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Corrosion and Surface Chemistry of Metals

Solution Manual

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Solutions to Problems in Annexe 3

CHAPTER 1

1.1

Fe + H_2SO_4 --> $FeSO_4$ + H_2

Cu + H_2SO_4 + ½ O_2 --> $CuSO_4$ + H_2O

2 Cu + ½ O_2 + 4 HCl --> 2 $CuCl^-$ + 3 H+ + H_2O

Zn + 2 HCl --> $ZnCl_2$ + H_2

1.2

v_{cor} = 30µm/year

i = nF v_{cor}

table 1.3: 1 mm/year = 3.06 n ρ /M

iron: ρ = 7.86 g/cm^3, M = 55.8 g/mol, n = 2 (in deaerated solution)

1 mm/year = 3.06 (2) (7.86)/55.8 = 0.862 A/m^2

30 mm/year = (0.862) ($30x10^{-3}$) = 2.59 $x10^{-2}$ A/m^2 = 2.6 µA/cm^2

1.3

2 Al + 6 H^+ --> $2Al^{3+}$ + 3 H_2

2 mol Al yield 3 mol H_2 ,

M_{Al} = 27.0 g/mol, 1 g Al = 0.0370 mol Al

0.0379 mol Al --> $5.56x10^{-2}$ mol H_2

V_{H2} = N_{H2} RT/P = ($5.56x10^{-2}$)(8.3)(298)/10^5 = $1.35x10^{-3}$ m^3 = 1.375 liter

1.4

dV_{H2}/dt = 0.5 ml/h

dN_{H2}/dt = P (dV_{H2}/dt)/RT

= ($10^5N/m^2$)($0.5cm^3/h$)($10^{-6}m^3/cm^3$)/(8.3Nm/molK)(298K) = $2.02x10^{-5}$ mol H_2/h

= $5.62x10^{-9}$ mol H_2/s

Ni + $2H^+$ --> Ni^{2+} + H_2

v_{cor} = (5.62x10-9 mol Ni/s)/(20 cm^2) = 2.81x10-10 mol Ni/ cm^2s

table 1.3: 1 mol/cm^2s = $3.5x10^8$ (M/ρ) mm/year

$M_{Ni} = 58.7$ g/mol, $\rho_{Ni} = 8.9$ g/cm^3

$v_{cor} = (3.15\text{x}10^8)(58.7)(2.81\text{x}10^{-10})/8.9 = \underline{0.58 \text{ mm/year}}$

1.5

Convert weight percent of Fe-13Cr into mol percent:

$M_{Fe} = 55.8$ g/mol , $M_{Cr} = 52.0$ g/mol

1 g alloy contains 0.87 g Fe = 0.87/55.8 = 1.559 x 10^{-2} mol Fe

0.13 g Cr = 0.13/52.0 = 0.250 x 10^{-2} mol Cr

Total 1.809 x 10^{-2} mol

%mol Cr: $(0.250\text{x}10^{-2})(100)/1.809\text{x}10^{-2}$) = 13.8 mol %Cr ---> mol fraction Cr: $\underline{X_{Cr} = 0.138}$

mol% Fe: 86.2 mol% Fe ---> mol fraction Fe: $\underline{X_{Fe} = 0.862}$

Anodic current density: $i_a = i_{a,Fe} + i_{a,Cr} = 2$ mA/cm^2

$i_{a,Cr} = X_{Cr}\, i_a = (0.138)(2) = 0.276$ mA/cm^2

$i_{a,Fe} = X_{Fe}\, i_a = (0.862)(2) = 1.724$ mA/cm^2

Table 1.3: 1 μA/cm^2 = $8.95\text{x}10^{-2}$ mg/dm^{2}day

Cr: $v_{cor,Cr} = (0.276\text{x}10^3)(8.95\text{x}10^{-2})(52.0)/2 = 642$ mg/dm^{2}day

Fe: $v_{cor,Fe} = (1.724\text{x}10^3)(8.95\text{x}10^{-2})(55.8)/2 = 4305$ mg/dm^{2}day

Alloy: Vcor = $v_{cor,Cr} + v_{cor,Fe}$ = $\underline{4947 \text{ mg/dm}^2\text{day}}$

1.6

$Fe + 2\, O_2 \rightarrow Fe_3O_4$

All the oxygen present reacts: (8mg/l) (10^{-3}g/mg) (300 l) /(32g/mol) = $7.50\text{x}10^{-2}$ mol O_2

this corresponds to (3/2)($7.50\text{x}10^{-2}$) = 0.113 mol Fe

surface: 10 m^2

Thickness corroded:

$L = (0.133\text{mol})(55.8\text{g/mol})/10\text{m}^2)(7.86\text{g/cm}^3)(10^4\text{cm}^2/\text{m}^2) = 9.44\text{x}10^{-6}$ cm = $\underline{0.094\ \mu\text{m}}$

CHAPTER 2

2.1

$4\, Cu + O_2 \rightarrow 2\, Cu_2O$

From Fig.2.2: $\Delta G^o \cong -130$ kJ/mol for 1200°C

$\Delta G^o = - RT \ln K = + RT \ln P_{O2}$

$P_{O2} = \exp(\Delta G^o/RT) = \exp\{(- 130\text{x}10^3 \text{J/mol})/ (8.3\text{J/molK})(1473\text{K})\} = \underline{2.4 \text{ x}10^{-5} \text{ bar}}$

2.2

$Fe + CO_2 = FeO + CO$ T = 1373 K

$\Delta G^o = - RT \ln K = - RT \ln (P_{co}/P_{CO2})$

$\Delta G^o = \sum \nu_i \Delta G_i^o$

$\Delta G^o_{FeO} = -264 + 64.7\text{x}10^{-3}$ T kJ/mol For T= 1373K: $\Delta G^o_{FeO} = - 175$ kJ/mol

$\Delta G^o_{CO2} = -394 - 1.13\text{x}10^{-3}$ T kJ/mol $\Delta G^o_{CO2} = - 392$ kJ/mol

$\Delta G^o_{CO} = -112 - 87.8 \text{ x}10^{-3}$ T kJ/mol $\Delta G^o_{CO2} = + 8.55$ kJ/mol

$\Delta G^o = = -175 + 8.55 -(-392) -(0) = 225.5$ kJ/mol

$P_{CO}/P_{CO2} = \exp(-\Delta G^o/RT) = \exp\{(-225.5\text{x}10^3)/(8.3)(1373)\}= 19.8$

$P_{CO} + P_{CO2} = 1$ bar

$19.2\ P_{CO2} + P_{CO2} = 1$ bar ------> $\underline{P_{CO2} = 4.8\text{x}10^{-2} \text{ bar}}$

2.3

$Co + H_2O = CoO + H_2$

$\Delta G^o = \Delta G^o_{CoO} + \Delta G^o_{H2} - \Delta G^o_{Co} - \Delta G^o_{H2O}$

$\Delta G^o_{H2} = 0,\ \Delta G^o_{Co} = 0$

$\Delta G^o_{CoO} = -240 + 78.0 \text{ x}10^{-3}$ T kJ/mol For 1223K : $\Delta G^o_{CoO} = -144.6$ kJ/mol

$\Delta G^o_{H2O} = -246 + 54.9 \text{ x}10^{-3}$ T kJ/mol $\Delta G^o_{H2O} = -178.9$ kJ/mol

$\Delta G^o = -144.6 -(-178.9) = 34.3$ kJ/mol

$K = \exp(-\Delta G^o/RT) = \exp\{-(34.3\text{x}10^3)/(8.3)(1223)\}= 3.38$

$K = P_{H2}/P_{H2O}$ -------> $P_{H2} = 3.38\ P_{H2O}$

$P_{H2} + P_{H2O} = 1$ bar ---> $3.38P_{H20} + P_{H2O} = 4.38\ P_{H2O}$

$P_{H2} = 1/4.38 = \underline{0.23 \text{ bar}}$

$P_{H2O} = 1- 0.23 = \underline{0.77 \text{ bar}}$

2.4

Guntelberg equation: $\log f_{\pm} = -\frac{A_{DB}|z_+ z_-| J^{1/2}}{1 + J^{1/2}}$ with $J = \frac{1}{2} \sum z_i^2 c_i$

a) 0.01 M $FeCl_2$ solution

$J = (1/2)[2^2(0.01)+(-1)^2(0.02) = 0.06/2 = 0.03$ mol/l

$\log f_{\pm} = -(0.51)(2x1)(0.03)^{1/2} / (1+(0.03)^{1/2}) = -0.150$

$f_{\pm} = \underline{0.708}$

b) Solution of 0.01 M $FeCl_2$ + 0.05M HCl

$J = (1/2) [(2^2)(0.01)+(1^2)(0.02) + 0.05 + 0.05] = 0.08$ mol/l

$\log f_{\pm} = -[0.51)(2)(0.08)^{1/2} / 1.283] = -0.225$

$f_{\pm} = \underline{0.596}$

2.5

$E_{rev} = 0 + (RT/nF) \ln [a_{H+}^{2} / P_{H2}]$

$n = 2$ for $2 H^+ + 2 e = H_2$; $T = 60^oC = 333K$; $P_{H2} = 0.5$ bar; pH = 8

$E_{rev} = [(8.3)(333) / (2)(96485)] \ln [10^{-8})^2 / 0.5] = \underline{-0.518 \text{ V}}$

2.6

The corrosion reaction $Cu + 2 H^+ \dashrightarrow Cu^{2+} + H_2$ occurs spontaneously provided $E_{rev,Cu} < E_{rev,H}$

$T = 25^oC$, $P_{H2} = 1$ bar, $c_{Cu2+} = 10\text{-}6$ mol/l :

$E_{rev,Cu} = 0.34 + (0.059/2)\log a_{Cu2+}$

$= 0.34 + (0.059/2)\log 10^{-6} = 0.163$ V

$E_{rev,H} = 0.0 - 0.059$ pH

$= -0.059 (0.5) = -0.030$ V

It follows that $E_{rev,Cu} > E_{rev,H}$ -------> no corrosion

2.7

$Fe^{3+} + H_2O = FeOH^{2+} + H^+$ $K_1 \cong c_{H+}\, c_{FeOH2+} / c_{Fe3+}$

$FeOH^{2+} + H_2O = Fe(OH)_2^{+} + H^+$ $K_2 \cong c_{H+}\, c_{Fe(OH)2+} / c_{Fe3+}$

Calculate K_1, K_2: $-RT \ln K_1 = \Delta G_1$ and $-RT \ln K_2 = \Delta G_2$

$\Delta G^o{}_1 = \mu^o{}_{H+} + \mu^o{}_{FeOH2+} - \mu^o{}_{Fe3+} - \mu^o{}_{H2O}$

$= 0 + (-229.4) - (-4.6) - (-237.2) = 12.6$

$K_1 = \exp(-\Delta G^o{}_1/RT) = \exp[-(12.6x10^3)/(8.3)(298)] = 6.1x10^{-3}$ [mol/l]

$\Delta G^o{}_2 = \mu^o{}_{H+} + \mu^o{}_{Fe(OH)2+} - \mu^o{}_{FeOH2+} - \mu^o{}_{H2O}$

$= 0 + (-438.1) - (-229.4) - (-237.2) = 28.5$

$K_2 = \exp(-\Delta G^o{}_2/RT) = \exp[-(28.5\mathrm{x}10^3)/(8.3)(298)] = 9.91\mathrm{x}10^{-6}$ [mol/l]

For pH = 4:

$c_{FeOH2+} / c_{Fe3+} = K_1/c_{H+} = 6.1\mathrm{x}10^{-3} / 10^{-4} = 61$

$c_{Fe(OH)2+} / c_{FeOH2+} = K_2 / H_+ = 9.9\mathrm{x}10^{-6} / 10^{-4} = 0.099$

total concentration of Fe :

$c_{tot} = c_{Fe3+} + c_{FeOH2+} + c_{Fe(OH)2+} = 0.1$ mol/l

$= (1/61)\, c_{FeOH2+} + c_{FeOH2+} + 0.099\, c_{FeOH2+} = 1.12\, c_{FeOH2+}$

It follows:

$c_{FeOH2+} = 0.1/1.12 = \underline{0.090 \text{ mol/l}}$

$c_{Fe3+} = (1/61)\, c_{FeOH2+} = \underline{0.001 \text{ mol/l}}$

$c_{FeOH2+} = 0.099\, c_{FeOH2+} = \underline{0.009 \text{ mol/l}}$

2.8

$Ag^+ + 2\, CN^- = Ag(CN)_2^-$ $\qquad K = \dfrac{a_{Ag(CN)_2^-}}{a_{Ag^+}\, a^2_{CN^-}}$

Table 2.8 : $Ag^+ + e = Ag$ $\qquad E^o = 0.799$ V

Table 2.115: $Ag(CN)_2^- + e = Ag + 2\, CN^-$ $\qquad E^{o'} = -0.31$ V

Equilibrium if:

$$E_{rev} = E^{o\prime} + \frac{RT}{F} \ln \frac{a_{Ag(CN)_2^-}}{a^2_{CN^-}} = E^o + \frac{RT}{F} \ln a_{Ag^+}$$

$E^{o'} - E^o = (RT/F) \ln (a_{Ag+}\, a_{CN-}{}^2 / a_{Ag(CN)2-}) = (RT/F) \ln (1 / K)$

25°C :

$E^{o'} - E^o = -0.31 - 0.799 = -1.109 = 0.059 \log_{10} (1/K) = -0.059 \log K$

$\log K = 18.8 \rightarrow K = \underline{6.3\mathrm{x}10^{18}}$

2.9

Cell voltage at equilibrium: $U = \Phi'' - \Phi' = 0.342$ V

Cell reaction: $1/2\, H_2 + AgCl = H^+ + Ag^+ + Cl^-$

- The cell voltage U is equal to the reverible potentialof the cell reaction E_{rev}.
- The standard potential for the cell reaction is equal to that of the halfcell

$AgCl + e = Ag + Cl^-$ which according to equation (2.117) is $E^o = 0.222$ V.

Fre energy of reaction: $\Delta G = - nF\, E_{rev}$

$\Delta G = \Delta G^o + RT \ln(a_{H+}\, a_{Cl-} / P_{H2}^{1/2}) \;\text{-->}\; E_{rev} = E^o - (RT/nF) \ln(a_{H+}\, a_{Cl-} / P_{H2}^{1/2})$

For $P_{H2} = 1$ bar :

$E_{rev} = E^o - (RT/nF) \ln(a_{H+}\, a_{Cl-}) = E^o - (RT/nF) \ln (f_+ c_{H+}\, f_- c_{Cl-}) = E^o - (RT/nF) \ln$

For 25°C: $0.342 = 0.222 - 0.059 \log (f_\pm^2\, (0.12)^2) = 0.331 - 0.059 \log f_\pm^2$

$0.059 \log f_\pm^2 = - 0.186 \;\rightarrow\; f_\pm = \underline{0.807}$

2.10

Pt’¦ O_2(0.002bar) ¦ KOH(0.01M) ¦ O_2(0.2bar) ¦ Pt’’

$U = \Phi'' - \Phi' = E_{rev}'' - E_{rev}'$

$= (RT/nF) \ln P_{O2}'' / P_{O2}' = (8.3)(353)/(4(96485)) \ln (0.2/0.002)$

$= 3.50\text{x}10^{-2}$ V $\rightarrow$ $U = \underline{0.035 \text{ V}}$

In this cell Pt’’ is the positive electrode (cathode) and Pt’ is the anode.

