MSE 112
Mid-Term EXAM, SPRING 2014

NAME:

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
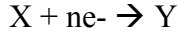
All voltages are measured with respect to SHE.

Logs are in base 10.

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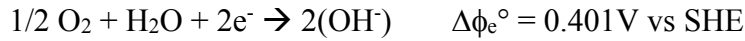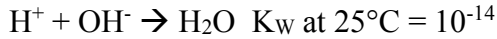R=gas constant = 1.9872 cal/(mole°K)
F= Faraday's Constant ≈ 96,500 coulombs/equivalent

Problem	*Point Value*
1	30
2	20
3	50

$X + ne- \rightarrow Y$

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

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

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

$Au^{+3} + 3e^- -> Au$ $\qquad\qquad$ $\Delta\phi_e° = 1.300V$ vs SHE

$Pt^{+2} + 2e^- \rightarrow Pt$ $\qquad\qquad$ $\Delta\phi_e° = 1.118V$ vs SHE

$2I^- + 2e^- -> I_{2(g)}$ $\qquad\qquad$ $\Delta\phi_e° = 0.535V$ vs SHE

$1/2\ O_2 + H_2O + 2e^- \rightarrow 2(OH^-)$ $\qquad$ $\Delta\phi_e° = 0.401V$ vs SHE

$Cu^{++} + 2e^- \rightarrow Cu$ $\qquad\qquad$ $\Delta\phi_e° = 0.337V$ vs SHE

$2H^+ + 2e^- \rightarrow H_2$ $\qquad\qquad$ $\Delta\phi_e° = 0.0V$ vs SHE

$H_2O + e^- \rightarrow 1/2\ H_2 + (OH^-)$ $\qquad$ $\Delta\phi_e° = -0.828V$ vs SHE

$Fe^{++} + 2e^- \rightarrow Fe$ $\qquad\qquad$ $\Delta\phi_e° = -0.447V$ vs SHE

$Zn^{++} + 2e^- \rightarrow Zn$ $\qquad\qquad$ $\Delta\phi_e° = -0.760V$ vs SHE

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

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

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

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

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

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

1.　　　　　　Equal surface areas of palladium (Pd) and thallium (Tl) are immersed in $N_{2(g)}$-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 Pd^{++} and Tl^{+3} are given by the following reactions

$Pd^{+2} + 2e^- \rightarrow Pd$　　$\Delta G° = $ -42,206 cal/mole

$Tl^{+3} + 3e^- \rightarrow Tl$　　$\Delta G° = $ -49,807 cal/mole

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.)

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.

3. The corrosion rate and corrosion potential of nickel are 10 mA/cm^2 and -0.224V, respectively, in an air-saturated aqueous electrolyte of pH=4. When the aqueous solution is saturated with nitrogen gas the corrosion rate of nickel is lowered to 17.3x10^{-6} A/cm^2 and its corrosion potential is -0.500V. In the nitrogen-saturated solution, the slope of the reduction reaction (i.e., $\partial \log_{10} i_{red} / \partial \Delta \phi$) on the surface of nickel is -(1/0.118)V^{-1}. The rate determining step of the reduction of hydrogen ions is: $H^+ + e^- \rightarrow H$.

The steady-state corrosion rate must be further lowered to 5x10^{-6} 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 5x10^{-6} A/cm^2.