MSE 112
Mid-Term EXAM, SPRING 2006

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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(a,b)	10 (5,5)
2	15
3	25
4(a,b,c,d,e,f)	50 (2,2,3,8,24,9)

$X + ne- \rightarrow Y$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1. (a.) In an aqueous solution of 0.1M Na_2SO_4 (pH = 8, T=25°C), at what value of the dissolved oxygen concentration will the thermodynamic driving force for corrosion of iron be the same as in an oxygen-free solution of 0.1M Na_2SO_4 (pH = 8)?

pH = 8

$$\Delta\phi_e(O) = \Delta\phi_e(H)$$

Calc. P_{O_2}

$$H_2O + e^- \rightarrow \tfrac{1}{2}H_2 + OH^- \quad \Delta\phi_e^\circ = -0.828V$$

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH^-) \quad \Delta\phi_e^\circ = 0.401$$

$$\Delta\phi_e(H) = -0.828 - 0.0592 \log \underset{10^{-6}}{[OH^-]}\,\cancel{P_{H_2}^{1/2}}$$

$$= -0.828 - 0.0592(-6)$$

+2 $$= -0.4728V$$

$$-0.4728 = \Delta\phi_e(\text{oxy}) = 0.401 - \frac{0.0592}{2}\log\frac{[OH^-]^2}{P_{O_2}^{1/2}}$$

$$-0.4728 = 0.401 - 0.0592 \log 10^{-6} + \frac{0.0592}{2}\log P_{O_2}^{1/2}$$

$$3.018\times10^{-42} = P_{O_2}^{1/2}$$

+3 $$9.109\times10^{-84}\,\text{atm} = P_{O_2}$$

(b) Explain why at steady-state, the partial pressure of hydrogen gas is one atmosphere on the surface of iron immersed in an oxygen-free aqueous solution at 25°C.

If greater ⇒ would bubble, would need to be pressurized
If less ⇒ would not be @ equil.

$2H^+ + 2e^- \rightarrow H_2$

$$\Delta\phi_e = 0 - \frac{0.0592}{2} \log \frac{P_{H_2}}{[H^+]^2}$$

Initially, $P_{H_2} = 0\,atm \Rightarrow \Delta\phi_e \rightarrow \infty$

As oxidation of metal occurs and reduction of H^+ occurs, P_{H_2} increases and $\Delta\phi_e$ decreases. The more oxidation that occurs, the more H^+ are reduced, causing P_{H_2} to increase. As P_{H_2} increases, $\Delta\phi_e$ decreases, causing the corrosion potential to decrease, which causes the oxidation rate to decrease. When P_{H_2} reaches 1 atm, further increases in P_{H_2} are not possible, unless the system is pressurized. Hence, steady-state value of $\underline{P_{H_2} = 1 atm}$

2. Waste from a plastics' manufacturing plant is being stored in a galvanized steel container, which is corroding on its inside surface. The rate of corrosion is too high for the vessel to meet its 10-year lifetime. As an initial remedial action, the waste solution was de-oxygenated, which significantly lowered the vessel's corrosion rate. The corrosion rate in deoxygenated waste, which consists of 0.1M HCl, is still too high and needs to be lowered by 50%.

   The slopes of the anodic and cathodic polarization curves of zinc in oxygen-free 0.1M HCl at 25°C are +10 decades/volt and –10 decades/volt, respectively. The corrosion potential of zinc is –600 mV vs SHE and the corrosion rate of zinc is 10 mA/cm^2. By how much should the pH of the solution be increased in order to decrease the corrosion rate by 50%?

de-oxygenated 0.1M HCl

$M_{ox} = 10 \quad M_{red} = -10$

$\Delta\Phi_{corr}(Zn) = -0.6V$

$i_{corr}(Zn) = 10 mA/cm^2$

$H^+ + e^- \rightarrow \frac{1}{2}H_2$

$\Delta\phi_e = \underset{0}{\Delta\phi_e^\circ} - \frac{RT}{F}\ln\frac{\overset{1}{\cancel{P_{H_2}^{1/2}}}}{[H^+] \rightarrow 0.1}$

