} = -\frac{z(1-\beta)F}{RT(2.303)} = \frac{-z(1-\beta)}{0.059} = -\frac{1}{0.118}$

(5)  $\rightarrow \Rightarrow \beta = \frac{1}{2}$

$\therefore i_0 = D [\text{H}^+]^{\frac{1}{2}}$

(5)  $\rightarrow \therefore D = \frac{1.0175 \times 10^{-7}}{[10^{-4}]^{\frac{1}{2}}} = 1.0175 \times 10^{-5}$

(OVER  $\rightarrow$ )

At

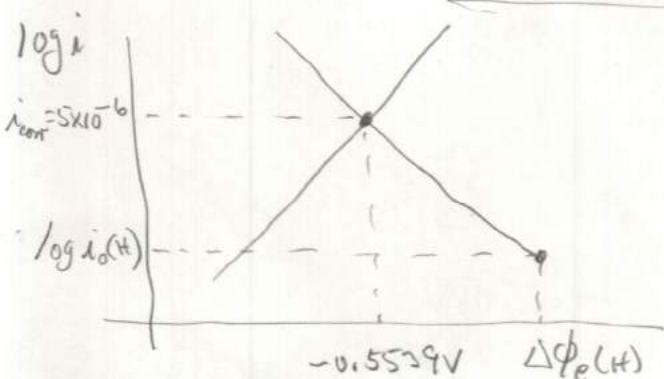
$$i_{\text{corr}} = 5 \times 10^{-6} \text{ A/cm}^2 \quad \Delta\phi_{\text{corr}} \text{ is given by}$$

$$\log \frac{5 \times 10^{-6}}{17.3 \times 10^{-6}} = 10 \text{ V}^{-1} (\Delta\phi_{\text{corr}} - (-0.50))$$

$$-0.5391 = 10 \text{ V}^{-1} [\Delta\phi_{\text{corr}} + 0.50]$$

$$\Delta\phi_{\text{corr}} = -0.5539 \text{ V}$$

(10) →



Determine the required pH by expressing  $i_0(\text{H})$  and  $\Delta\phi_e(\text{H})$  in terms of pH :

$$\log \frac{5 \times 10^{-6}}{i_0(\text{H})} = \frac{-1}{0.118 \text{ V}} [-0.5539 - \Delta\phi_e(\text{H})] \quad \Delta\phi_e = 0 - \frac{0.0592}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$\log \frac{5 \times 10^{-6}}{1 \times 10^{-5} [\text{H}^+]^{1/2}} = \frac{-1}{0.118} [-0.5539 - 0.0592 \log [\text{H}^+]]$$

$$\log 0.5 - \frac{1}{2} \log [\text{H}^+] = 4.6941 + \frac{1}{2} \log [\text{H}^+]$$

$$\therefore \log [\text{H}^+] = -4.9951$$

$$\text{pH} = 4.9951 \approx 5$$

(10) →