2.11

$E_{prot} = E^o + (RT/nF) \ln 10^{-6}$ (mol/l)

$Ni^{2+} + 2e = Ni$ $\qquad E^o = - 0.257$ V

$E_{prot,Ni} = -0.257 + (RT/nF) \ln 10^{-6}$

25°C : $E_{prot,Ni} = -0.257 + (0.059/2) \log 10^{-6} = - 0.434$ V

$E_{calomel} = 0.241$V

Protection potential versus saturated calomel electrode :

$E_{prot,Ni} = - 0.434 \text{ V} - 0.241 \text{ V} = \underline{- 0.675 \text{ V vs SCE}}$

2.12

maximum corrosion rate : $v_{cor} = k_L\, c_s$ $\qquad$ (mol/m^2 s)

surface concentration of Cu^{2+} ions : $c_s = c_{Cu2+,s}$

$Cu^{2+} + 2\, e = Cu$ $\qquad E^o = 0.340$ V

$E = E^o + (0.059/2) \log c_{Cu2+,s}$ $\qquad$ (25°C)

$0.160 = 0.340 + (0.059/2) \log c_{Cu2+,s}$

$\log c_{Cu2+,s} = - 6.10$ --> $c_s = 7.91\text{x}10^{-7}$ mol/l

$v_{cor} = (10^{-5} \text{ m/s})(7.91\text{x}10^{-7} \text{ mol/dm}^3)(10^3 \text{ dm}^3/\text{m}^3) = \underline{7.91\text{x}10^{-9} \text{ mol/cm}^2 \text{ s}}$

2.13

Pt ¦ H_2(1bar) ¦ Ni^{2+}, OH^-, H_2O ¦ $Ni(OH)_2$ ¦ Ni

$Ni(OH)_2 \ = \ Ni^{2+} \ + 2\ OH^-$

Solubility constant : $K_s = \ a_{Ni2}{}^{+} \ a_{OH-}{}^{2} \ = \ 1.6x10^{-16}$ $(mol^3 l^{-3})$

Water dissociation constant : $K_w = a_{H+}\, a_{OH-} \ = \ 10^{-14}$ $(mol^2 l\text{-}^2)$

For pH 8 : $a_{H+} = 10^{-8}$, $a_{OH-} = K_w / a_{H+} = \ 10^{-6}$ mol/l

$a_{Ni2+} = Ks / a_{OH-}{}^{2} \ = 10^{-16} / 10^{-12} = 1.6x10^{-4}$ mol/l

$U = E_{rev,Ni} - E_{rev,H}$

$E_{rev,Ni} = -0.257 + (0.059/2)\log a_{Ni2+} \ = 0.257 + (0.059/2)\log 1.6x10^{-4} = -0.369$ V

$E_{rev,H} \ = 0 - 0.059$ pH = -0.472 V

U = (-0.369) – (-0.472) = $\underline{0.103 \text{ V}}$

2.14

a) Calculation of standard potential::

$Cu(NH_3)_2{}^{+} + e = Cu + 2\ NH_3$ $\qquad E^o{}_1 = -0.10$ V $\qquad$ (1)

$Cu(NH_3)_4{}^{2+} + e = Cu(NH_3)_2{}^{+} + 2\ NH_3$ $\qquad E^o{}_2 = \ 0.10$ V $\qquad$ (2)

$Cu(NH_3)_4{}^{2+} + 2e = Cu \ + 4 \ NH_3$ $\qquad E^o{}_3$ $\qquad$ (3)

(3) = (1) + (2) :

$E^o{}_3 = \ (n_1/n_3)\, E^o{}_1 + (n_2/n_3)\, E^o{}_2 = \ ½\,(-0.1) + ½\,(0.1) = \ \underline{0 \text{ V}}$

b) Dominating species in equilibrium with Cu metal : $Cu(NH_3)_2{}^{+}$ (because $E^o{}_1 < \ E^o{}_3$)

For reaction 1: $\qquad E_{rev,1} = E^o{}_1 + 0.059 \log a_{Cu(NH3)2+} / a_{NH3}{}^{2}$

Protection potential: $\quad E_{prot} \ = E^o{}_1 + 0.059 \log (10^{-6}/(0.1)^2\,)$

$= -0.1 + (0.059)(-4) = \underline{-0.336 \text{ V}}$

Note that in ths case the value of the protection potential depends on the ammonia concentration!

c) From table 2:

$Cu^+ + \quad e \ = Cu$ $\qquad E^o = 0.520$ V $\qquad = \ E^o{}_4$ $\qquad$ (4)

$Cu^{2+} + 2\ e \ = \ Cu$ $\qquad E^o = 0.340$ V $\qquad = \ E^o{}_5$ $\qquad$ (5)

Complexation reactions:

$Cu^{+} + 2\,NH_3 = Cu(NH_3)_2^{+}$ (6)

$Cu^{2+} + 4\,NH_3 = Cu(NH_3)_4^{2+}$ (7)

Monovalent copper:

$(6) = (4) - (1) \rightarrow \quad \Delta G^o_6 = \Delta G^o_4 - \Delta G^o_1 = -F\,(E^o_4 - E^o_1) = -RT \ln K_6$

where $K_6 = a_{Cu(NH3)2+} / a_{Cu+}\, a_{NH3}^{2}$

$(RT/F) \ln K_6 = 0.520 - (-0.1) = 0.420$ V

25^oC: $\log K_6 = 0.420/0.059 = 7.119 \rightarrow \underline{K = 1.3\text{x}10^{7}}$

Divalent copper:

$(7) = (5) - (3) \rightarrow \quad \Delta G^o_7 = \Delta G^o_5 - \Delta G^o_3 = -F\,(E^o_5 - E^o_3) = -RT \ln K_7$

where $K_6 = a_{Cu(NH3)42+} / a_{Cu2+}\, a_{NH3}^{4}$

$(RT/2F) \ln K_7 = 0.340 - (0.0) = 0.340$ V

25^oC: $\log K_7 = 0.34/0.0295 = 11.5 \rightarrow \underline{K = 3.3\text{x}10^{11}}$

2.15

$Cr^{2+} + 2e = Cr \qquad E° = -0.90$ V (1)

$Cr^{3+} + 3e = Cr \qquad E° = -0.74$ V (2)

a) Equilibrium with Cr metal: $E_{rev,1} = E_{rev,2}$

$-0.90 + (RT/2F)\ln a_{Cr2+} = -0.74 + RT/3F \ln a_{Cr3+}$

$(-0.90) - (-0.74) = -0.16 = (RT/F)\ln a_{Cr3+}^{1/3} - (RT/F)\ln a_{Cr2+}^{1/2} = (RT/F)\ln (a_{Cr3+}^{1/3} / a_{Cr2+}^{1/2})$

For 25^oC and replacing activities by concentrations:

$-0.16/0.059 = -2.71 = \log (c_{Cr3+}^{1/3} / c_{Cr2+}^{1/2}) \rightarrow c_{Cr3+}^{1/3} / c_{Cr2+}^{1/2} = 1.94\text{x}10^{-3}$

$c_{Cr3+} = (1.94\text{x}10^{-3})^3\, c_{Cr2+}^{3/2} = 7.31\text{x}10^{-9}\, c_{Cr2+}^{3/2}$

from this we deduce that in contact with chromium metal $c_{Cr3+} << c_{Cr2+}$.

b) Mol fraction of Cr^{3+}: $X_{Cr3+} = c_{Cr3+}/c$

$X_{Cr3+} = 7.31\text{x}10^{-9}\, c_{Cr2+}^{3/2}/c = 7.31\text{x}10^{-9}\, c^{1/2}\, X_{Cr2+}^{3/2}$ with $X_{Cr2+} = c_{Cr2+}/c$

$X_{Cr3+} + X_{Cr2+} = 1$

Hence : $X_{Cr3+} = 7.31\text{x}10^{-9}\, c^{1/2}\, (1 - X_{Cr3+})^{3/2}$

c) Concentration ratio Cr^{3+}concentration in contact with chromium metal at a total chromium ion concentration of 0.01 M:

Set $X_{Cr3+} << 1$: $X_{Cr3+} = 7.31\text{x}10^{-9}\, c^{1/2}$

c = 0.01: $X_{Cr3+} = 7.31x10^{-10}$

it follows:

$c_{Cr3+} = X_{Cr3+}$ c = $\underline{7{,}31x10^{-8}\ mol/l}$

$c_{Cr2+} \approx \underline{0.01\ mol/l}$

CHAPTER 3

3.1

Kelvin: RT ln $(P'/P_o) = 2\gamma M\ /r\rho$

P_o = 0.023 bar, T = 25°C

$\gamma = 0.072\ Nm^{-1}$ (table 3.4)

ρ_{H2O} = 1g/cm3, M_{H2O} = 18 g/mol

ln $(P'/P_o) = 2\gamma M\ / RT\ r\ \rho = (2)\ (0.072)\ (18)\ /\ (88.3)\ (298)\ (1x10^{-6}\ (1)) = 1.048x10^{-3}$

$P'/P_o = 1.001$ --> $\underline{P' = 0.023\ bar}$

The small drop size has a negligible effect

3.2

Pressure difference to be applied : $\Delta P = 2\ \gamma\ /\ r_{pore}$

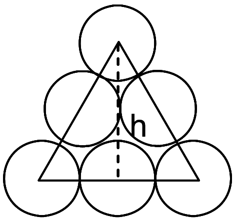
$\gamma = 0.0720$, $r_{pore} = 3x10^{-6}$ m

$\Delta P = 2\ (0.072)/\ (3x10^{-6}) = 4.80x10^4\ N/m^2$

1 bar = $10^5\ N/m^2$ ---> $\underline{\Delta P = 0.48\ bar}$

3.3

(111) plane, r = atom radius, h = (4 r) sin 60° = 3.464 r



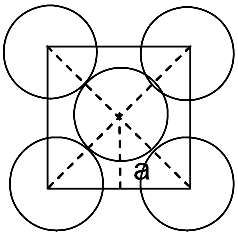
surface of triangle: A = (4 r)(h) / 2 = 2 r h = $6.928\ r^2$

number of atoms per triangle: (3) (1/6) + (3) (½) = 2

For copper: r = $0.1278x10^{-9}$ m

number of atoms per m^2: $N = 2\ /(6.928)(0.1278x10^{-9})^2 = \underline{1.76\ x10^{19}\ atoms\ Cu\ /\ m^2}$

(100) plane, r = atom radius, a = 4 r cos45^o = 2.828 r



surface of square: $A = a^2 = 7.952\ r^2$

number of atoms per square: (4) (1/4) + 1 = 2

For copper: $r = 0.1278 \times 10^{-9}$ m

number of atoms per m^2: $N = 2 / 7.952\ r^2$ = $\underline{1.54 \times 10^{19}}$ <u>atoms Cu / m^2</u>

3.4

$v_{ads} = s_{CO}\, P_{CO} / (2\pi\, M_{CO}\, RT)^{1/2}$

$P_{CO} = 10^{-5}$ Pa

$s_{CO} = 0.5$

M_{CO} = 28 g/lmol = 28x10$_{-3}$ kg/mol

T = 298 K

One gets: $(2\pi\, M_{CO}\, RT)^{1/2}$ = 20.85 Ns/mol

$v_{ads} = (0.5)(10^{-5})/20.85 = 2.40 \times 10^{-7}$ mol/m^{2}s

The number of moles forming a monolayer is obtained by dividing the number of adsorption divided by the Avogadro number: $N_{mono} = 10^{-19} / 6 \times 10^{23} = 1.67 \times 10^{-5}$ mol/m^2

Time to form a monolayer: $t_{mono} = N_{mono} / v_{ads}$

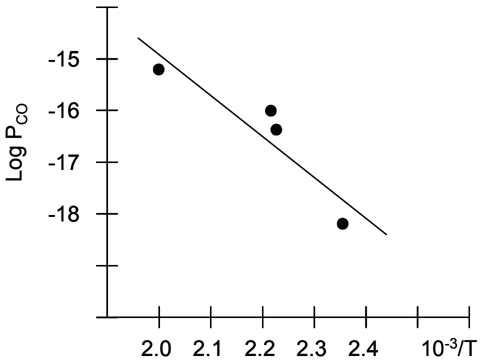
t = (1.67x10^{-5} mol m^{-2}) / (2.40x10^{-7} mol m^{-2}s) = <u>70 s</u>

3.5

$Q_{ads}/R = -\, d \ln P / d(1/T)$ for θ = const, here: $\theta = 0.5$

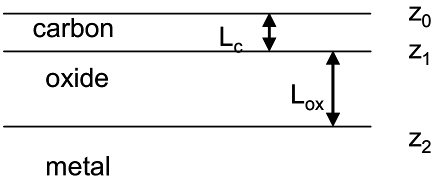
from Figure:

T (K)	425	448	453	493
10^{-3}/T (K-1)	2.35	2.23	2.21	2.03
10^8 P_{CO} (Torr)	1.2	9	11	25
ln pCO	-18.2	-16.2	-16	-15.2



From this: $Q_{ads}/R = 8.57\times10^3$ (J mol^{-1}/J mol^{-1} K) ---> $Q_{ads} = 7.1\times10^4$ J/mol = <u>71 kJ/mol</u>

3.6



Cr^{3+} signal from the oxide film without contamination:

$$I_o = \kappa \int_0^{Lox} c_{Cr3+} \exp(-z/\Lambda)dz$$

integration yields: $I_o = -\kappa\, c_{Cr3+}\, \Lambda\, [\exp(-L_{ox}/\Lambda) - 1] = \kappa\, c_{Cr3+}\, \Lambda\, [1 - \exp(-L_{ox}/\Lambda)]$

Cr^{3+} signal from the oxide film with carbon contamination:

$$I_c = \kappa \int_{z1}^{z2} c_{Cr3+} \exp(-z/\Lambda)dz$$

integration yields:

$I_c = -\kappa\, c_{Cr3+}\, \Lambda\, [\exp(-z_2/\Lambda) - \exp(-z_1/\Lambda)]$ with $z_1 = L_c$ and $z_2 = L_c + L_{ox}$

From this:

$I_c/I_o = [\exp(-z_1/\Lambda) - \exp(-z_2/\Lambda)] / [1 - \exp(-L_{ox}/\Lambda)]$

$= [\exp(-L_c/\Lambda) - \exp((-L_c+L_{ox})/\Lambda)] / [1 - \exp(-L_{ox}/\Lambda)]$

$= \exp(-L_c/\Lambda)\, [1 - \exp((L_{ox})/\Lambda)] / [1 - \exp(-L_{ox}/\Lambda)] = \exp(-L_c/\Lambda)$

L_c = 0.18nm (= 2 x atomic radius) , Λ = 1.9 nm :

--> $I_c/I_o = \exp(-0.18/1.9) = \underline{0.91}$

3.7

Energy of ISS signals (E_P = energy of primary beam) :

Fe: $E_{Fe}/E_P = (M_{Fe} - M_{He})/(M_{Fe} + M_{He})$

Ni: $E_{Ni}/E_P = (M_{Ni} - M_{He})/(M_{Ni} + M_{He})$

M_{He} = 4 g/mol

M_{Fe} = 55.8 g/mol

M_{Ni} = 58.7 g/mol

Relative energy resolution:

$\Delta E/E_P = [(M_{Ni} - M_{He})/(M_{Ni} + M_{He})] - [(M_{Fe} - M_{He})/(M_{Fe} + M_{He})]$

$= [(58.7-4)/(58.7+4)] - [(55.8-4)/(55.8+4)] = 0.8724 - 0.8662 = 0.0062$

Absolute energy resolution for E_P = 1KeV:

$\Delta E = (\Delta E/E_P)\, E_P = (1000\text{ eV})\,(0.0062) = \underline{6.2\text{ eV}}$

3.8

$$C = \left(\frac{2z^2F^2\varepsilon\varepsilon_o c_b}{RT}\right)^{1/2} \cosh\left(\frac{zF\Delta\Phi_{GC}}{2RT}\right)$$

z = 1, ε = 78, $\varepsilon_o = 8{,}95\text{x}10^{-12}$ C/V m, T = 298 K,

$$\left(\frac{2z^2F^2\varepsilon\varepsilon_o}{RT}\right)^{1/2} = 7.15\text{x}10^{-2}\ \text{As/Vm}^2$$

$$\cosh\left(\frac{zF\Delta\Phi_{GC}}{2RT}\right) = 1.51$$

Double layer capacity: $C = (7.15\text{x}10^{-2})(1.51)\, c^{1/2} = 0.110\, c^{1/2}$

For c = 0.001 mol/l: $C = 0.110\ \text{As/Vm}^2 = 0.110\ \text{F/m}^2 = \underline{11.0\ \mu\text{F/cm}^2}$

3.9

Mott-Schottky: $\frac{1}{C^2} = \left(\frac{2l_c}{\varepsilon\varepsilon_o}\right)^2\left(\frac{F\Delta\Phi_{SC}}{RT} - 1\right)$ or $\frac{1}{C^2} = \left(\frac{2l_c}{\varepsilon\varepsilon_o}\right)^2 \frac{F}{RT}\Delta\Phi_{SC} - \left(\frac{2l_c}{\varepsilon\varepsilon_o}\right)^2$

Flatband potential, $E_{(\Delta\Phi sc=0)}$: from the potential of intersect of ($1/C^2$) vs E with x-axis:

$1/C^2 = 0$: $E = E_{intersect}$

$$0 = \left(\frac{2l_c}{\varepsilon\varepsilon_o}\right)^2 \left(\frac{F\Delta\Phi_{SC}}{RT} - 1\right)$$ --> $E = E_{intersect} : \Delta\Phi_{SC} = RT/F$

For semiconductor electrodes : $\Delta\Phi_{SC} = E - E_{(\Delta\Phi sc=0)}$

Therefore : $E_{(\Delta\Phi sc=0)} = E_{intersect} - \Delta\Phi_{SC} = E_{intersect} - RT/F$

Charge carrier density: from slope of $1/C^2 = f(E)$

$$a = d(1/C^2)/d\,\Delta\Phi_{SC} = \left(\frac{2l_c}{\varepsilon\varepsilon_o}\right)^2 \frac{F}{RT} \quad \text{with } l_c^2 = \varepsilon\varepsilon_o RT/2F^2 n_o$$

$a = [4\,\varepsilon\varepsilon_o RT/2F^2 n_o(\varepsilon\varepsilon_o)^2](F/RT) = 2/F\, n_o\, \varepsilon\varepsilon_o$

Measured values:

E(V)	-0.1	0	0.1	0.2	0.3	0.5	0.7
$10^3 C$ (F/m^2)	14.0	7.7	6.0	5.0	4.4	3.6	3.2
$10^{-3} C^{-2}$ (m^2/F^2)	5.1	16.9	27.8	40.0	51.7	77.2	97.7

From these values we get:

intersect : $E_{intersect} = -0.15$ V

--> Flatband potential: $E_{(\Delta\Phi sc=0)} = E_{intersect} - RT/F = (-0.15)-(0.026) = \underline{-0.176\text{ V}}$

slope: $a = 1.19\text{x}10^5\ \ m^4/V\,F^2$

Charge carrier density: $n_o = 2/aF\varepsilon\varepsilon_o$

$\varepsilon = 8,\ \varepsilon_o = 8.95\text{x}10^{-12}$ As/Vm

$n_o = 2/(1.119\text{x}10^5)(8)(8.95\text{x}10^{-12})(96485) = 2.43\text{ mol/m}^3 = \underline{2.43\text{x}10^{-6}\text{ molcm}^3}$

CHAPTER 4

4.1

BV equation: $i = i_o\,[\,\exp(\eta/\beta_a) - \exp(-\eta/\beta_c)\,]$

Applied potential: E = - 0.6V vs SCE = - 0.359 V (NHE)

equilibrium potential: $E_{rev} = 0 - 0.059\text{ pH} = -0.177$ V

overvoltage: $\eta = E - E_{rev} = -0.359 - (-0.177) = -0.182$ V

cathodic Tafel region: $i = -\ i_o\ \exp(-\eta/\beta_c) = -10^{-4}\exp(-(-0.182)/0.055) = \underline{-2.74\text{x}10^{-3}\text{ A/cm}^2}$

4.2

$i_o = F\, k_a\, c_{Fe2+} \exp(E_{rev}/\beta_a) = F\, k_c\, c_{Fe3+} \exp(-\, E_{rev}/\beta_c)$

solution I: $c_{Fe3+} = 10^{-3}$ mol/l, $c_{Fe2+} = 10^{-3}$ mol/l

$E_{rev,I} = E^o + (RT/F) \ln (10^{-3}/10^{-3}) = E^o$

solution II: $c_{Fe3+} = 10^{-3} + 0.019 = 0.020$ mol/l, $c_{Fe2+} = 10^{-3}$ mol/l