$\Delta\phi_e = 0.0592 \log 0.1 = \boxed{-0.0592V}$ +3

$\log i_{corr} - \log i_o = -m(\Delta\Phi_{corr} - \Delta\phi_e)$

$\log i_o = \underline{\log(10)} + 10(-0.6 + 0.0592)$

$\log i_o = -4.408$

$\boxed{i_o = 3.91 \times 10^{-5} mA/cm^2}$ +5

$i_o = D P_{H_2}^{(1-\beta)/2} [H^+]^{\beta}$

$-\frac{(1-\beta)ZF}{2.303RT} = -10$

$\frac{(1-\beta)}{0.0592} = 10$

$1 - \beta = 0.592 \Rightarrow \beta = 0.408$ +2

$3.91 \times 10^{-5} = D(1)[0.1]^{0.408}$

$1 \times 10^{-4} = D$ +2

New Case : Want to decrease corrosion rate by 50%

$i_{corr,new} = 5 mA/cm^2$

Reduction Rxn : $H^+ + e^- \longrightarrow \tfrac{1}{2} H_2$ $\quad$ pH = unknown

$$\left.\begin{aligned} \Delta\phi_e &= 0 - 0.0592 \log \frac{P_{H_2}}{[H^+]} \\ &= 0 + 0.0592 \log [H^+] = -0.0592\,\mathrm{pH} \\ i_o &= 1\times10^{-4}\,(1)\,[H^+]^{0.408} \end{aligned}\right\} +4$$

$$\log i_{corr} - \log i_o = m_{red}(\Delta\phi_{corr} - \Delta\phi_e)$$

① $$\log 5 - \log\left(1\times10^{-4}[H^+]^{0.408}\right) = -10\left(\Delta\phi_{corr,\,new} - 0.0592 \log [H^+]\right)$$

To determine $\Delta\phi_{corr}$, must use oxidation reaction

Oxidation Rxn : $Zn^{2+} + 2e^- \longrightarrow Zn$ $\quad \Delta\phi_e^\circ = -0.760\,V$

$$\Delta\phi_e = -0.760 + \frac{0.0592}{2} \log [\underset{10^{-6}}{Zn^{2+}}] = -0.938\,V$$

$$\log i_{corr,new} - \log i_{corr} = m_{ox}(\Delta\phi_{corr,\,new} - \Delta\phi_{corr})$$

$$\log(5) - \log(10) = 10\left(\Delta\phi_{corr,\,new} + 0.6\right)$$

$$\Delta\phi_{corr,\,new} = -0.63\,V \qquad +5$$

Now plugging back into equation ① above :

$$\log 5 - \log\left(1\times10^{-4}[H^+]^{0.408}\right) = -10\left(-0.63 - 0.0592 \log [H^+]\right)$$

$$\left.\begin{aligned} &\text{Solving} \Longrightarrow [H^+] = 0.025\,M \\ &\boxed{\mathrm{pH} = -\log [H^+] = 1.6} \end{aligned}\right\} +4$$

3. The sketch (on the next page) shows an electrochemical cell in which the anodic and cathodic polarization curves of iron were measured in air-free 0.1M H_2SO_4. The second sketch shows the polarization curves.

+2 (a). On the sketch of the polarization curves, label the corrosion potential and indicate the approximate corrosion rate of iron immersed in air-free 0.1M H_2SO_4.

+2 (b) Identify the reaction whose approximate rate is given at point A.

$H^+ + e^- \rightarrow \frac{1}{2}H_2$

+2 (c) Identify the reaction whose approximate rate is given at point B.

$Fe \rightarrow Fe^{++} + 2e^-$

(d) State all of the oxidation and reduction reactions that take place on the surface of iron at potential $\Delta\phi_1$. What reaction is occurring at the highest rate?

+4

$Fe \rightarrow Fe^{++} + 2e^- \Longleftarrow$ highest rate

$Fe^{++} + 2e^- \rightarrow Fe$

$2H^+ + 2e^- \rightarrow H_2$

$H_2 \rightarrow 2H^+ + 2e^-$

+1 (e) Indicate on the sketch the direction of electron flow in the external circuit connecting iron and platinum when the potential of iron is $\Delta\phi_1$.

