1. (a) A copy of the Figure on the next page was handed out in class earlier this semester. The Figure lists the alloys (on the right hand side of the figure) in order of their corrosion potentials in sea water. Briefly indicate how you would make use of this information to ~~solve~~ address a problem of galvanic corrosion in sea water of two alloys that are listed in the Figure.

⑧ Alloys at the bottom of the list have corrosion potentials greater than alloys at the top of the list. Therefore, in a galvanic couple, the corrosion potential of an alloy at the top of the list will be raised and the corrosion potential of an alloy at the bottom of the list will be lowered. For non-passive metals, the corrosion rate of an alloy at the top of the list will be raised while the corrosion potential of an alloy at the bottom of the list will be lowered.

(b) Would the ranking of the alloys in the attached Figure change if the environment was changed from sea water to boiling 1M H_2SO_4 (sulfuric acid)? Explain your answer.

⑩ Yes. In general, the concentration of Cl^- and the pH will affect the kinetics of the oxidation of a metal. In addition, the reduction reaction will change from O_2 reduction to H^+ reduction. Thus, both the kinetics of oxidation and reduction will change. Since both the kinetics of oxidation and reduction are changed, the corrosion potential will almost certainly change. Most likely the changes in the kinetics of oxidation and reduction will be different for the different alloys. Hence, there likely will be changes in the relative locations of the alloys in the list of corrosion potentials.

2. As described in lecture, "Blue Water" was a consequence of the localized corrosion of copper pipes in tap water in which pH = 8, the concentration of chloride ions = 4 ppm (by weight), and the buffering capacity was essentially negligible. The remedial action identified in lecture was to increase the buffering capacity of the water. Name two other changes of the chemistry of the water that would stop the Blue Water problem. Indicate the reason(s) why each change would eliminate the Blue Water problem. (Do NOT identify any changes in water chemistry that would cause accelerated failure of the copper piping.)

(a) ③ Decrease the dissolved oxygen concentration of the water. ③ Copper is thermodynamically stable in oxygen-free water.

(b) $pH = 8 \Rightarrow [OH^-] = 10^{-6}$ M

$$[Cl^-] = 4\text{ppm} \approx \frac{4\times10^{-3}\text{ gm}}{10^{3}\text{ gm of water}} \approx 10^{-4}\text{M}$$

④ Therefore, decrease the chloride concentration to $\simeq 10^{-7}$ M (i.e. 4 pp$\underline{b}$).

⑧ For $[Cl^-] = 10^{-7}$M, OH^- rather than Cl^- will be the dominant anion that migrates into the occluded volumes of water trapped between the film of Cu_2O and copper.

The OH^- will neutralize any H^+ in the water trapped in the occluded regions and prevent acidification of the trapped water. Although there is a local anode (i.e. in the occluded region) and a local cathode (i.e., outside the occluded region), the separation of anode and cathode is not harmful in the absence of Cl^-.

3. On the Pourbaix Diagram for iron in water (25°C, 1 atm of pressure) what will be the slope of the line that separates the region of (potential, pH) in which iron is thermodynamically stable from the region of (potential, pH) in which Fe_3O_4 is thermodynamically stable?

$3Fe + 4\,H_2O \rightarrow Fe_3O_4 + 8\,H^+ + 8\,e^-$

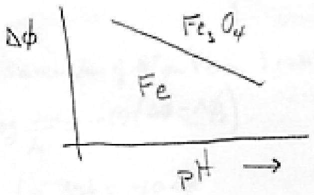
⑨

$$\Delta\phi_e = \Delta\phi_e^\circ - \frac{.0592}{8}\log\frac{1}{[H^+]^8}$$

$$\Rightarrow \quad \frac{\partial(\Delta\phi_e)}{\partial(-\log[H^+])} = -0.0592\,V/_{pH}$$

(b.) On the Pourbaix Diagram for Fe in water (25°C, 1 atm pressure), which phase, Fe or Fe_3O_4, lies above the line that describes equilibrium between Fe and Fe_3O_4? Briefly explain your reasoning.

⑨

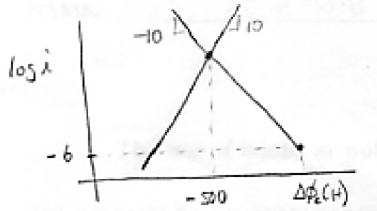


either one

(1) At a given value of pH, as the iron surface is made more positive w.r.t the water, Fe_3O_4 is more stable.