$E_{rev,I} = E^o + (RT/F) \ln (2\text{x}10^{-2}/10^{-3}) = E^o + 0.077$ V

$i_{o,II}/i_{o,I} = F\, k_c\, (2\text{x}10^{-2}) \exp(-\, (E^o+0.077)/\beta_c) \,/\, F\, k_c\, (10^{-3}) \exp(-\, E^o/\beta_c)$

$= 20 \exp[(-E^o-0.077+E^o)/\beta_c)] = 20 \exp(-0.077/\, \beta_c)$

numerical values: $i_{o,I} = 5\text{x}10^{-3}$ A/cm^2, $\beta_c = 0.05$V

$i_{o,II} = i_{o,I}\, 20 \exp(-0.077/\, \beta_c) = (5\text{x}10^{-3})20 \exp(-0.077/\, 0.05) =$ $\underline{0.021 \text{ A/cm}^2}$

4.3

Equilibrium potential for pH = 1 : $E_{rev} = 0 - 0.059 = -\, 0.059$ V

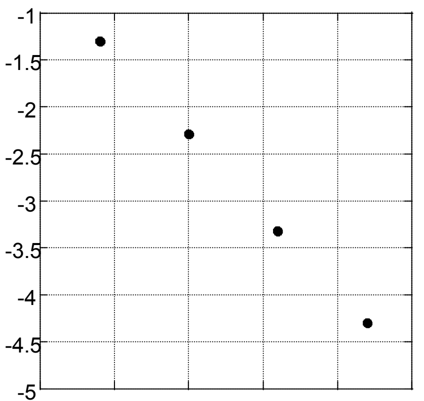
Saturated calomel electrode (SCE): $E_{rev} = 0.241$ V

equilibrium potential versus SCE : E_{rev} (SCE) = -0.059 +0.241 = - 0.300 V

Surface area: 6 cm^2 : i = I/A = I/6 A/cm^2

Experimental data:

E(SCE)	η (V)	I (A)	i (A/cm2)	log│i│
-0.360	-0.060	-0.0003	$-5.0\text{x}10^{-5}$	-4.30
-0-480	-0.180	-0.0029	$-4.83\text{x}10^{-4}$	-3.32
-0.600	-0.300	-0.0310	$-5.17\text{x}10^{-3}$	-2.29
0.720	-0.420	-0.3010	$-5.02\text{x}10^{-2}$	-1.30

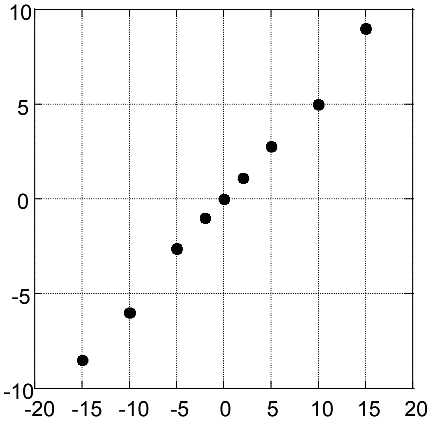


From graph $\log|i|$ vs η :

intercept with $\eta = 0$ ---> $\log i_o = -4.8$ --> $i_o = 1.6 \times 10^{-5}$ A/cm^2

slope: $(d \log|i|)/d\eta = 8.40 = 1/(2.3\,\beta_c)$ ---> $\beta_c = \underline{0.052 \text{ V}}$

4.4



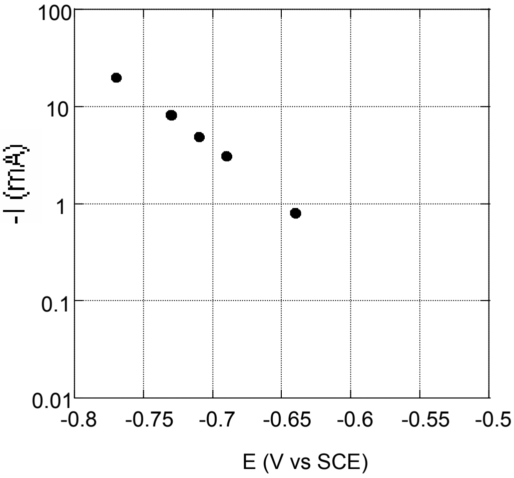
slope: $di/dE = 1/r_c \cong 0.58$ mA/cm^{2}mV = 0.58 Ω^{-1}cm^{-2} ---> $r_c = 1.72\ \Omega$cm^2

$i_{cor} = (1/r_c)[(1/b_a) + (1/b_c)]^{-1}$

$= 0.58\,[(1/0.03)+(1/0.05)]^{-1} = 0.58/53.3 = 0.011$ Acm^{-2}

$i_{cor} = \underline{11 \text{ mA/cm}^2}$

4.5



$E_{cor} = -\,0.55$ V vs SCE

from figure extrapolation: $I_{cor} \cong 0.07$ mA/cm^2 ---> $i_{cor} \cong 0.035$ mA/cm^2

Table 1.1: $1\ \mu A/cm^2 = 3.27\times10^{-3}\ (M/n\rho)$ mm/year

Ni: $n = 2$, $M = 58.7$ g/mol , $\rho = 8.9$ g/cm^3

$i_{cor} = 35\ \mu A/cm2 = (35)(3.27\times10^{-3})(58.7)/(2)(8.9) =$ <u>0.377 mm/year</u>

4.6

$i_{cor} = i_{o,Fe} \exp[(E-E_{rev,Fe})/\beta_{a,Fe}]$ (1)

$i_{cor} = i_{o,H} \exp[-(E-E_{rev,H})/\beta_{c,H}]$ (2)

(2 equations with 2 unknowns: E_{cor}, i_{cor})

$E_{rev,H} = 0 - 0.059\ pH = -0.059$ V

$E_{rev,Fe} = -0.44 + (0.059/2) \log 10^{-2} = -0.499$ V

$\beta_{a,Fe} = 0.0174$ V, $\beta_{c,H} = 0.052$ V

Corrosion potential:

$i_{o,Fe} \exp[(E-E_{rev,Fe})/\beta_{a,Fe}] = i_{o,H} \exp[-(E-E_{rev,H})/\beta_{c,H}]$

$\ln i_{o,Fe} + (E_{cor}/\beta_{a,Fe}) - (E_{rev,Fe}/\beta_{a,Fe}) = \ln i_{o,H} - (E_{cor}/\beta_{c,H}) + (E_{rev,H}/\beta_{c,H})$

$\ln 10^{-8} + (E_{cor}/0.0174) - (-0.499/0.0174) = \ln 10^{-7} - (E_{cor}/0.052) + (-0.059/0.052)$

--> $E_{cor} =$ <u>-0.359 V</u>

Corrosion current density:

$i_{cor} = i_{o,Fe} \exp[(E-E_{rev,Fe})/\beta_{a,Fe}]$

$\ln i_{cor} = \ln i_{o,Fe} + (E_{cor}/\beta_{a,Fe}) - (E_{rev,Fe}/\beta_{a,Fe}) = -18.42 + (-20.61) + 28.68 = -10.36$

--> $i_{cor} =$ <u>3.2×10^{-5} A/cm^2</u>

Note: The same result for i_{cor} ccould also be obtained from equation (2)

4.7

$i_{cor} = i_{o,H} \exp[-(E-E_{rev,H})/\beta_{c,H}]$ Unknowns: i_{cor} , $i_{o,H}$

$E_{cor} = -0.520$ V (SCE) $= -0.279$ V (NHE)

$b_{c,H} = 0.12$ V ---> $\beta_{c,H} = 0.052$ V

pH 4 : $E_{rev,H} = 0 - 0.059\ pH = -0.236$ V

Calculation of $i_{o,H}$ from cathodic polarization:

For 1 mA/cm^2 $E = -0.90$ v (SCE) $= -0.659$ V (NHE)

$i = i_{o,H} \exp[-(E-E_{rev,H})/\beta_{c,H}]$

$10^{-3} = i_{o,H} \exp[-(-0.659 + 0.236)/0.052] = i_{o,H} \exp[8.135] = i_{o,H}\ (3.41\text{x}103)$

---> $i_{o,H} =$ <u>2.9×10^{-7} A/cm^2</u>

Corrosion current density:

$i_{cor} = (2.9\text{x}10^{-7})\ \exp[-(-0.279 + 0.236)/0.052]$

---> $i_{cor} = \underline{6.6\text{x}10^{-7}\ \text{A/cm}^2}$

4.8

pH 3 : $E_{cor} = -0.50$ V, $i_{cor} = 10^{-6}$ A/cm^2 $E_{rev} = 0 - 0.059\ (3) = -0.177$ V

pH 1 : $E_{cor} = ?$, $i_{cor} = 10^{-5}$ A/cm^2 $E_{rev} = 0 - 0.059\ (1) = -0.059$ V

Corrosion current density: $i_{cor} = i_{o,H} \exp[-(E_{cor} - E_{rev,H})/\beta_{c,H}]$ with $\beta_{c,H} = 0.053$

pH 3 : $10^{-6} = i_{o,H(pH3)} \exp[-((-0.50) - (-0.177))/0.053]$

→ $i_{o,H(pH3)} = 10^{-6}/(4.43\text{x}10^{2}) = \underline{2.26\text{x}10^{-9}\ \text{A/cm}^2}$

Exchange curent density: $i_{o,H} = n\ F\ k_c\ c_{H+} \exp[-E_{rev,H}/\beta_{c,H}]$

pH 3 : $i_{o,H(pH3)} = n\ F\ k_c\ (10^{-3}) \exp[-(-0.177)/0.053] = n\ F\ k_c\ (28.2\text{x}10^{-3})$

pH 1 : $i_{o,H(pH1)} = n\ F\ k_c\ (10^{-1}) \exp[-(-0.059)/0.053] = n\ F\ k_c\ (3.04\text{x}10^{-1})$

$i_{o,H(pH1)} / i_{o,H(pH3)} = 0.304/(28.2\text{x}10^{-3}) = 10.8$

$i_{o,H(pH1)} = \underline{2.44\text{x}10^{-8}}$

Corrosion potential: $E_{cor} - E_{rev} = -\beta_{c,H} \ln i_{cor}/i_{o,H}$

$E_{cor} = E_{rev} - \beta_{c,H} \ln i_{cor}/i_{o,H}$

For pH 1: $E_{cor} = -0.059 - 0.053 \ln (10^{-6}/2.44\text{x}10^{-8}) = -0.059 - 0.197 = \underline{-0.256\ \text{V}}$

4.9

$i_l = 0.62\ n\ F\ D^{2/3}\ \nu^{-1/6}\ c_b\ \omega^{1/2}$

$n = 4$

$D = 2.51\text{x}10^{-5}$ cm^2/s → $D^{2/3} = 8.57\text{x}10^{-4}$ (cm^2/s)$^{2/3}$

$\nu = 10^{-2}$ cm^2/s → $\nu^{-1/6} = 2.15$ (cm^2/s)$^{-1/6}$

$c_b = 8$ mg/l $= (8\text{x}10^{-3}/32)10^{-3} = 0.25\text{x}10^{-6}$ mol/cm^3

$\omega = 1200$ rpm $= 2\pi\ (1200/60) = 126$ rad/s → $\omega^{1/2} = 11.21$ (rad/s)$^{1/2}$

Limiting current density at 1200 RPM:

$i_l = (0.62)(4)(96585)(8.57\text{x}10^{-4})(2.15)(0.25\text{x}10^{-6})(11.21) = \underline{1.23\text{x}10^{-3}\ \text{A/cm}^2}$

Diffusion layer thickness:

$i_l = n\ F\ D\ c_b/\delta$ → $\delta = n\ F\ D\ c_b / i_l$

$\delta = 4\ (96585)(2.51\text{x}10^{-5})(0.25\text{x}10^{-6})/(1.23\text{x}10^{-3}) = 2.05\text{x}10^{-3}$ cm $= \underline{20.5\ \mu\text{m}}$

4.10

Mass transport controlled corrosion: $i_{cor} = i_{l,O2}$

Mass transport rate for turbulent pipe flow: $Sh = 0.0115\ Re^{7/8}\ Sc^{1/3}$

Re = 42000, Pipe diameter L = 1.9 cm , $D_{O2} = 2.5\text{x}10^{-5}\ cm^2/s$

$c_{O2} = 7\ mg/l = 2.19\text{x}10^{-4}\ mol/l = 2.19\text{x}10^{-7}\ mol/cm^3$

$Sc = \nu/D_{O2} = 0.01/(2.5\text{x}10^{-5}) = 400$

$Sh = (0.0115)(\ 42\text{x}103)^{7/8}(400)^{1/3} = 9.39\text{x}10^2$

$Sh = i_{l,O2}\ L\ /\ 4F\ D_{O2}\ c_{O2}$ $\rightarrow$ $i_{l,O2} = Sh\ 4F\ D_{O2}\ c_{O2}\ /\ L$

$i_{l,O2} = (9.39\text{x}10^2)(4)(96485)(\ 2.5\text{x}10^{-5})(\ 2.19\text{x}10^{-7})\ /1.9 = 1.05\text{x}10^{-3}\ A/cm^2 = \underline{1.05\ mA/cm^2}$

4.11

Table 4.27 : $Sh = 0.079\ Sc^{0.35}\ Re^{0.7}$

$Re = \omega\ r\ L\ /\nu$ $L = 2r = 0.04\ m$ $\omega = 2\pi(4000/60) = 419\ rad/s$

$Sc = \nu/D_H$ $\nu = 10^{-6}\ m^2/s$ $D_H = 9.32\text{x}10^{-9}\ m^2/s$

$Sh = i_l\ L\ /n\ F\ D_H\ c_b$ $c_b = 0.001 mol/l = 1\ mol/m^3$ $n = 1$

$Re = (419)(0.02)(0.04)/(10^{-6}) = 3.35\text{x}10^5$

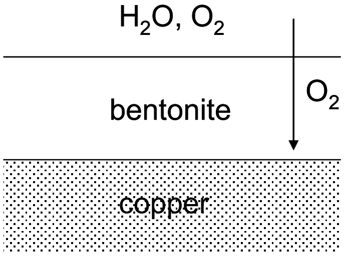
$Sc = (10^{-6})/9.32\text{x}10^{-9} = 1.072\text{x}10^2$

$Sh = (0.079)(\ 1.072\text{x}10^2)^{0.35}(3.35\text{x}10^5)^{0.7} = 2.99\text{x}10^3$

$i_l = Sh\ (n\ F\ D_H\ c_b)/L = (2.99\text{x}10^3)(1)(96485)(\ 9.32\text{x}10^{-9})(1)/(0.04) = \underline{67.2\ A/m^2}$

Corrosion rate: $1\ A/m^2 = 0.327\ (M/n\ \rho)$ mm/year (Table 1.1); $M_{Mg} = 24.3$ g/mol, $\rho_{Mg} = 1.74$ g/cm^3 , n = 2 : --> $v_{cor} = (67.2)(0.327)(24.3)/(2)(1.74) = \underline{1.53\ mm/year}$

4.12



$2\ Cu + O_2 + 2\ H_2O \rightarrow 2\ Cu(OH)_2$

Oxygen flux across bentonite layer of thickness L = 2 m : $N_{O2} = D_{O2}\ c_{O2}\ /L$

$D_{O2} = 8\text{x}10^{-11}\ m^2/s$,

$c_{O2} = 5.4\ ppm = 5.4\ g/10^6\ g\ H_2O = 5.4 g/m^3 H_2O = (5.4/32)\ mol/m^3 = 0.169\ mol/m^3$

$N_{O2} = (8\text{x}10^{-11})(0.169)\ /2 = 6.76\text{x}10^{-12}\ mol/m^2s$

Corrosion rate of copper:

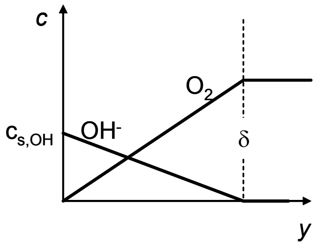
$N_{Cu} = 2\ N_{O2}$ → $N_{Cu} = 1.35\text{x}10^{-11}$ mol/m^{2}s

1 mm/year = $(3.15\text{x}10^4)(M/\rho)$ mol/m^{2}s where $M_{Cu} = 63.5$ g/mol, $\rho_{Cu} = 8.96$ g/cm^3

$v_{cor} = (1.35\text{x}10^{-11})\ (3.15\text{x}10^4)(63.5/8.96) = \underline{3.01\ \text{x}10^{-6}\ \text{mm/year}}$

Thickness corroded in 100000 years: $\underline{0.3\ \text{mm}}$

4.13



$O_2 + H_2O + 4\ e \rightarrow 4\ OH^-$

hydroxyl ion flux: $N_{OH} = 4\ N_{O2}$

$N_{O2} = i_{l,O2}/4F = 0.62\ D_{O2}^{2/3}\ \nu^{-1/6}\ c_{b,O2}\ \omega^{1/2}$

$N_{OH} = 0.62\ D_{OH}^{2/3}\ \nu^{-1/6}\ c_{s,OH}\ \omega^{1/2}$ assuming $c_{b,OH} \approx 0$

$N_{OH} / N_{O2} = D_{OH}^{2/3}\ c_{s,OH}/\ D_{O2}^{2/3}\ c_{b,O2} = 4$ → $c_{s,OH} = 4\ (D_{O2}/D_{OH})^{2/3}\ c_{b,O2}$

$D_{O2} = 2.5\text{x}10^{-9}$, $D_{OH} = 5.25\text{x}10^{-9}$, $c_{b,O2} = 8$ mg/l $= 2.5\text{x}10^{-4}$ mol/l

$c_{s,OH} = 4\ (2.5/5.25)^{2/3}\ (2.5\text{x}10^{-4}) = 6.1\text{x}10^{-4}$ mol/l

Water dissociation equilibrium: $c_{OH}\ c_{H+} \approx 10^{-14}$ (mol/l)^2

$c_{H+} \approx 1.6\text{x}10^{-11}$ mol/l or pH ≈ 10.8

Note: The surface pH does not vary with the rotation rate.