(f) State all of the oxidation and reduction reactions that take place on the surface of platinum when the potential of iron is $\Delta\phi_1$. What reaction on platinum is occurring at the highest rate?

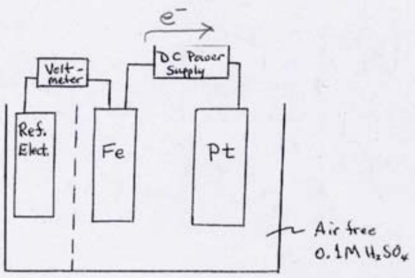
+4

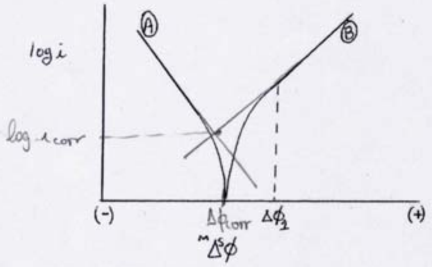
$Pt^{++} + 2e^- \rightarrow Pt$

$Pt \rightarrow Pt^{++} + 2e^-$

$2H^+ + 2e^- \rightarrow H_2 \Longleftarrow$ Highest Rate

$H_2 \rightarrow 2H^+ + 2e^-$


e⁻
Volt-meter
D.C. Power Supply
Ref. Elect.
Fe
Pt
Air free 0.1M H₂SO₄


log i
A
B
log i corr
(-)
Δφcorr
Δφ1
(+)
MΔSφ

4. The Pourbaix diagram for iron at 25°C is presented on page 10. In this problem, ignore the "short-dashed" lines, i.e., the lines that are labeled as **N'** (where N is a number, i.e., ignore lines such as 2', 3', 4', 5', etc.).
Solid phases are written in boldface, e.g., **Fe, and Fe(OH)$_2$**. All other species are soluble in water.

(a) Write down the reaction whose equilibrium potential as a function of pH is given by the "long-dashed" line "a".

+2

$H^+ + e^- \rightarrow \frac{1}{2}H_2$

$H_2O + e^- \rightarrow \frac{1}{2}H_2 + (OH^-)$

(b) Write down the reaction whose equilibrium potential as a function of pH is given by line "long-dashed" line "b".

+2

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

$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH^-)$

(c) Identify the reaction whose equilibrium potential as a function of pH is described by the 4 parallel lines labeled "23". Note: the same reaction describes each of the four lines. The highest of the four lines is labeled "0" and describes the equilibrium potential for the case in which the soluble species has a concentration of 10^0 moles/liter. The lowest of the four lines is labeled "-6" and this line describes the equilibrium potential for the case in which the soluble species has a concentration of 10^{-6} moles/liter.

+3

$Fe \rightleftharpoons Fe^{++} + 2e^-$

(d) With a pencil/pen trace the entire Pourbaix Diagram of iron for the case in which all water-soluble species of iron have a concentration of 10^{-6} moles/liter.

+8

(e) Identify the reactions whose equilibrium potentials as functions of pH are described by the following lines: "18", "28", "20", "16", "12", "19", "24", and "29".