(2) At a given value of potential, increasing $[H^+]$ drives the reaction $3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^-$ to the left $\Rightarrow$ Fe is more stable than Fe_3O_4 at lower pH.

4. At steady-state , the slopes of the anodic and cathodic polarization curves of iron in oxygen-free 1M HCl (pH=0) at 25°C are +10 decades/volt and –10 decades/volt, respectively. The corrosion potential of iron is –500 mV vs SHE and the exchange current density for the reduction of hydrogen ions on the surface of iron in 1M HCl is 10^{-6} A/cm^2. At any given potential the rate of oxidation of iron is inversely proportional to the concentration of hydrogen ions. What is the steady state corrosion potential of iron if the pH of the solution is raised to 1 (without changing the concentration of chloride ions)?



$$\Delta\phi_e(H) = 0 - \frac{0.0592}{2}\log\frac{\overset{1}{P_{H_2}}}{\underset{1}{[H^+]}} = 0$$

(a) ∴ Kinetics of reduction of H^+ on Fe in 1MHCl are described by

$$\log\frac{i_{red}}{i_o} = -10(\Delta\phi - \Delta\phi_e)$$

⑤ $$\therefore \log\frac{i_{red}}{10^{-6}} = -10\Delta\phi$$

(b) ∴ Corrosion rate of Fe in 1M HCl is given by

$$\log\frac{i_{corr}}{10^{-6}} = -10(-0.5V)$$

⑤ $$i_{corr} = 10^{-1}\ A/cm^2$$

$\log i_{ox} + \log\frac{1}{10^{1}} = 10\Delta\phi + 5$

$\log i_{ox} = 10\Delta\phi + 4$

(c) ∴ Kinetics of oxidation of Fe in 1MHCl are given by

$$\log\frac{i_{ox}}{10^{-1}} = 10(\Delta\phi + 0.5V) \longrightarrow \log i_{ox} = 10\Delta\phi + 4$$

(d) It's stated that the kinetics of oxidation of iron are inversely proportional to $[H^+]$.

$$\therefore \frac{i_{ox}(pH=1)}{i_{ox}(pH=0)} = \frac{10^0}{10^{-1}} = 10$$

⑤ ∴ Kinetics of oxidation of Fe in 0.1M HCl are given by

$$i_{ox}(pH=1) = 10\, i_{ox}(pH=0) = 10^{10(\Delta\phi + 0.5V)}$$

(e) Kinetics of reduction of H^+ in 0.1MHCl can be obtained from kinetics of reduction of H^+ in 1MHCl by taking into account the change in i_o and the change in $\Delta\phi_e$.

⑤ (i) In 1MHCl, $i_o = D[H^+]^{\beta} P_{H_2}^{(1-\beta)/2} = 10^{-6}$

$\Rightarrow D = 10^{-6}$

(over→)

(i) (Continued)

In 0.1M HCl

$$i_0 = 10^{-6}[0.1]^{\beta}[1]^{(1-\beta)/2}$$

$$i_0 = 10^{-6}[0.1]^{\beta}$$

$\beta = 0.41$ (See below)

$$\therefore i_0 = 10^{-6}[0.1]^{0.41}$$

⑤ $= 3.89 \times 10^{-7}\ A/cm^2$

Calculation of β:

$$i_{red} = A \exp -\frac{ZF(1-\beta)\Delta\phi}{RT}$$

$$\therefore \ln i_{red} = \ln A - \frac{ZF(1-\beta)}{RT}\Delta\phi$$

or

$$\log i_{red} = \log A - \frac{ZF(1-\beta)}{2.303RT}\Delta\phi$$

$$= \log A - \frac{(1-\beta)}{0.059V}\Delta\phi$$

$$\therefore 10 = \frac{(1-\beta)}{.059V}$$

⑤ $\Rightarrow \beta = 0.41.$

(ii) In 0.1MHCl

$$\Delta\phi_e(H) = 0 - .0592 \log\frac{1}{[10^{-1}]}$$

$$= -.0592V$$

$\therefore$ Kinetics of reduction of H^+ on Fe in 0.1MHCl are given by:

⑤ $$\log\frac{i_{red}}{3.89\times10^{-7}} = -10(\Delta\phi + 0.0592)$$

Solve the above equation and the equation in (i) simultaneously for

$i_{ox} = i_{red} = i_{corr}$

$$10^{10(\Delta\phi_{corr}+0.5V)} = 3.89\times10^{-6.0592}\ 10^{-10\Delta\phi_{corr}}$$

⑥ $\Rightarrow \Delta\phi_{corr} = -0.550\ V.$