4.14

Limiting current density at RDE in a binary electrolyte:

$i_l = (1-(z_+/z_-))\ 0.62\ n\ F\ D_+^{2/3}\ \nu^{-1/6}\ (c_{+s} - c_{+b})\ \omega^{1/2}$

$FeCl_2$: $z_+ = 2$, $z_- = 1$ → $1-(z_+/z_-) = 3$

$D_+ = 0.72\text{x}10^{-9}$ m^2/s

$c_{+s} = 4.25$ mol/l, $c_{+b} = 2.0$ mol/l → $c_{+s} - c_{+b} = 2.25$ mol/l

$\nu = 10^{-6}$ m^{2}s , $\omega = 200$ RPM $= (200)2\pi/60 = 20.9$ rad/s

$i_l = (3)(0.62)(2)(96485)(\ 0.72\text{x}10^{-9})^{2/3}(10^{-6})^{-1/6}(2.25)(20.9)^{1/2} = 2.97\text{x}10^4$ A/m^2

$i_l = \underline{2.97\ \text{A/cm}^2}$

4.15

$\kappa = (F^2/RT) \sum z_i^2 D_i c_i$

$M_{NaCl} = 58.5$ g/mol, $\quad M_{Ca(HCO3)2} = 162.1$ g/mol

$c_{NaCl} = 1$ mg/l $= (10^{-3}/58.5) = 1.71\text{x}10^{-5}$ mol/l $= 1.71\text{x}10^{-2}$ mol/m^3 $= c_{Na+} = c_{Cl-}$

$c_{Ca(HCO3)2} = 15$ mg/l $= (15\text{x}10^{-3}/162.1) = 9.25\text{x}10^{-5}$ mol/l $= 9.25\text{x}10^{-2}$ mol/m^3 $= c_{Ca+} = ½\, c_{HCO3-}$

25^{o}C: $F^2/RT = (96485)^2/(8.3)(298) = 3.76\text{x}10^6$ As/Vmol

Na^+ : $D_{Na+} = 1.33\text{x}10^{-9}$ m^2/s $\quad z_{Na+} = 1$

Cl^- : $D_{Cl-} = 2.03\text{x}10^{-9}$ m^2/s $\quad z_{Cl-} = -1$

Ca^{2+} : $D_{Ca2+} = 0.79\text{x}10^{-9}$ m^2/s $\quad z_{Ca2+} = 2$

HCO_3^- : $D_{HCO3-} = 1.18\text{x}10^{-9}$ m^2/s $\quad z_{HCO3-} = -1$

$$\kappa = (3.76\text{x}10^6)[\, z_{Na+}{}^2 D_{Na+}\, c_{Na+} + z_{Cl-}{}^2 D_{Cl-}\, c_{Cl-} + z_{Ca2+}{}^2 D_{Ca2+}\, c_{Ca+} + z_{HCO3-}{}^2 D_{HCO3-}\, c_{HCO3-}]$$

$$= (3.76\text{x}10^6)[(1.33\text{x}10^{-9})(1.71\text{x}10^{-2}) + (2.03\text{x}10^{-9})(1.71\text{x}10^{-2})$$

$$+ (4)(0.79\text{x}10^{-9})(9.25\text{x}10^{-2}) + (1.18\text{x}10^{-9})(18.5\text{x}10^{-2})] = \underline{2.14\text{x}10^{-3}\ \Omega^{-1}\text{m}^{-1}}$$

Units: (As/molV)(m^2/s)(mol/m^3) = A/Vm = Ω^{-1}m^{-1}

4.16

steady motion: $\quad z_i\, q_i\, (d\Phi/dy) = 6\pi\, r_i\, \eta_i\, v_i$

Definition of electric mobility: $u_{e,i} = v_i /(d\Phi/dy)$ [(m/s)/(V/m)]; $u_{e,i} = z_i\, F\, u_i$ with $u_i = D_i/RT$

Fe^{2+} : $D_{Fe2+} = 0.72\text{x}10^{-9}$m^2/s → $u_{e,Fe2+} = (2)(96485)(0.72\text{x}10^{-9})/(8.3)(298) = 5.61\text{x}10^{-8}$ m^2/Vs

Fe^{3+} : $D_{Fe3+} = 0.61\text{x}10^{-9}$m^2/s → $u_{e,Fe2+} = (3)(96485)(0.61\text{x}10^{-9})/(8.3)(298) = 7.13\text{x}10^{-8}$ m^2/Vs

ionic radius: $\quad r_i = z_i\, q_i /6\pi\, \eta\, u_{e,i}$

Fe^{2+} : $r_{Fe2+} = (2)(1.6\text{x}10^{-19}) /(6\pi)(10^{-3})(5.61\text{x}10^{-8}) = 3.03\text{x}10^{-10}$ m

Fe^{3+} : $r_{Fe3+} = (3)(1.6\text{x}10^{-19}) /(6\pi)(10^{-3})(7.13\text{x}10^{-8}) = 3.57\text{x}10^{-10}$ m

$r_{Fe3+} > r_{Fe2+}$ because the higher charge leads to stronger hydration

CHAPTER 5

5.1

$Fe^{3+} + 2\,e = Fe^{2+}$ $\quad E^o = 0.771$ V

$c_{Fe3+} = c_{Fe2+} = 0.001$ mol/l

$E_{rev} = 0.771 + (RT/F) \ln (a_{Fe3+}/a_{Fe2+}) \approx 0.771 + (RT/F) \ln (c_{Fe3+}/c_{Fe2+}) = 0.771$ V

Applied potential E = 0.595 V

Overvoltage : $\eta = E - Erev = 0.595 - 0.771 = - 0.176$ V

Assuming that the rection is charge transfer controlled (Tafel region):

$$i_c = - i_o \exp(-\eta/\beta_c) = - 5x10^{-3} \exp(+0.176/0.05) = - 0.169 \text{ A/cm}^2$$

Assuming that the reaction is transport controlled (limiting current):

$$i_l = - nF\, D_{Fe3+}\, c_{Fe3+} / \delta$$

$$i_l = - (1)(96485)(0.61x10^{-5})(10^{-5})/10^{-3}) = - 5.89x10^{-3} \text{ A/cm}^2$$

Comparison of i_c and i_l shows: il <<ic. Under the conditions of the experiment Fe^{3+} will be reduced at the limiting current density under mass transport control.

5.2

I $Fe + OH^- \rightarrow FeOH_{ads} + e$

II $FeOH_{ads} \rightarrow FeOH_{ads}^+ + e$

III $FeOH_{ads}^+ + H^+ \rightarrow Fe^{2+} + H_2O$

I : $k_{I,a}\, c_{OH}\, (1-\theta) \exp(\alpha\, f\, E) = k_{I,c}\, \theta \exp(-(1-\alpha)\, f\, E)$

where θ = surface coverage of $FeOH_{ads}$ and $f = F/RT$

for $\theta << 1$: $\theta/(1 - \theta) \approx \theta = (k_{I,a} / k_{I,c})\, c_{OH} \exp(\alpha\, f\, E + (1-\alpha)\, f\, E) = K_I\, c_{OH} \exp(f\, E)$

where $K_I = (k_{I,a} / k_{I,c})$

II: $v_{II} = k_{II,a}\, \theta \exp(\alpha\, f\, E) = k_{II,a}\, K_I\, c_{OH} \exp(f\, E) \exp(\alpha\, f\, E) = k_{II,a}\, K_I\, c_{OH} \exp [(1+ \alpha)\, f\, E)]$

anodic current density:

$i_a = i_I + i_{II} = F\, v_I + F\, v_{II} = 2\, F\, v_{II}$

$$i_a = 2F\, k_a\, c_{OH} \exp [(1+ \alpha)\, f\, E)] \qquad \text{where } k_a = k_{II,a}\, K_I$$

Charge transfer coefficient:

$1/ \beta_a = d \ln i_a/dE = (1 + \alpha)\, f \rightarrow \beta_a = 1/((1+\alpha)\, f\,)$

$\alpha = 0.5$; $1/f = (RT/F) = (8.3)(298)/96485 = 0.0256$ V : $\beta_a = 0.0256 /1.5 = \underline{0.0171 \text{ V}}$

Reaction order for OH^- :

$$p_{OH} = \left(\frac{d \ln i}{d \ln c_{OH^-}}\right)_{c_{Fe2+}} = \underline{1}$$

Variation of exchange current density with Fe^{2+} cocnetration: $i_o = 2\, F\, k_a\, c_{OH} \exp [(1+ \alpha)\, f\, E_{rev})]$

$d \ln i_o /d \ln c_{Fe2+} = d[(1+\alpha)\, f\, E_{rev}] / d \ln c_{Fe2+}$

$$E_{rev} \approx E^o + (RT/2F) \ln c_{Fe2+}$$

$(1+\alpha)\, f\, E_{rev}) = (1+\alpha)\, f\, E^{o}) + ((1+\alpha)/2)\ \ln c_{Fe2+}$

$d[(1+\alpha)\, f\, E_{rev}] / d \ln c_{Fe2+} = (1+\alpha)/2 = 0.75$

$$\left(\frac{\mathrm{d}\ln i_0}{\mathrm{d}\ln c_{\mathrm{Fe2+}}}\right)_{c_{\mathrm{OH-}}} = \underline{0.75}$$

Potential shift with c_{OH-} at constant i and c_{Fe2+}:

$\ln i_a = \ln (2F\, k_a\, c_{OH}\ ) + (1+\alpha) f\, E$

$E = [1/(1+\alpha) f]\ [\ln i_a - \ln (2F\, k_a - \ln c_{OH})]$

$$\left(\frac{\mathrm{d}E}{\mathrm{d}\ln c_{\mathrm{OH-}}}\right)_{i,c_{\mathrm{Fe2+}}} = -\ 1/(1+\alpha) f \quad = \quad \underline{-\ 0.0171\ \mathrm{V}}$$

5.3

Volmer-Tafel mechanism: $H^+ + e \rightarrow H_{ads}$ 2x I
$H_{ads} + H_{ads} \rightarrow H_2$ II

I at quasi equilibrium: $k_{Ic}\, c_{H+}\, (1-\theta) \exp(-(1-\alpha) f E) = k_{Ia}\, \theta \exp(\alpha\, f\, E)$

for small coverage: $\theta/(1-\theta) \approx \theta$

$\theta = (k_{Ic} / k_{Ia})\, c_{H+} \exp[-(1-\alpha)\, f\, E - \alpha\, f\, E) = (k_{Ic} / k_{Ia})\, c_{H+} \exp(-f\, E)$

II (RDS) : $v_{II} = k_{IIc}\, \theta^2 = k_{IIc}\, (k_{Ic} / k_{Ia})^2 c_{H+}^{\ 2} \exp(-2f\, E)$

$i_c = -\ 2\, F\, k_{IIc}\, (k_{Ic} / k_{Ia})^2 c_{H+}^{\ 2} \exp(-2f\, E) = -\ 2\, F\, k_{IIc}\, (k_{Ic} / k_{Ia})^2 c_{H+}^{\ 2} \exp(-E/\beta_c)$

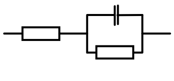
$\beta_c = dE/d\ln i_c \rightarrow 1/\beta c = d \ln i / dE = -(-2f) = 2f \rightarrow \beta_c = 1/(2f)$

$1/f = (RT/F) = (8.3)(298)/96485 = 0.0256\ V \rightarrow \beta_c = 0.0128\ V$

$b_c = 2.3\ \beta_c = 0.0295\ V \approx \underline{30\ mV}$

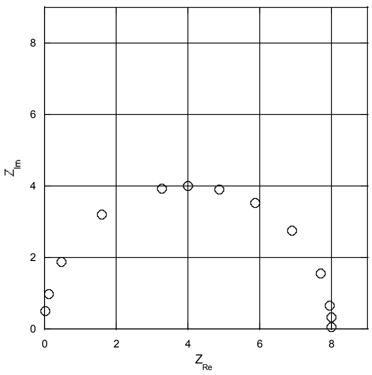
5.4

For a charge transfer controlled reaction:



$$Z_{\mathrm{Re}} = \frac{R_t/\omega^2 C^2}{R_t^2 + 1/\omega^2 C^2} \qquad Z_{\mathrm{Im}} = \frac{R_t^2/\omega C}{R_t^2 + 1/\omega^2 C^2}$$

A Nyquist plot of the tabulated data yields a hemi-circle:



ω=∞ ω=0

Charge transfer resistance from graph: $R_t = Z_{Re}(\omega=0) - Z_{Re}(\omega=\infty) = 8\ \Omega$

A = 2 cm2 → $r_t = R_t A = (8)(2) = 16\ \Omega\text{cm}^2$

Double layer capacity from the maximum: $|Z_{Re}| = |Z_{Im}|$

$$\frac{R_t/\omega^2C^2}{R_t^2+1/\omega^2C^2} = \frac{R_t^2/\omega C}{R_t^2+1/\omega^2C^2} \rightarrow 1/\omega C = R_t$$

$\omega_{max} = 1.25$ kHz (see figure and table) ; $R_t = 8\ \Omega$ → $C = 1/\omega R_t = 10^{-4}$ Farad

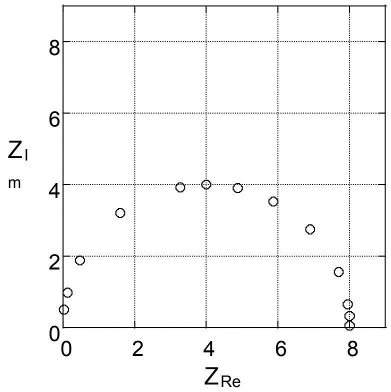
$c_{dl} = C/A = 0.5 \times 10^{-4}\ \text{F/cm}^2 = 50\ \mu\text{F/cm}^2$

Exchange current density:

At the equilibrium potential : $r_t = RT/nFi_o$ → $i_o = RT/nFr_t$

n = 2; RT/F = 0.026V ; $r_t = 16\ \Omega\text{cm}^2$ → $i_o = 0.013/16 = 8.1\text{x}10^{-4}\ \text{A/cm}^2$

5.5



From graph: $R_\Omega = 2\ \Omega$,

$R_t = 8 - 2 = 6\ \Omega$

A = 5 cm2 ; $r_t = R_t A = 30\ \Omega cm^2$

Tafel region: $r_t = dE/di = (dE/d \ln i)(d \ln i/di) = \beta_a/ i$

i = 1 mA/cm2 → $\beta_a = r_t\ i = (30\ \Omega cm^2)(10^{-3}\ A/cm^2) = \underline{0.030\ V}$

5.6

$$\begin{array}{ll} (I) & Ni + H_2O = NiOH_{ads} + H^+ + e \\ (II) & NiOH_{ads} \rightarrow NiOH^+ + e \\ (III) & NiOH^+ + H^+ = Ni^{2+} + H_2O \end{array}$$

I : $k_{a,I}\,(1-\theta) \exp(\alpha fE) = k_{c,I}\ \theta\ c_{H+}^{-1} \exp(-(1-\alpha)fE)$

$\theta/(1-\theta) \approx \theta = (k_{a,I} /k_{c,I})\ c_{H+}^{-1} \exp(fE)$

II: $v_{II} = k_{a,II}\ \theta \exp(\alpha fE) = k_{a,II}\ [(k_{a,I} /k_{c,I})\ c_{H+}^{-1} \exp(fE)] \exp(\alpha fE)$

$= (k_{a,II}\ k_{a,I} /k_{c,I})\ c_{H+}^{-1} \exp((1+\alpha)fE))$

$i_a = 2\ F\ v_{II} = 2F\ k_a\ c_{H+}^{-1} \exp((1+\alpha)\ f\ E))$ where $k_a = (k_{a,II}\ k_{a,I} /k_{c,I})$

Exchange current density:

$i_o = 2F\ k_a\ c_{H+}^{-1} \exp((1+\alpha)\ f\ E_{rev})$

$\ln i_o = \ln (2F\ k_a) – \ln c_{H+} + (1+\alpha)\ f\ E_{rev}$

$\log i_o = \log (2F\ k_a) – \log c_{H+} + (1+\alpha)\ f\ E_{rev} /2.3$

$d \log i_o / d\ pH \approx - d \log i_o / d \log c_{H+} = 1$

$$\left(\frac{d \log i_0}{d\,pH}\right)_{c_{Ni2+}} = \underline{1}$$

$d \log i_o / d \log c_{Ni2+} = (d \log i_o / dE_{rev})(dE_{rev} / d \log c_{Ni2+}) = ((1+\alpha)\ f /2.3)(2.3/2f) = (1+\alpha)/2$

(setting $E_{rev} \approx E^o + (RT/2F) \ln c_{Ni2+} = E^o + (2.3/2f) \log c_{Ni2+}$)

$$\left(\frac{d \log i_0}{d \log c_{Ni2+}}\right)_{pH} = (1 + 0.5)/2 = \underline{0.75}$$

5.7

I Cu = $Cu^+ + e$

II Cu+ → $Cu^{2+} + e$

$\alpha_I = \alpha_{II} = \alpha$; f = F/RT $\eta = E - E_{rev}$

(a)

reaction step I:

$i_I = F\ k_{a,I} \exp(\alpha\ f\ E) – F\ k_{c,I}\ c_{Cu+} \exp(-(1-\alpha)f\ E)$

$i_{o,I} = F\ k_{a,I} \exp(\alpha\ f\ E_{rev}) = F\ k_{c,I}\ c_{Cu+(eq)} \exp(-(1-\alpha)f\ E_{rev})$

$\rightarrow \quad i_I = i_{o,I} \exp(\alpha f \eta) - i_{o,I} (c_{Cu+}/ c_{Cu+(eq)}) \exp(-(1-\alpha)f \eta)$

eliminate $(c_{Cu+}/ c_{Cu+(eq)})$:

$i_I = i_{o,I} \exp(\alpha f \eta) - i_{o,I} (c_{Cu+}/ c_{Cu+(eq)}) \exp(-(1-\alpha)f \eta)$