$H_2O \rightleftharpoons H^+ + OH^-$

+3 18: $Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$

+3 28: $Fe^{2+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ + e^-$

+3 20: $Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$

+3 16: $Fe(OH)_2 + H_2O \rightleftharpoons Fe(OH)_3 + H^+ + e^-$

+3 12: $Fe + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+ + 2e^-$

+3 19: $Fe(OH)_2 \rightleftharpoons HFeO_2^- + H^+$

+3 24: $Fe + 2H_2O \rightleftharpoons HFeO_2^- + 3H^+ + 2e^-$

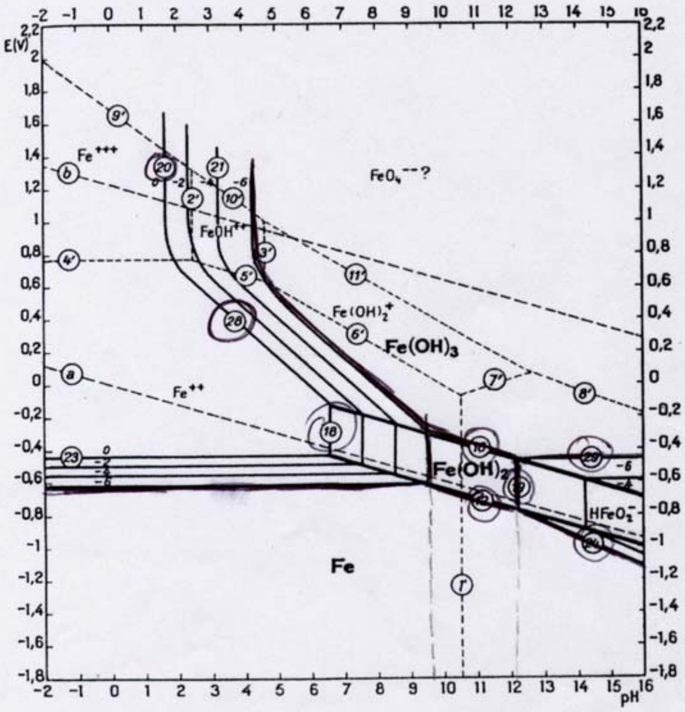
+3 29: $Fe(OH)_3 + e^- \rightleftharpoons HFeO_2^- + H_2O$

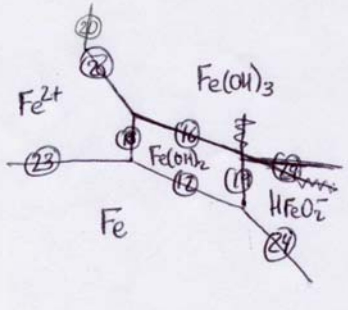
(f) An alkaline solution (pH=14) is used for refining ore at Homestake Mining's gold mine, which is located close to Clearwater, CA. After refining of the ore, the alkaline solution is stored in a large, carbon steel (approximately, unalloyed iron) vessel. When a new batch of ore is processed, the stored alkaline solution is reused. Under the operating conditions described above, the carbon steel vessel is corroding at a rate that will lead to failure of the vessel in less than two years. The vessel's intended lifetime is 40 years. Because of the vessel's size, it is very expensive.

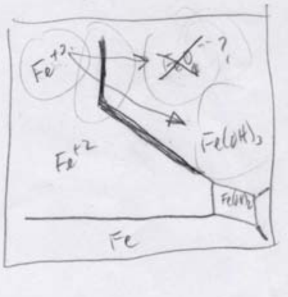
Imagine yourself as the materials engineer at Homestake Mining. You need to explain to your supervisor the likely cause of corrosion of the vessel. In addition, you need to solve the corrosion problem (i.e., lower the vessel's corrosion rate to close to zero). You can accomplish both goals by using the Pourbaix Diagram of iron. Specifically, using the Pourbaix Diagram for which the concentration of all water soluble species of iron is 10^{-6} moles/liter, (a) explain the likely reason why the vessel is corroding at present, and (b) identify the pH-range (i.e., the minimum value and the maximum value (approximate)) in which the alkaline solution's pH must be lowered while in storage in order to guarantee that the vessel is either immune to corrosion, or forms a passive film at all potentials?

+11 +5 (a) Only soluble species @ pH = 14 is $HFeO_2^-$

+6 (b) ~ 9.7 to 12.1 since Fe, $Fe(OH)_2$, & $Fe(OH)_3$ stable


E(V)
pH
2,2
2
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
-0,2
-0,4
-0,6
-0,8
-1
-1,2
-1,4
-1,6
-1,8
-2
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Fe⁺⁺⁺
Fe⁺⁺
FeOH⁺⁺
Fe(OH)₂⁺
FeO₄⁻⁻?
Fe(OH)₃
Fe(OH)₂
HFeO₂⁻
Fe
9'
b
4'
a
2'
3'
5'
6'
7'
8'
10'
11'
1'
20
21
28
18
16
12
19
23
24
29
0
-2
-4
-6


20
26
Fe²⁺
Fe(OH)₃
18
16
23
Fe(OH)₂
12
19
29
HFeO₂⁻
Fe
24


Fe⁺²
FeO₄⁻⁻?
Fe⁺²
Fe(OH)₃
Fe(OH)₂
Fe