$(c_{Cu+}/ c_{Cu+(eq)}) = - i_I + i_{o,I} \exp(\alpha f \eta) / i_{o,I} \ \exp(-(1-\alpha)f \eta)$

$= - (i_I/ i_{o,I}) \exp((1-\alpha)f \eta) + \exp(\alpha f \eta)/ \exp(-(1-\alpha)f \eta)$

$= - (i /2 i_{o,I}) \exp((1-\alpha)f \eta) + \exp(f \eta)$ because at steady state $i_I = i_{II} = i/2$

reaction step II:

$i_{II} = i_{o,II} (c_{Cu+}/ c_{Cu+(eq)}) \exp(\alpha f \eta) - i_{o,II} \exp(-(1-\alpha)f \eta)$ (using same reasoning as for step I)

$= i_{o,II} [- (i /2 i_{o,I}) \exp((1-\alpha)f \eta) + \exp(f \eta)] \exp(\alpha f \eta) - i_{o,II} \exp(-(1-\alpha)f \eta)$

$= (-i_{o,II}\ i /2 i_{o,I}) \exp((1-\alpha)f \eta) + i_{o,II} \exp(f \eta)] \exp(\alpha f \eta) - i_{o,II} \exp(-(1-\alpha)f \eta) = i/2$

rearrange:

$(i/2)[1 + (i_{o,II} /i_{o,I}) \exp(f \eta)] = i_{o,II} [\exp((1+\alpha) f \eta) - \exp(-(1-\alpha)f \eta)]$

$\underline{i = 2\, i_{o,II} [\exp((1+\alpha) f \eta) - \exp(-(1-\alpha)f \eta)] / [1 + (i_{o,II} /i_{o,I}) \exp(f \eta)]}$ q.e.d

(b) For $i_{o,I} >> i_{o,II}$ and $\eta >> 0$ (anodic Tafel region) :

from above equation it follows (setting $i_{o,I} = \infty$) : $i = i_a = 2\, i_{o,II} \exp ((1+\alpha) f \eta)$

$\underline{\beta_a = 1/(1+\alpha)f}$

For $i_{o,I} >> i_{o,II}$ and $\eta << 0$ (cathodic Tafel region) :

$i = i_c = - i_{o,II} \exp (-(1-\alpha) f \eta)$

$\underline{\beta_c = 1/(1-\alpha)f}$

CHAPTER 6

6.1

The standard potential of the halfcell reaction

$Fe_2O_3 + 6 H^+ + 6 e = 2 Fe + 3 H_2O$

corresponds to the standard free energy change of the reaction (Chapter 2):

$Fe_2O_3 + 3H_2 = 2 Fe + 3 H_2O$

$\Delta G^o = 3\, \Delta G^o_{(H2O)} - \Delta G^o_{(Fe2O3)} = 3 (-237.2) -(-742.2) = + 30.6$ kJ/mol

$E^o = -\Delta G^o/nF = (-30.6x10^3) /(6)(96485) = - 0.053$ V

Equilibrium potential in 0.5M H_2SO_4 of pH ≈ 0 :

$E_{rev} = E^o + RT/6F \ln (1/a_{H+}^6) = - 0.053 - 0.059\, pH = \underline{- 0.053 \text{ V}}$

Passivation potential at pH ≈ 0 (from Fig. 6.9) : Ep = 0.86 V

→ $E_p >> E_{rev}$!

6.2

$3\ Fe_2O_3 + 2\ H^+\ 2\ e = 2\ Fe_3O_4 + H_2O$ (1) E_1^o =?

One finds in Table 6.9 :

$Fe_3O_4 + 8\ H^+ + 8\ e = 3\ Fe + 4\ H_2O$ (2) $E_2^o = - 0.087$ V

$Fe_2O_3 + 6\ H^+ + 6\ e = 2\ Fe + 3\ H_2O$ (3) $E_3^o = - 0.053$ V

----

reaction (1) = 3 x reaction (3) – 2 x reaction (2)

$\Delta G^o{}_1 = 3\ \Delta G^o{}_3 - 2\ \Delta G^o{}_2$

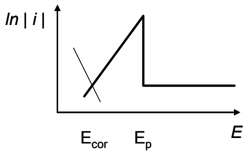
$-n_1\ F\ E^o{}_1 = - 3\ n_3\ F\ E^o{}_3 + 2\ n_2\ F\ E^o{}_2$

→ $E^o{}_1 = 3\ (n_3/n_1)\ E^o{}_3 - 2\ (n_2/n_1)\ E^o{}_2$

$n_1 = 2,\ n_2 = 8,\ n_3 = 6$:

$E^o{}_1 = 3\ (3)\ (- 0.053) - 2\ (4)\ (- 0.087) = \underline{0.219\ V}$

6.3



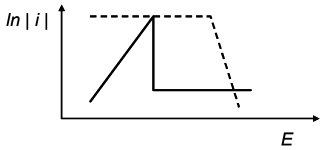
$i_p = i_{cor}\ \exp[(E_p - E_{cor})/\beta_a]$ Tafel region

$E_p = 0.15 - 0.059$ pH → for pH = 2: Ep = 0.138 V

$E_{cor} = - 0.05$ V; $i_{cor} = 0.1$ mA/cm^2; $\beta_a = 30$ mV

$i_p = (0.1x10^{-3})\ \exp[(0.138 + 0.05) / 0.03)] = 0.053\ A/cm^2 = \underline{53\ mA/cm^2}$

6.4



Cathodic partial reaction: $Fe^{3+} + e \rightarrow Fe^{2+}$; anodic partial reaction : $M \rightarrow M^{z+} + z\ e$

What value of $c_{Fe3+,b}$ is needed to passivate the electrode: Passivation if $i_{l,Fe3+} \geq i_p$

Rotating cylinder: $Sh = 0.079\ Re^{0.7}\ Sc^{0.35}$

$Sh = i_{l,Fe3+}L / nFc_{Fe3+,b}D_{Fe3+}$ $\rightarrow$ $i_{l,Fe3+} = Sh\ nF\ c_{Fe3+,b}\ D_{Fe3+} / L$

with L = cylinder diameter: $L = 2r$; $Re = \omega\ r\ L/\nu = 2\ \omega\ r^2/\nu$

$Sc = \nu/D_{Fe3+}$

$i_{l,Fe3+} = (nFc_{Fe3+,b}D_{Fe3+}/2r)(0.079)\ (2\ \omega\ r^2/\nu)^{0.7}(\ \nu/D_{Fe3+})^{0.35}$

$i_{l,Fe3+} = 0.0642\ nF\ \ c_{Fe3+,b}\ D_{Fe3+}^{0.65}\ \nu^{-0.35}\ r^{0.4}\ \omega^{\ 0.7}$

$\rightarrow$ $c_{Fe3+,b} = i_{l,Fe3+} / 0.0642\ nF\ D_{Fe3+}^{0.65}\ \nu^{-0.35}\ r^{0.4}\ \omega^{\ 0.7}$

100 RPM = $1000(2\pi/60) = 104.7$ rad/s

$i_p = 0.03$ A/cm^2 ; $\nu = 0.011$ cm^2/s; $D_{Fe3+} = 0.5 \times 10^{-5}$ cm^2/s; $n = 1$; $i_{l,Fe3+} = 3 \times 10^{-2}$ A/cm^2

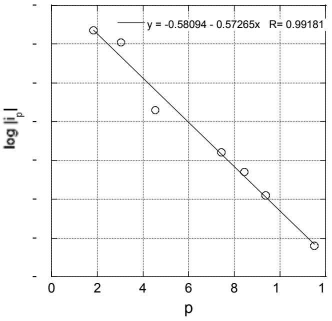
$\rightarrow$ $c_{Fe3+,b} = \underline{6.55 \times 10^{-5}\ \text{mol/cm}^3}$

6.5

From Fig. 6.16 we read:

pH	log $|i_p|$
1.8500	-1.6500
3.0200	-1.9500
4.5500	-3.7000
7.4500	-4.8000
8.4200	-5.3000
9.3700	-5.9000
11.500	-7.2000

A plot of log $|i_p|$ versus pH of yields:



By regression analysis: log $|i_p| = -0.08 - 0.57$ pH

To reach spontaneous passivation $i_{l,O2} \geq i_p$ (cf. problem 6.4)

Limiting current density for oxygen reduction:

$i_{l,O2} = 4\ F\ D_{O2}\ c_{O2,b} / \delta$ with

$c_{O2,b} = 0.5$ ppm = 0.5 mg/l = $0.5x10^{-3}/32 = 1.56x10^{-5}$ mol /l = $1.56x10^{-8}$ mol O_2 /cm^3

$D_{O2} = 2.5x10^{-5}$ cm^2/s (from Table 4.1) ; $\delta = 10^{-2}$ cm

→ $i_{l,O2} = 7.53x10^{-6}$ A/cm^2 or $\log |i_{l,O2}| = -\ 5.12$ (A/cm$^{2)}$

$\log |i_{l,O2}| = \log |i_p|$

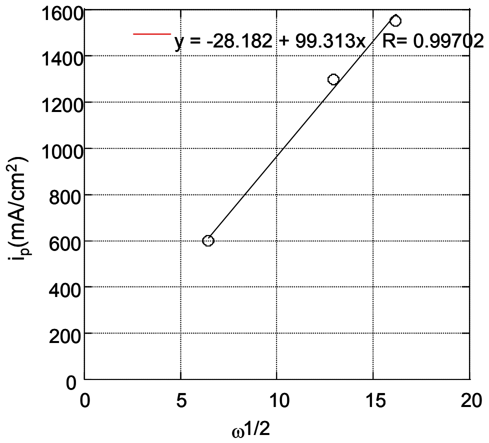
$-\ 5.12 = -0.08 - 0.57$ pH → pH = (-5.12+0.08)/0.57 = - 7.97 ≈ 8.0

--> Spontaneous passivation for pH ≥ 8

6.6

From Fig. 6.15 :

ω(rad/s)	$\omega^{1/2}$	i_p (mA/cm^2)
261.80	16.180	1550.0
167.60	12.940	1300.0
41.900	6.4700	600.00



regression analysis: $i_p \approx 99\ \omega^{1/2}$ mA/cm^2 = $99x10^{-3}$ A/cm^2

Levich equation: $i_l = 0.62\ nF\ D^{2/3}\ c_{sat}\ \nu^{-1/6}\ \omega^{1/2}$

$i_l = i_p \approx 99\ \omega^{1/2}$

Saturation concentration at electrode surface:

$c_{sat} = i_l / 0.62\ nF\ D^{2/3}\ \nu^{-1/6}\ \omega^{1/2} = 99x10^{-3}\ \omega^{1/2} / 0.62\ nF\ D^{2/3}\ \nu^{-1/6}\ \omega^{1/2} = 99x10^{-3} / 0.62\ nF\ D^{2/3}\ \nu^{-1/6}$

For $D = 10^{-5}$cm^2/s ; $\nu = 10^{-2}$ cm^2/s ; n =2 :

→ c_{sat} = (99x10-3)/[(0.62)(2)(96485)(2.92x10-4)(2.15)] = $1.29\ x10^{-3}$ mol/cm^3 ≅ <u>1.3 mol/l</u>

6.7

$2\ CrO_{3(s)} + 6\ H^+ + 6\ e = Cr_2O_{3(s)} + 3\ H_2O$

$3H_2 \qquad\qquad\qquad = 6\ H^+ + 6\ e$

$2\ CrO_3\ + 3H_2 \qquad\qquad = \ Cr_2O_3 + 3\ H_2O$

For this reaction: $\Delta G^o\ = \Delta G^o_{Cr2O3} + 3\ \Delta G^o_{H2O} - 2\ \Delta G^o_{CrO3}$

Using Tables 6.8 and 2.9 :

$\Delta G^o = (-1058) + 3(-237.2)-2(-510) = -\ 749.6$ kJ/mol Cr_2O_3

$E^o = -\ \Delta G^o / nF = -\ (-\ 749.6x103)/(6)(96485) = 1.295$ V

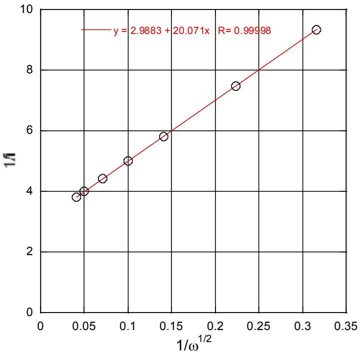
pH 5 : $E_{rev} = E^o + RT/nF\ \ln(1/a_{H+}^{\ 2}) = E^o - 0\text{-}059$ pH

$E_{rev} = 1.295 - (0.059)\ (5) = \underline{1.00V}$

6.8

Data points:

ω(rad/s)	i(A/cm^2)	1/i	1/ω$^{1/2}$
600.00	0.26200	3.8170	0.041000
400.00	0.25000	4.0000	0.050000
200.00	0.22700	4.4050	0.071000
100.00	0.20000	5.0000	0.10000
50.000	0.17200	5.8140	0.14100
20.000	0.13400	7.4630	0.22400
10.000	0.10700	9.3460	0.31600



Regression analysis: $(1/i) = 2.99 + 20.1\ (1/\omega^{1/2})$

$\omega \rightarrow \infty$: $1/i = 2.99 \cong 3.0$ or $i_{(\omega = \infty)}\ =\ \underline{0.33\ A/cm^2}$

6.9

$H_2CrO_4\ =\ HCrO_4^-\ + H^+$ $\qquad$ $K_1 = 6.3$

$HCrO_4^-\ == CrO_4^{2-}\ + H^+$ $\qquad$ $K_2 = 3.3x10\text{-}^7$

$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$ $\qquad$ $K_3 = 33.9$

To solve this problem we replace all activities by concentrations.

$K_1 \approx\ c_{H+}\, c_{HCrO4-} / c_{H2CrO4}\ = 6.3$ (1)

$K_2 \approx\ c_{H+}\, c_{CrO4--} / c_{HCrO4-}\ = 3.3x10^{-7}$ (2)

$K_3 \approx\ c_{Cr2O7} / c_{HCrO4-}{}^2\ = 33.9$ (3)

$a_{H+} \approx\ c_{H+} = 10^{-3}$ $\qquad$ (pH = 3) (4)

Total chromium concentration: $c = c_{H2CrO4} + c_{HCrO4-} + c_{CrO4--}\ + c_{Cr2O7}$ (5)

→ 5 equations with 5 unknowns: c_{H+}, c_{HCrO4-}, c_{CrO4--} , c_{H2CrO4} , c_{Cr2O7}

Approximate solution:

(1): $c_{HCrO4-} / c_{H2CrO4} = 6.3/10^{-3} = 6.3x10^3$ $\qquad$ → $c_{HCrO4-} >> c_{H2CrO4}$

(2): $c_{CrO4--} / c_{HCrO4-} =\ 3.3x10^{-7} / 10^{-3} = 3.3x10^{-4}$ $\qquad$ → $c_{CrO4--} << c_{HCrO4-}$

(3): $c_{Cr2O7} / c_{HCrO4-}{}^2 = 33.9$ $\qquad$ → $c_{Cr2O7} = 33.9\ c_{HCrO4-}{}^2$

(5): $c = 0.1$ mol/l $= c_{HCrO4-} + c_{CrO4--} + c_{H2CrO4} + c_{Cr2O7} \approx c_{HCrO4-} + c_{Cr2O7} = c_{HCrO4-} + 33.9\ c_{HCrO4-}{}^2$

solving for (5) c_{HCrO4-} yields : $\qquad$ $c_{HCrO4-} =\ \underline{0.042\ \text{mol/l}}$

with (3): $c_{Cr2O7} = 33.9\ (0.042)^2$ $\qquad$ $c_{Cr2O7}\ =\ \underline{0.058\ \text{mol/l}}$

with (1) $c_{H2CrO4} = 0.042/6.3x10^3$ $\qquad$ $c_{H2CrO4} = \underline{6.7x10^{-6}\ \text{mol/l}}$

with (2): $c_{CrO4--} = (3.3x10^{-4})(\ 0.042)$ $\qquad$ $c_{CrO4--}\ = \underline{1.4x10^{-5}\ \text{mol/l}}$

CHAPTER 7

7.1

$E_{rev} = E^o + (RT/F)\ \ln a_{Cu2+}$ $\qquad$ $E^o = 0.340$ V

$0.1\ \text{ppm} = (0.1x10^{-6}g/g)(10^3g/l)/63.5g/mol = 1.57x10^{-6}$ mol/l

$a_{Cu2+} \cong c_{Cu2+} = 1.57x10^{-6}$ mol/l

$95^oC = 368\ K$: $\qquad$ $E_{rev,95} = 0.340 + (8.3)(368)/896485)\ln(1.57x10^{-6}) = 0.128\ V$

$55^oC = 338\ K$: $\qquad$ $E_{rev,55} = 0.340 + (8.3)(338)/896485)\ln(1.57x10^{-6}) = 0.146\ V$

$\Delta E = E_{rev,95} - E_{rev,55} = 0.018\ V$

For corrosion cells: $E_{anode} < E_{cathode}$ $\quad$ --> Metal at 95^oC is anodic and corrodes preferentially.

7.2

Cell voltage for $I = 0$: $U_{(I=0)} = 2.0$ V

Cell voltage for $I \neq 0$: $U_{(I)} = U_{(I=0)} - \zeta_a - |\zeta_c| - I\,R_{int}$

with $\zeta_a = 0.18 + 0.12 \log I$

$\zeta_c = -\,0.20 - 0.09 \log |I|$

$R_{int} = 0.14\ \Omega$

$I = 0.1$A : $U_{(I=0.1)} = U_{(I=0)} - \zeta_a - |\zeta_c| - I\,R_{int}$

$U_{(I=0.1)} = 2.0 - (0.18 + 0.12 \log 0.1) - |(-0.20-0.09 \log 0.1)| - 0.1(0.14)$

$= 2.0 - 0.06 - 0.11 - 0.014 = \underline{1.816\ \text{V}}$

$I = 1$A : $U_{(I=1)} = U_{(I=0)} - \zeta_a - |\zeta_c| - I\,R_{int}$

$U_{(I=1)} = 2.0 - (0.18 + 0.12 \log 1) - |(-0.20-0.09 \log 1)| - 1(0.14)$

$= 2.0 - 0.18 - 0.20 - 0.\,14 = \underline{1.480\ \text{V}}$

7.3

$Fe + \frac{1}{2} O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O$ --> $V_{cor} = N_{Fe2+} = 2\,N_{O2}$ (mol/cm2s)

$A = A_{Fe} + A_{Cu} = 2500 = A_{Fe} + 5(0.5)$ cm^2 --> $A_{Cu} = 2.5\ cm^2$

$A_{Fe} = 2497.5\ cm^2 \approx 2500\ cm^2$

$N_{O2} = 4x10^{-11}\ mol/cm^2s$

Number of moles O_2 reacting per second: $J_{O2} = N_{O2}\ A = (4x10^{-11})(2500) = 1.0x10^{-7}\ mol\ O_2/s$

number of moles Fe reacting per second: $J_{Fe} = 2\,J_{O2} = 2.0\ x10^{-7}\ mol\ Fe/s$

(a) Rivets made of iron: $A_{Fe} = 5x0.5\ cm^2$

$v_{cor} = N_{Fe} = 2.0\ x10^{-7}/2.5 = 8.0x10^{-8}\ molFe/cm^2s$

Table 1.3: $1\ mol/cm^2s = 3.15x10^8\ (M/\rho)$ mm/year

$M_{Fe} = 55.8$ g/mol ; $\rho_{Fe} = 7.86\ g/cm^3$ --> $\underline{v_{cor} = 179\ \text{mm/year}}$

(b) Rivets made of copper: $A_{Fe} = 2500\ cm^2$

$v_{cor} = N_{Fe} = 2.0\ x10^{-7}/2500 = 8.0x10^{-11}\ molFe/cm^2s$ --> $\underline{v_{cor} = 0.179\ \text{mm/year}}$

7.4

Anodic partial reaction: $i_{a,Zn} = i_{cor,Zn} \exp(E_{Zn}-E_{cor,Zn})/\beta_{a,Zn}$

$A_{Zn} = A_{Cu} = 10cm^2$; $i_{l,O2} = 0.05\ A/cm^2$;

$E_{cor,Zn} = -\,0.765$ V ; $E_{cor,Cu} = 0.01$ V ; $R_{int} = 1\ \Omega$; $\beta_{a,Zn} = 0.04$V

For $I_{a,Cu} \approx 0$: $I_{a,Zn} = i_{l,O2}\,(A_{Cu} + A_{Zn}) = (0.05)(20) = 1.0$ A

(a) $i_{a,Zn} = I_{a,Zn} / A_{Zn} = 1.0/10 = \underline{0.1\ A/cm^2}$

(b) $E_{Zn} - E_{cor,Zn} = \beta_{a,Zn} \ln (i_{a,Zn} / i_{cor,Zn})$

With $i_{a,Zn} = 1.0$ A/cm2 ; $i_{cor,Zn} = i_{l,O2} = 0.05\ A/cm^2$:

$E_{Zn} = 0.765 + 0.04 \ln (0.1 / 0.05) = \underline{- 0.737\ V}$

(c) $I = I_{a,Zn} + I_{c,Zn} \cong I_{a,Zn} + i_{l,O2}\ A_{Zn} = 1.0 – 0.05\ (10) = \underline{0.5\ A}$

(d) $E_{Cu} – EZn = I\ R_{int}$ --> $E_{Cu} = E_{Zn} + I\ R_{int} = -0.737 + (0.5)(1) = \underline{- 0.273\ V}$

7.5

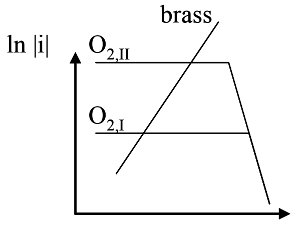
(a) Noble electrode, equilibrium conditions for oxygen: $O_2 + 4H^+ + 4e = 2\ H_2O$

$E_{rev,I} = E^o + (RT/4F) \ln(P_{O2,I}\ a_{H+})$

$E_{rev,II} = E^o + (RT/4F) \ln(P_{O2,II}\ a_{H+})$

$E_{rev,I} - E_{rev,II} = (RT/4F) \ln(P_{O2,I} /P_{O2,II}) = 0.0064 \ln(0.01/1.0) = \underline{- 0.0295\ V}$

(b)



$k_H = 1.3\ x10^{-3}\ mol/dm^3\ bar$

$P_{O2,I} = 0.01$ bar : $c_{O2,I} = k_H(0.01) = 1.3x10^{-5}$ mol/l

$P_{O2,II} = 1.0$ bar : $c_{O2,II} = k_H(1.0) = 1.3x10^{-3}$ mol/l

$i_{lO2} = - nFD_{O2}C_{O2}/\delta$ —> $i_{lO2,I}/ i_{lO2,II} = c_{O2,I} / c_{O2,II}$

Dissolution of brass: $i_a = i_{cor} \exp(E-E_{cor})/\beta_a$

It follows for electrodes I and II: $E_I – E_{cor} = \beta_a \ln(i_{a,I}/i_{cor})$ and $E_{II} – E_{cor} = \beta_a \ln(i_{a,II}/i_{cor})$

--> $E_I – E_{II} = \beta_a \ln(i_{a,I}/i_{a,II}) = \beta_a \ln(i_{lO2,I}/i_{lO2,II})$

$= 0.017 \ln(1.3x10\text{-}5/1.3x10\text{-}3) = \underline{- 0.078\ V}$ --> E_{II} is more noble than E_I

7.6

Steel pipe: $E_{cor,I} = 0.1$ V

Rebar : $E_{cor,II} = 0.6$ V

soil resistance: $\rho_e = 3000\ \Omega cm^2 = 1/\kappa$

Ohmic resistance at coating defect: $R_{int}\ (1/2\ d\ \kappa\ ) = 3000 /(2)(1) = 1500\ \Omega$

Ohmic control: $E_{cor,II} - E_{cor,I} = I\ (R_{int} + R_{ext}) \cong I\ R_{int}$

--> $I = (0.6 – 0.1)/1500 = 3.33x10^{-4}$ A

$i_{a,I} = I/A_I = 3.33x10^{-4}/0.785 = 4.25x10^{-4}$ A/cm^2

Table 1.3: 1µA/cm^2 = $3.27x10^{-3}(M/n\rho)$ mm/year

vcor = (425) $(3.27x10^{-3})(55.8)/(2)(7.86) = 4.92$ mm/year

Wall thickness: 6 mm

Time to perforation: $t_p = 6/4.92 =$ 1.22 years

7.7

Fe-18w%Cr-8w%Ni-0.4w%C: $C_{dissolved} \dashrightarrow C_{23}Cr_6$

initial concentrations of Cr and C :

18gCr/100g steel = (18/52.0)/100g steel = 0.346 molCr/100g steel $M_{Cr} = 53.0$ g/mol

0.4gC/100g steel = (0.4/12.0)/100g steel = 0.0333 molC/100g steel $M_C = 12.0$ g/mol

Reaction of 0.0333 mol C with 23 Cr/ 6C :

(0.033/6) 23 = 0.128 mol Cr/100g steel = 0.128(53.0) g Cr/100g steel = 6.64 g Cr/100g steel

Remaining Cr concentration : 18g/100g steel – 6.64 g/100 g steel = 11.36 g Cr/100g steel

Chromium concentration in w% : 11.4 w%

7.8

Pit growth rate: $(dL/dt) = (i_a/nF)(M/\rho) = [D\,(c_{sat}-c_b)/L]\,(M/r)$

For $c_b = 0$: $L = (2\,D_{Fe2+}\,c_{sat}\,M/\rho)^{1/2}\,t^{1/2}$ L = pit depth

$M_{Fe} = 55.8$ g/mol; $\rho_{Fe} = 7.86$ g/cm^3

$c_{sat} = 4.25$ mol/l

$D_{Fe2+} = 0.72x10^{-5}$ cm^2/s (Table 4.)

--> $L = [(2)(0.72x10^{-5})(4.25x10^{-3})(55.8)/(7.86)]^{1/2}\,t^{1/2} = 6.66x10^{-4}\,t^{1/2}$

Wall thickness 3 mm :

Time to perforation: $tp^{1/2} = (0.3\text{ cm})/(6.66x10^{-4}\text{ cm s}^{1/2}) = 455\text{ s}^{-1/2}$

$tp = 2.07x10^5\text{ s} = 2.07x10^5 / 3600 =$ 57.5 h

(b) Binary electrolyte , 0.1 M $FeCl_2$

$(dL/dt) = (i_a/nF)(M/\rho) = [(1 - z_+/z_-)\,D_{Fe+}\,(c_{sat}-c_b)/L]\,(M/\rho)$

with $(1 - z_+/z_-) = 1 - 2/(-1) = 3$; $(c_{sat}-c_b) = 4.25 - 0.1 = 4.15$ mol/l

--> $L = [(2)(3)(0.72x10^{-5})(4.15x10^{-3})(55.8)/(7.86)]^{1/2}\,t^{1/2} = 1.13\,x10^{-3}\,t^{1/2}$

$tp = (0.3/(1.13x10^{-4})^2 = 6.94x10^{-4}\text{ s} =$ 19.2 h

7.9

Pitting criterion: $E_b < E_{rev,O2}$

$E_b = 0.60$ V(SCE) = <u>0.86 V</u> (NHE)

$O_2 + 4\ H^+ + 4\ e\ =\ 2\ H_2O \qquad E^o = 1.23$ V

$E_{rev,O2} = 1.23 + (RT/4F)\log(P_{O2}\ a_{H+}{}^4) = 1.23 - (2.3\ RT/F)\ pH + (2.3\ RT/4F)\log P_{O2}$

$T = 40^oC = 313$ K

pH = 8 ; $P_{O2} = 0.2$ bar (air)

$E_{rev,O2} = 1.23 - (0.062)(8) + (0.0155)(-0.699) = 1.23 - 0.495 - 0.011 = \underline{0.724\ V}$

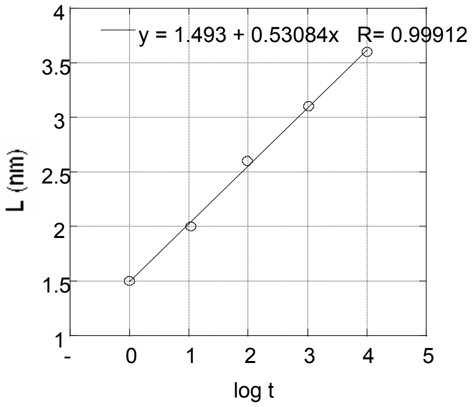
--> $E_{rev,O2} < E_b$, no pitting corrosion

CHAPTER 8

8.1

Plot L versus log t:

L (nm	t (min)	Log t
1.5	1.0	0
2.0	11.0	1.04
2.6	98	1.99
3.1	1050	3.02
3.6	9960	4.0



Regression line : 1.50 + 0.53 log t

10 years = $5.25\mathrm{x}10^5$ min

Oxide thickness after 10 years : $L = 1.5 + 0.53\log(5.25\mathrm{x}10^5) = \underline{4.5\ nm}$

8.2

Kelvin equation: $\ln (P_c/P_{sat}) = - 2\gamma\, M/\rho\, RT\, r_c$ → $r_c = - 2\gamma\, M / \rho\, RT \ln(P_c/P_{sat})$

$P_c/P_{sat} = 0.85$ → $\ln(P_c/P_{sat}) = -0.163$

$\gamma = 0.072$ J/m^2 (Table 3.1)

M = 18 g/mol = 18x10^{-3} kg/mol

r = 1 g/cm^3 = 10^3 kg/m^3

$r_c = - (2)(0.072)(18\text{x}10^{-3}) /(10^3)(8.31)(298)(-0.163) = 6.42\text{x}10^{-9}$ m = <u>6.4 nm</u>

8.3

T = 30°C ; relative humidity: RH = 53 %

From Fig. 8.10: absolute humidity for these conditions AH ≈ 16 g /m3

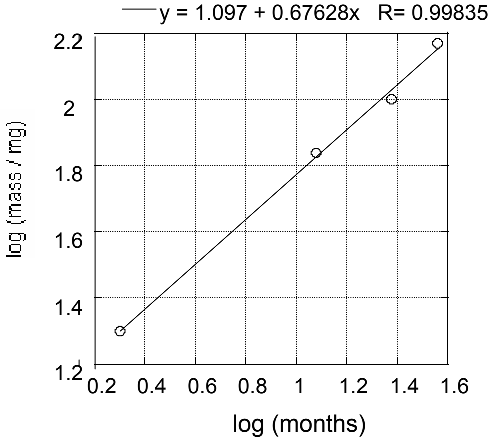
for T = 20°C and AH = 16 g/m3 → RH ≈ 95 %

Saturation in presence of ZnSO4 : (Table 8.11) : $\text{RH}_{\text{sat, ZnSO4}}$ = 90%

→ RH at 20°C > $\text{RH}_{\text{sat, ZnSO4}}$ condensation is possible

8.4

months	mass (mg)	log t	log m
2	20	0.301	1.30
12	69	1.08	1.84
22	101	1.38	2.00
36	148	1.56	2.17



Regression line: log m = 1.097 + 0.676 log t

20 years = 240 months

log m = 1.097 + 0.676 log (240) = 2.71 --> corroded mass : m = 508 mg steel: $\rho = 7.86$ g/cm^3 ; surface : A = 25 cm^2

Corroded depth after 20 years:

$L = (508\text{mg})(10^{-3}\text{g/mg}) / (7.86\ \text{g/cm}^3)(25\text{cm}^2) = 2.6\text{x}10^{-3}\ \text{cm} = \underline{26\ \mu\text{m}}$

8.5

Reaction number	Oxidation state of iron	Equation	Equilibrium constant
1	Fe(II)	$Fe(OH)_2 = Fe^{2+} + 2\ OH^-$	$K_1 = 8\text{x}10^{-16}$
2	Fe(II)	$Fe(OH)_2 = FeOH^+ + OH^-$	$K_2 = 4\text{x}10^{-10}$
3	Fe(III)	$Fe(OH)_3 = Fe^{3+} + 3OH^-$	$K_3 = 10^{-36}$
4	Fe(III)	$Fe(OH)_3 = FeOH^{2+} + 2OH^-$	$K_4 = 6.8\text{x}10^{-25}$
5	Fe(III)	$Fe(OH)_3 = Fe(OH)_2^+ + OH^-$	$K_5 = 1.7\text{x}10^{-15}$

Water dissociation equilibrium:

$a_{OH-}\ a_{H+} = 10^{-14}$ → $\log a_{OH-} = -14 + pH$; pH = 6: $\log a_{OH-} = -8$

a) Fe(II):

Reaction (1): $K_1 = a_{Fe2+}\ a_{OH-}^2$

$\log K_1 = -15.1 = \log a_{Fe2+} + 2 \log a_{OH-} = \log a_{Fe2+} - 16$

$\log a_{Fe2+} = -15.1 + 16 = +0.9$ → $c_{Fe2+} \approx a_{Fe2+} = \underline{7.9\ \text{mol/l}}$

Reaction (2): $K_2 = a_{FeOH+}\ a_{OH-}$

$\log K_2 = -9.4 = \log a_{FeOH+} + \log a_{OH-} = \log a_{FeOH+} - 8$

$\log a_{Fe2+} = -9.4 + 8 = -1.4$ → $c_{FeOH+} \approx a_{FeOH+} = \underline{3.6\text{x}10^{-2}\ \text{mol/l}}$

b) Fe(III):

Reaction (3): $K_3 = a_{Fe3+}\ a_{OH-}^3$

$\log K_1 = \log a_{Fe3+} + 3 \log a_{OH-} = \log a_{Fe2+} - 24$

$\log a_{Fe3+} = -36 + 24 = -12$ → $c_{Fe3+} \approx a_{Fe3+} = \underline{10^{-12}\ \text{mol/l}}$

Reaction (4): $K_3 = a_{FeOH2+}\ a_{OH-}^2$

$\log K_4 = \log a_{FeOH2+} + 2 \log a_{OH-} = \log a_{FeOH2+} - 16$

$\log a_{FeOH2+} = -24.2 + 16 = -8.2$ → $c_{FeOH2+} \approx a_{FeOH2+} = \underline{6.3\text{x}10^{-9}\ \text{mol/l}}$

Reaction (5): $K_5 = a_{Fe(OH)2+}\ a_{OH-}$

$\log K_5 = \log a_{Fe(OH)2+} + \log a_{OH-} = \log a_{Fe(OH)2+} - 8$

$\log a_{Fe(OH)2+} = -14.8 + 8 = -6.8$ → $c_{Fe(OH)2+} \approx a_{Fe(OH)2+} = \underline{1.6\text{x}10^{-7}\ \text{mol/l}}$

c)

Dominant Fe(II) species: Fe^{2+} (saturation concentration at pH 6 ≈ 7.9 mol/l)

Dominant Fe(III) species: $Fe(OH)_2^+$ (saturation concentration at pH 6 ≈ $1.6x10^{-7}$ mol/l)

→ Because of the lower saturation concentration of Fe(III) species oxidation of Fe(II) favors precipitation of $Fe(OH)_3$.

8.6

$4Fe + 3O_2 + 2 H_2O \rightarrow 4 FeOOH$

Maximum rate = limiting current density for O_2

Oxygen flus to surface: $N_{O2} = D_{O2}\, c_{O2}/\delta$

$D_{O2} = 2.5x10^{-9}\ m^2/s$ (Table 4. x)

$c_{O2} = c_{O2,\ saturation} = 2.5x10^{-4}\ mol/l = 2.5x10^{-1}\ mol/m^3$

$\delta = 1\ \mu m = 10^{-6}\ m$

$N_{O2} = (2.5x10^{-9})(2.5x10^{-9})/(10^{-6}) = 6.25x10^{-4}\ mol/m^2s$

$N_{Fe} = (4/3)\ N_{O2}$

Corrosion rate: $N_{Fe} = 8.33x10^{-4}\ mol/m^2s$

Table 1.1 : $1\ mol/m^2s = (3.15x10^{-4})(M/\rho)$ mm/year

Vcor = $(3.15x10^{-4})\ (8.33x10^{-4})(55.8)/7.86$ = <u>186.3 mm/year</u>

The actual values are usually lower because of the precipitation of corrosion products on the surface

CHAPTER 9

9.1

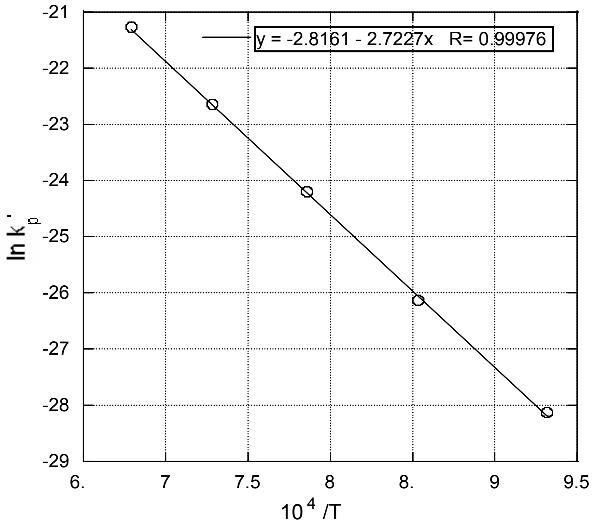
$k_p = k_p'\ P_{O2}^{1/n}$

$k_p' = k_o \exp(-\Delta G^\#/RT)$ --> $\ln k_p' = \ln k_o - \Delta G^\#/RT$

Activation energy at P_{O2} = 1bar: $d \ln kp' / d(1/T) = -\Delta G^\#/R$

Estimated from Fig. 9.13 for 1 bar :

T	$(1/T)x10^4$	k_p'	$\ln k_p'$
1073	9.32	6.1E-13	-28.128
1173	8.53	4.5E-12	-26.135
1273	7.86	3.1E-11	-24.209
1373	7.28	1.5E-10	-22.649
1473	6.79	5.8E-10	-21.269



Slope: $\Delta G^{\#}/R = 2.72\text{x}10^4$ K

--> $\Delta G^{\#} = (8.3)(2.72\text{x}10^4) = 22.6\text{x}10^4$ J/mol = <u>226 kJ/mol</u>

(b) $\ln k_p = \ln k_p' + (1/n) \ln P_{O2}$

$d \ln k_p/d(1/T) = d \ln k_p'/d(1/T) + [d(1/n)/d(1/T)] \ln P_{O2}$

--> Only if n is independent of T do we find the same activation energy at 1 bar and 0.01 bar oxygen pressure.

9.2

n-type oxide M_2O :

$M_2O = ½\, O_2 + 2M_i^{\bullet} + 2\, e$

$K = P_{O2}^{1/2}\, c_{Mi\bullet}^{2}\, c_e^{2}$ where M_i = interstitial cation

$c_{Mi\bullet} = c_e$ --> $K = P_{O2}^{1/2}\, c_{Mi\bullet}^{4}$

$c_{Mi\bullet}^{4} = K\ P_{O2}^{-1/2}$ --> $c_{Mi\bullet} \propto P_{O2}^{-1/8}$

\---------------------

p-type oxide M_2O :

$M_2O + 2\, V_M' + 2h = ½\, O_2$

$K = P_{O2}^{1/2}\, c_h^{-2}\, c_{VM'}^{-2} = P_{O2}^{1/2}\, c_{VM'}^{-4}$ (since $c_h = c_{VM'}$)

$c_{VM'}^{4} = P_{O2}^{1/2}\, K^{-1}$ --> $c_{VM'} \propto P_{O2}^{1/8}$

\----------------

9.3

Cu_2O is a p-type semiconductor that conducts by movement of metal vacancies V_M'

Ni^{2+} is an electron donor in a monovalent copper oxide:

$c_{D\bullet} = c_{VM'}$

Wagner Hauffe rules: oxidation rate of Cu_2O should increase in presence of Ni

9.4

$600^{o}C = 873$ K

From Table 2.1:

$Ni + ½ O_2 = NiO$ $\Delta G^{o}_{NiO} = -245000+(98.5)(873) = -159000$ J/mol

$Ni + ½ S_{2(g)} = NiO$ $\Delta G^{o}_{NiS} = -187000+(72.0)(873) = -124100$ J/mol

$½ S_{2(g)} + O_2 = SO_2$ $\Delta G^{o}_{SO2} = -362000+(73.1)(873) = -290200$ J/mol

The following equilibria will be considered:

(1) $Ni + ½ O_2 = NiO$ $K_1 = P_{O2}^{-1/2}$ $\log K_1 = (-1/2) \log P_{O2}$

(2) $Ni + SO_2 = NiS + O_2$ $K_2 = P_{O2}P_{SO2}^{-1}$ $\log K_2 = \log P_{O2} - \log P_{SO2}$

(3) $NiO + SO_2 = NiS + (3/2)\, O_2$ $K_3 = P_{O2}^{3/2}P_{SO2}^{-1}$ $\log K_3 = (3/2)\log P_{O2} - \log P_{SO2}$

Reaction (1): $\ln K_1 = - \Delta G^{o}_1/RT$

$\log K_1 = - (-159000)/(2.3)(8.3)(873) = 9.54$

$= (-1/2) \log P_{O2}$

--> $\underline{\log P_{O2} = -19.8}$

Reaction (2): $\ln K_2 = - \Delta G^{o}_2/RT = - (\Delta G^{o}_{NiS} - \Delta G^{o}_{SO2})/RT$

$\log K_2 = (-159000)/(2.3)(8.3)(873) = -((-124100)-(-290200))/RT = -166100/RT$

$= (-166100)/ (2.3)(8.3)(873) = - 9.97$

$= \log P_{O2} - \log P_{SO2}$

--> $\underline{\log P_{SO2} = 9.97 + \log P_{O2}}$

Reaction (3): $\ln K_3 = - \Delta G^{o}_3/RT$ with $\Delta G^{o}_3 = \Delta G^{o}_{NiS} - \Delta G^{o}_{NiO} - \Delta G^{o}_{SO2}$

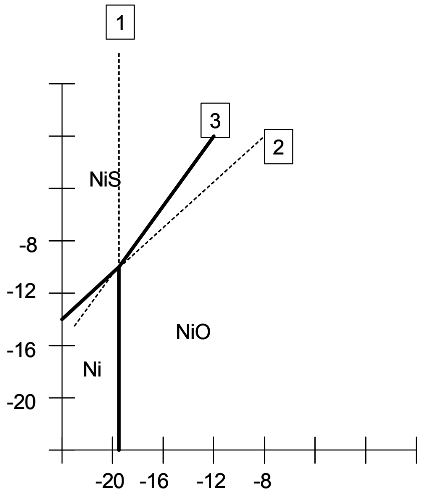
$\ln K_3 = -[(-124100)-(-159000)-(-290200)]/RT = -325100 /RT$

$\log K_3 = - (-325100)/ (2.3)(8.3)(873)= -19.48$

$= (3/2)\log P_{O2} - \log P_{SO2}$

--> $\underline{\log P_{SO2} = 19.48 +(2/3) \log P_{O2}}$

Plot these equations:



(b) $P_{tot} = 1$ bar : 2vol% SO_2 --> $P_{SO2} = 2x10^{-2}$ bar

$P_{O2} = 10^{-16}$ bar

from diagram: --> NiS is the stable product

9.5

From Fig. 9.1 (Ellingham diagram) for 900^{o}C:

$\Delta G^{o}_{TiC} > \Delta G^{o}_{Cr23C6} > \Delta G^{o}_{MoC} > \Delta G^{o}_{Fe3C}$

→ all Ti will react with C to TiC, the rest forms $Cr_{23}C_6$. (If there were still C left it would form MoC and Fe_3C).

Element	w-%	M (g/mol)	Mol /g alloy
Fe	75	55.8	$1.34x10^{-2}$
Cr	23.4	52.0	$4.50x10^{-3}$
Ti	0.05	47.9	$1.04x10^{-5}$
Mo	0.015	95.9	$1.56x10^{-5}$
C	0.05	12.0	$4.17x10^{-5}$

Ti + C → TiC : $1.04x10^{-5}$ mol TiC formed

$M_{TiC} = 47.9 + 12 = 59.9$ g/mol

→ $1.04x10^{-5}$ mol TiC = $(1.04x10^{-5})(59.9) = 6.20x10^{-4}$ g TiC/g alloy

C available for reaction with Cr: $4.17x10^{-5} - 1.04x10^{-5}$ mol = $3.13\ x10^{-5}$ mol C

23 Cr + 6 C → $Cr_{23}C_6$ $3.13\ x10^{-5}$ mol C / 6 = $0.522\ x10^{-5}$ mol $Cr_{23}C_6$

$M_{Cr23C6} = (23)(52)+(6)(12) = 1268$ g / mol

→ $0.522\ x10^{-5}$ mol $Cr_{23}C_6$ = $(0.522\ x10^{-5})(1268) = 6.62x10^{-3}$ g $Cr_{23}C_6$ / g alloy

Result: TiC: $\underline{0.062\text{ w-\%}}$ $Cr_{23}C_6$: $\underline{0.66\text{ w-\%}}$

CHAPTER 10

10.1

(a) Energy dissipation: $Q_f = f\ F_N\ v_s / A$ (J/m2s) where v_s = sliding velocity

$Q_f = (0.1)\ (100N)(50s^{-1}x\ 2mm)(10^{-3}m/mm) / (3x10\text{-}6\ m^2\ ) = \underline{3.33x105\ J/m^2s}$

(b) Temperature incease: $T - To = (\theta_1\ l_H\ /k_1)\ Q_f$

where θ_1 = ½ ; l_H = thermal conduction length; k_1 = thermal conductivity

$T - To = (0.5)(0.01m)\ /0.46\ Jcm^{-1}sK)(10^2\ cm/m))\ (3.33x105\ J/m^2s) = \underline{36.2\ ^oC}$

10.2

Adhesive wear rate : $v_w = K_{WA}\ (F_N\ l_s\ / 3H)$

wear resistance $\propto\ (1/v_W)\ \propto\ (H/\ K_{WA})$

If K_{WA} is independent of hardness H the adhesive wear should vary hardness in the same way as abrasive wear.

10.3

Dimensionless force: $F^* = F_N/A\ H$

$H = 250\ kg/mm^2 = 2450\ MPa$

$F^* = (50N)/(4x10^{-6}m^2)(2450x10^6\ Ns/m^2) = 5.10x10^{-3}$

Dimensionless sliding velocity: $v^* = v_s\ r_o\ /\alpha_T$

$v_s = 2\pi\ f\ r_o = 2\pi\ (3/60)(8) = 2.57\ cm/s$

Thermal conductivity $\alpha_T = h_T/c_p\ \rho$

with $h_T = 0.46\ J/cm\ s\ K$; $c_p = 490\ J/kg\ K$; $\rho_{Fe} = 7.86\ g/cm^3$

$\alpha_T = (0.46\ J/cm\ s\ K\ ) / (490\ J/kg\ K\ )\ (7.86\ g/cm^3) = 0.117\ cm^2/s$

$v^* = (2.57\ cm/s\ )(8\ cm)/(\ 0.117\ cm^2/s) = 176$

Zone III, Severe oxidation wear

10.4

Friction coefficient: $f = (F_f/A)/E_k$

where F_f = friction force, A wall area, E_k = kinetic energy of fluid

Wall area: $A = 2\pi\ r\ L$ where L = 10 m (length of pipe)

Shear force acting on pipe wall: $F_f/A = \Delta P\ (4\pi r^2)/\ 2\pi\ r\ L = \Delta P\ 2r\ /\ L$

with $\Delta P = P_{inlet} - P_{outlet} = 0.15$ bar

$F_f/A = (0.15x10^5\ Pa)(2)(0.05)/10 = 150\ Pa = 150\ N/m^2$

Flow velocity: v = volume flow rate/cross section = $v_{vol}/\ 4\pi\ r^2$

$= 90x10^{-3}/4\pi(5.10^{-2})^2 = 2.87$ m/s

Kinetic energy: $E_k = \rho\ v^2\ /2$ $\qquad$ ρ = density of fluid

$E_k = (1/2)\ (10^3\ kg/m^3)(2.87m/s)^2 = 4.12x10^3\ J/m^3$

Friction coefficient: $f = (150\ N/m^2)/(4.12x10^3\ J/m^3) = \underline{0.036}$

10.5

Critical flow velocity : $v_{crit} = (2\ \tau_{crit}\ /\ \rho\ f)^{1/2}$

Friction coefficient: $\qquad f = 0.32\ Re^{-1/4}$ $\qquad$ with $Re = v\ L\ /\ \nu$

$\tau_{crit} = 9.6\ N/m^2$; $\rho = 10^3\ kg/m^3$; $\nu = 10^{-6}\ m^2/s$; (a) $L = 0.05$ m ; (b) $L = 0.20$ m

$$
\begin{aligned}
v_{crit} &= [2\ \tau_{crit}\ /\ (\rho\ 0.32\ Re^{-1/4})]^{1/2} = [2\ \tau_{crit}\ /\ (0.32\ \rho\ v_{crit}^{-1/4}\ L^{-1/4}\ \nu^{1/4}\ )]^{1/2} \\
&[2\ \tau_{crit}\ 0.32^{-1}\ \rho^{-1}\ v_{crit}^{+1/4}\ L^{+1/4}\ \nu^{-1/4}\ )]^{1/2} = [2\ \tau_{crit}\ (3.125)\ \rho^{-1}\ \nu^{-1/4}]^{1/2}\ v_{crit}^{1/8}\ L^{1/8} \\
&= [2\ (9.6)\ (3.125)\ (10^{-3})(10^{6/4})]^{1/2}\ v_{crit}^{1/8}\ L^{1/8} \\
&= [2\ (9.6)\ (3.125)\ (10^{-3})(31.62)]^{1/2}\ v_{crit}^{1/8}\ L^{1/8} = [1.90]^{1/2}\ v^{1/8}\ L^{1/8} = 1.377\ v_{crit}^{1/8}\ L^{1/8} \\
v_{crit}^{7/8} &= 1.377\ L^{1/8} \rightarrow v_{crit} = \underline{1.44\ L^{1/7}}
\end{aligned}
$$

(a) $L = 0.05$ m : $\qquad v_{crit} = 1.44\ (0.05)^{1/7} = \underline{0.93\ m/s}$

(b) $L = 0.20$ m : $\qquad v_{crit} = 1.44\ (0.20)^{1/7} = \underline{1.14\ m/s}$

10.6

$$T_{inst} - T_s = \frac{f\,\beta}{2N^{1/2}} F^{*1/2}\ v^*$$

with $\quad N \approx 1 + (4 \times 10^{-3}\ )\ F^*(1-F^*)$

$f = 0.5$

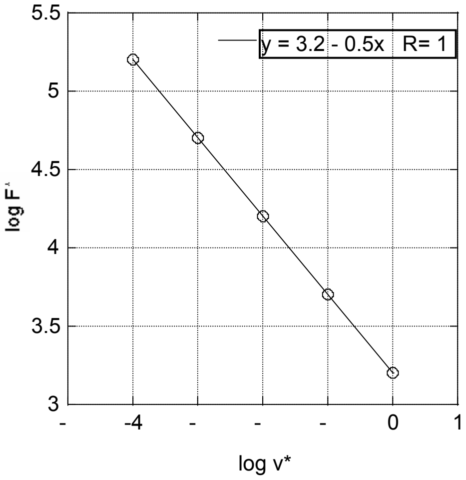
$b = 1$

$T_{inst}-T_s = 400^oC$

$F^{*1/2} = (400)\ (2/(0.5)(1)\ N^{1/2}\ /v^* = (1600/v^*)\ N^{1/2}$

$v^* = 1600\ N^{1/2}\ /\ F^{*1/2} = 1600\ (1 + (4 \times 10^{-3}\ )\ F^*(1-F^*))\ /\ F^{*1/2}$

F*	log F*	v*	log v*
10^{-4}	-4.0000	1.6×10^5	5.20
0.001	-3.0000	50400	4.70
0.01	-2.0000	16000	4.20
0.10	-1.0000	5000.0	3.70
1.0	0.0000	1600.0	3.20



Wear map showing isotherm for f = 0.5 and $\Delta T = 400$

Discussion: $v^* = v_{sl}\, r / \alpha_T$

$F^* = F_N / A\, H$

For a given set up the heating increases with either sliding velocity or applied normal force.

CHAPTER 11

11.1

Cold worked copper: $E_{rev,1} = E_{o,1} + (RT/2F) \ln a_{Cu2+}$

Annealed copper: $E_{rev,2} = E_{o,2} + (RT/2F) \ln a_{Cu2+}$

$Cu_{annealed}$ --> $Cu_{coldworked}$ $\Delta G^o = \Delta G^o_2 - \Delta G^o_1$

$\Delta G^o_2 = -nF\, E_{o,2}$

$\Delta G^o_1 = -nF\, E_{o,1}$

$\Delta G^o = -\, nF\, (E_{o,2} - E_{o,1}) = -\, nF\, E_{cell}$

$\Delta G^o = 12$ J/g = (12) (63.5) = 762 J/mol

$E_{cell} = -\, \Delta G^o / nF = E_{o,2} - E_{o,1} = -(762)/(2)(96485) = -\, 3.9 \times 10^{-3}$ V = $\underline{-\ 3.9 \text{ mV}}$

It follws :

$E_{o,2} < E_{o,1}$ The cold worked electrode is anodic and corrodes preferentially

note: The effect of cold work on the equilibrium potential is small, however.

11.2

$K_{ISCC} = f(a/w)\ \sigma_o\ (\pi\ a)^{1/2}$

$f(a/w) = 1$

$K_{ISCC} = 5$ MN $m^{-3/2} = 5\ x10^6$ N/$m^{3/2}$

σ_o = 700 MPa = 700 $x10^6$ N/m^2

$\pi^{1/2}\ a^{1/2} = K_{ISCC}/\sigma_o = 5x10^6/700x10^6 = 0.714\ x10^{-2}$

$a^{1/2} = (0.714x10^{-2})/1.772 = 0.403x10^{-2}\ m^{1/2}$

critical crack length: a = $0.162x10^{-4}$ m = <u>16.2 μm</u>

11.3

cross section: $A = \pi\ d^2/4 = 0.005^2\ \pi/4 = 1.96x10^{-5}\ m^2$

applied stress: $\sigma_{appl} = F/A = (1.5x10^4\ N)/(1.96x10^{-5}m^2) = 7.64x10^8\ N/m^2$

yield strength: $\sigma_e = 1100$ MPa = $1.1x10^9\ N/m^2$

(a) inert environment: $\sigma_e > \sigma_{appl}$ no rupture

(b) dissolved hydrogen:

in Fig. 11.27 we find for a steel with σ_e = 1100 MPa : $\sigma_{rupture} = 30 – 80\ N/mm^2$

or $\sigma_{rupture} = 30\ x10^7 – 80\ x10^7\ N/m^2$

In presence of dissolved H: $\sigma_{rupture} << \sigma_{appl}$ rupture occurs due to hydrogen embrittlement

11.4

½ $H_2 = H_{(m)}$ $\Delta G = \Delta G^o + RT\ ln\ (X_H\ /\ P_{H2}{}^{1/2})$ (setting $a_H = X_H$)

at equilibrium: $\Delta G = 0$ --> $ln\ X_H = -\Delta G^o/RT + ln\ P_{H2}{}^{1/2}$

P_{H2} = 20 bar --> $lnP_{H2}{}^{1/2} = 1.5$

$ln\ X_H = -\Delta G^o/RT + 1.5$

Table 11.20 for Fe_α :

ΔH^o = 26.3 kJ/mol ΔS^o = -50.3 J/mol K for 300- 900 °C; T = 200°C = 473 K

$\Delta G^o = \Delta H^o - T\ \Delta S^o$

$= 26.3x10^3 – (473)(-50.3) = 5.01x10^4$ J/mol $H_{(m)}$ = 50.1 kJ/mol mol $H_{(m)}$

$ln\ X_H = (-5.01x10^4)/(8.31)(473) + 1.5 = -12.74 + 1.5 = -11.24$

--> $\underline{X_H = 1.31\text{x}10^{-5}}$ [mol H/(mol H + mol Fe)] $\cong$ [mol H/mol Fe]

Volume H_2 dissolved per cm^3 Fe:

$\rho_{Fe} = 7.86\ g/cm^3$; $M_{Fe} = 55.8$ g/mol --> 1 cm^3 Fe = 7.86/55.8 = 0.14 mol Fe

set: $X_H = n_H/n_{Fe}$

where n_H , n_{Fe} are the number of mol of hydrogen and fer per cm^3 Fe

$n_H = X_H\ n_{Fe} = 1.31\text{x}10^{-5} / 0.14 = 1.85\text{x}10^{-6}$ mol H /cm^3 Fe

this corresponds to $n_H/2 = 9.23\text{x}10^{-7}$ mol H_2 /cm^3 Fe

25°C, 1bar : $V_{H2} = n_{H2}\ RT / P_{H2} = (9.23\text{x}10^{-7})(8.31)(298) / (10^5)$ (1 bar = 10^5 N/m2)

$V_{H2} = 2.28\text{x}10^{-8}\ m^3\ H_2/\ cm^3$ Fe = $\underline{2.28 \text{ x } 10^{-2}\ cm^3\ H_2 / cm^3 \text{ Fe}}$

11.5

reaction at anode : $H_{(m)}$ --> $H^+ + e$

diffusion controlled anodic current density: $i_a = 80\mu A/cm^2 = F\ [D_{H(m)}\ c_{Hsat(m)}/L]$

where L = thickness of Fe sheet; L = 20 μm

$c_{Hsat(m)}$ = hydrogen concentration in Fe on cathode side

$D_{H(m)}$ = diffusion coefficient of H in Fe

hydrogen solubility:

$c_{Hsat(m)} = 1.62\text{x}10^{-3}\ cm^3\ H_2$ /g Fe (25°C, 1 bar)

$= 1.62\text{x}10^{-3} / 7.86 = 1.27\text{x}10^{-2}\ cm^3\ H_2\ /cm^3$Fe ($\rho_{Fe} = 7.86\ g/cm^3$)

number of moles H_2:

$n_{H2} = PV/R\ T = (10^5)(1.27\text{x}10^{-8})/8.31)(298) = 5.13\text{x}10^{-7}$ mol H_2/cm^3 Fe

$n_H = 2\ n_{H2}$ --> $n_H = 10.26\text{x}10^{-7}$ mol H / cm^3 Fe

Diffusion coefficient : $D_{H(m)} = i_a\ L / F\ c_{Hsat(m)}$

$D_{H(m)} = (80\text{x}10^{-6}A/cm^2)(20\text{x}10^{-4}cm)/(96485As/mol)(\ 10.26\text{x}10^{-7}mol/cm3) = \underline{1.62\text{x}10^{-6}\ cm^2/s}$

CHAPTER 12

12.1

overall reaction: $Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2\ H^+$

anodic partial reaction: $H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2\ H^+ + 2\ e$ E = 0.085 + 0.065 ln

$i_{a,HP}$

cathodic partial reaction: $Ni^{2+} + 2\ e \rightarrow Ni$ $E = -0.542 - 0.039 \ln |i_{c,Ni}|$

at open circuit, $E = E_{ocp}$: $i_{a,HP} = - i_{c,Ni} = i_{dep}$ (i_{dep} = Ni deposition current density)

$0.085 + 0.065 \ln i_{dep} = -0.542 - 0.039 \ln i_{dep}$

$(0.065 + 0.039) \ln i_{dep} = - 0.542 - 0.085 = - 0.627$

$\ln i_{dep} = - 0.627/0.104 = - 6.026$ → $i_{dep} = 2.41 \times 10^{-3}$ A/cm^2

Ni deposition rate: $v_{dep} = (i_{dep}/2 F)(M/\rho)$ [cm/s]

with $M_{Ni} = 58.7$ g/mol ; $n = 2$; $\rho_{Ni} = 8.9$ g/cm^3

$v_{dep} = (2.41 \times 10^{-3}) (58.7) / (2)(96485)(8.9) = 8.23 \times 10^{-8}$ cm/s

Time to form 12 μm deposit:

$t = (12 \times 10^{-4}$ cm$)/(8.23 \times 10^{-8}$ cm/s$) = 1.46 \times 10^4$ s = $\underline{4.05 \text{ h}}$

12.2

French hardness = total concentration of Mg^{2+} and Ca^{2+} ions exprssed in mg CaCO3 /l :

10 mg $CaCO_3$ = 1°F

$c_{Ca2+} = 10^{-4}$ mol/l

$c_{Mg2+} = 4 \times 10^{-5}$ mol/l

$c_{tot} = c_{Ca2+} + c_{Mg2+} = 14 \times 10^{-5}$ mol/l

10 mg $CaCO_3 = 10^{-3}$ g / $M_{CaCO3} = 10^{-3}/100.1 = 10^{-5}$ mol $CaCO_3$ (M_{CaCO3} = 100.1 g/mol)

→ 10 mg $CaCO_3$/l corresponds to $c_{tot} = 10^{-5}$ mol Ca^{2+}/l

$c_{tot} = 14 \times 10^{-5}$ mol/l → $\underline{14 \text{ °F}}$

Although degree hardness is often used in practice this concentration unit should be avoided whenever possible.

12.3

$\Delta G°_{ads} = -RT \ln b_L$

(a) From Fig. 12.32: $c/\theta \cong 0.1 + c$ [mM/l]

Langmuir: $c/\theta = 1/b_L + c$

By comparison: $1/b_L = 0.1 \times 10^{-3}$ mol/l $= 10^4$ mol/l

$b_L = 10^4$ l/mol

$\Delta G°_{ads} = -RT \ln b_L = - (8.3)(298) \ln 10^4 = \underline{2.28 \times 10^4 \text{ J/mol}}$

(b) $\ln b_L = - \Delta G°_{ads} /RT$

$\Delta G°_{ads} = \Delta H°_{ads} - T \Delta S°_{ads}$

$R (d\ln b_L/dT) = - d(\Delta G°_{ads} /T)/dT$

$= -[(d\Delta G°_{ads} /dT) (1/T) - \Delta G°_{ads}/T^2] = -[-\Delta S°_{ads}/T - (\Delta H°_{ads} - T\Delta S°_{ads})/T^2]$

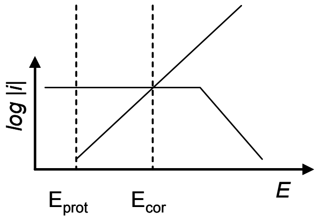
$d\ln b_L/dT = \Delta H^{\circ}_{ads}/ R\, T^2$

exothermic: $\Delta H^{\circ}_{ads} < 0$ --> $d\ln b_L/dT < 0$

by definition: $b_L = k_{ads} / k_{des}$; as T increases k_{ads} / k_{des} decreases. An increasing temperature therefore favors desorption.

12.4

$Fe + O_2 + H_2O \text{ --> } Fe^{2+} + 2OH^-$



$i_{cor} = - i_{l,O2} = nF\, v_{cor}$

$i_{prot} = - i_{cor} = i_{l,O2}$

$v_{cor} = 10$ mg/cm^2 day = $10\text{x}10^2$ mdd = 1000 mdd

Table 1.3 : 1 mdd = 0.112 (n/M) A/m^2 n = 2 ; M = 55.8 g/mol

v_{cor} = (1000) (0.112)(2)/ (55.8) = 4.01 /Am^2

A = 2 m^2 --> $\underline{I_{prot} = 8.02\text{ A}}$

12.5

$E_{prot} = E^o + (RT/nF) \ln 10^{-6}$ [mol/l] $E^o = -0.44$ V; T = 15°C = 288K

$E_{prot} = (-0.44) + [(8.31)(288)/(2)(96485)] \ln 10^{-6} = -0.44 - 0.171 = -0.611$ V

$E_{Cu/CuSO4} = 0.316$ V

E_{prot}(Cu/CuSO4) = -0.611- 0.316 = $\underline{-\ 0.927\text{ V}}$

12.6

Protection current: $I_{prot} = i_{prot}\, A = - i_{cor}\, A = i_{l,O2}\, A$

Estimation of corrosion current density from polarization resistance:

$r_p = (dE/di)_{E=Ecor}$ or $(1/ r_p) = (di/dE)_{E=Ecor}$

For charge transfer controlled anodic reaction and mass transport controlled cathodic reaction:

$i = i_{cor} \exp(\zeta /\beta_a) - i_{l,O2}$ where polarization $\zeta = (E-E_{cor})$

$(1/ r_p) = (di/dE)_{E=Ecor} = (di/d\zeta)_{\zeta=0} = i_{cor} (1/\beta_a)$ --> $i_{cor} = \beta_a / r_p$

$\beta_a = 20$ mV = 0.02 V ; $r_p = 4\text{x}10^4\ \Omega\text{cm}^2$; A = 9 m^2

$i_{cor} = 0.02/4\text{x}10^4 = 5\text{x}10^{-7}$ A/cm^2 = $5\text{x}10^{-3}$ A/m^2

$I_{prot} = - i_{cor} A = - (5x10^{-3}) (9) = - 0.045$ A

Charge for 6 years protection:

$Q = I t / \theta$

$t = (6x365x24x3600) = 1.89x10^8$ s

$\theta = 0.5$ (efficiency)

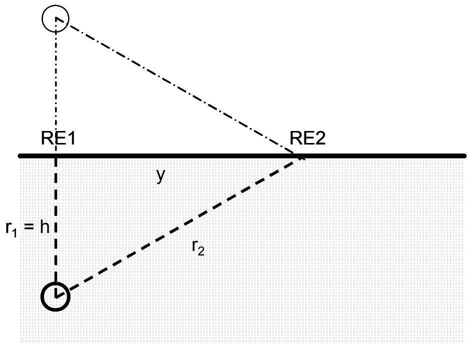
$Q = (0.045)(1.89x10^8)/0.5 = 1.70 \times 10^7$ Coulomb

Mass magnesium required:

$m_{Mg} = Q M_{Mg} /nF$ where $M_{Mg} = 24.3$ g/mol ; n=2

$m_{Mg} = (1.70 \times 10^7) (24.3) /(2)(96485) = 2.14 \times 10^3$ g = $\underline{2.14 \text{ kg}}$

12.7



The stray current creates a potential gradient in the soil. For cylindrical geometry in infinite space :

$d\Phi/dr = - i/\kappa = - \rho_e i = - \rho_e I / 2\pi r L$

where κ = conductivity; ρ_e = resisitivity; L = length of pipe, r = radial coordinate

integration yields: $\Phi_1 - \Phi_0 = -\frac{\rho_e I}{2\pi L}\int_{ro}^{r1}\frac{dr}{r} = -\frac{\rho_e I}{2\pi L}\ln\frac{r_1}{r_0}$

$$\Phi_2 - \Phi_0 = -\frac{\rho_e I}{2\pi L}\ln\frac{r_2}{r_0}$$

Here r_o is the pipe radius.

For a finite space we suppose a symetrical image field. The potential difference between reference electrodes RE1 and RE2 is then obtained from the sum of the two potential fields:

$\Phi_2' - \Phi_1' = 2 (\Phi_2 - \Phi_1) = - (\rho_e I/\pi L) \ln r_2/r_1$

set $r_1^2 = h^2$; $r_2^2 = h^2 + y^2$:

$\Phi_2' - \Phi_0' = - (\rho_e I/\pi L) \ln r_2/r_1 = (1/2)(\rho_e I/\pi L) \ln r_2^2/r_1^2 = (1/2)(\rho_e I/\pi L) \ln[(h^2+y^2)/h^2]$ q.e.d.

numerical values:

$L = 1$ m ; $h = 2$ m ; $y = 20$ m; $\rho_e = 3000\ \Omega$cm $= 30\ \Omega$m

$\Phi_2' - \Phi_1' = -(1/2)(30\ I)/\pi)\ \ln[(4+400)/4] = -(4.78\ I)\ (4.615) = -\ 22.1\ I$

Measured potential difference between RE2 and RE1: $\Phi_2' - \Phi_1' = 1.25$ V

Stray current per meter length: $I = 1.25/22.1 = \underline{5.7 \times 10^{-2}\ \text{A/m}}$

12.8

$Fe + 2\ H^+ \text{--} Fe^{2+} + H_2$

anodic partial reaction: $E = 0.08 + 0.05 \log i_{a,Fe}$

cathodic partial reaction: $E = -0.36 - 0.12 \log |i_{c,H}|$

(a) Corrosion current density, no inhibitor : $E = E_{cor}$

$E_{cor} = 0.08 + 0.05 \log i_{cor} = -0.36 - 0.12 \log i_{cor}$

$\log i_{cor} = (-0.36-0.08)/(0.05+0.12) = -0.44/0.17 = -\ 2.58$ --> $\underline{i_{cor} = 2.58\text{x}10^{-3}\ \text{A/cm}^2}$

Corrosion potential:

$E_{cor} = 0.08 + 0.05 \log i_{cor} = 0.08 + 0.05\ (-2.58) = \underline{-\ 0.05\ \text{V}}$

(b) Hydrogen exchange current density, no inhibitor

$i_c = i_{oH} \exp(-\eta/\beta_c)$ --> $\eta = -\ \beta_c \ln |i_c|/i_{oH} = \beta_c \ln i_{oH} - \beta_c \ln |i_{cH}|$

$E_{rev,H} = 0 - 0.059\ pH = -\ 0.059(0.2) = -\ 0.012$ V

at the corrosion potential $E = E_{cor}$; : $|i_{cH}| = i_{cor}$

$\eta_{(Ecor)} = E_{cor} - E_{rev,H} = -0.05 -(-0.012) = -\ 0.038$ V

$\eta_{(Ecor)} = \beta_c \ln i_{oH} - \beta_c \ln i_{cor}$

$\ln i_{oH} = (\eta_{(Ecor)} / \beta_c) + \ln i_{cor}$

$\beta_c = 0.12/2.3$ V $= 0.052$ V

$\ln i_{oH} = (-\ 0.038/0.052) + \ln(2.58\text{x}10^{-3}) = -0.731 - 5.96 = -\ 6.69$

$i_{oH} = \underline{1.24\text{x}10^{-3}\ \text{A/cm}^2}$

(c) with inhibitor: $i_{oH}' = 10^{-4}\ i_{oH} = 1.24\text{x}10^{-7}$

cathodic partial reaction, $E = E_{cor}$:

$\eta_{(Ecor)} = \beta_c \ln i_{oH}' - \beta_c \ln i_{cor}' = E_{cor} - E_{rev,H} = E_{cor} - (-\ 0.012)$

$E_{cor}' = -0.012 + \beta_c \ln i_{oH}' - \beta_c \ln i_{cor}$

$= -0.012 + 0.12 \log(1.24\text{x}10^{-7}) - 0.12 \log i_{cor}' = -6.92 - 0.12 \log i_{cor}$

anodic partial reaction:

$E_{cor}' = 0.08 + 0.05 \log i_{cor}'$ (same as without inhibitor)

Combine:

$E_{cor}' = -0.83 - 0.12 \log i_{cor}' = 0.08 + 0.05 \log i_{cor}'$

$(0.05+0.12) \log i_{cor}' = -0.83 - 0.08$

$0.17 \log i_{cor}' = -0.91$

$\log i_{cor}' = -5.35 \rightarrow i_{cor}' = \underline{4.4 \times 10^{-6}\ \text{A/cm}^2}$

$E_{cor}' = 0.08 + 0.05 \log i_{cor}' = 0.08 + 0.05\,(-5.35) = \underline{-0.19\ \text{V}}$

(d) Inhibition efficiency: $\theta = (i_{cor} - i_{cor}') / i_{cor}$

$\theta = (1.24\text{x}10^{-3} - 4.4\text{x}10^{-6}) / 1.24\text{x}10^{-3} = 0.997 \rightarrow \theta = \underline{99.7\%}$
