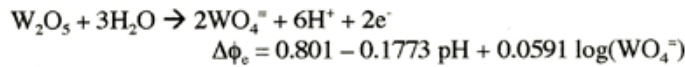
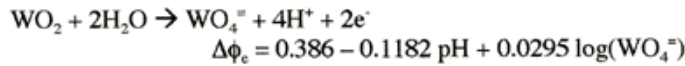
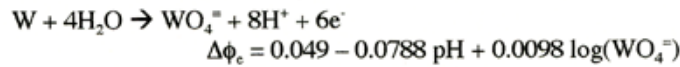
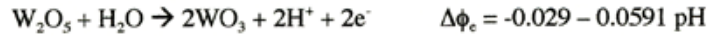
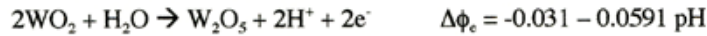
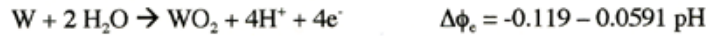


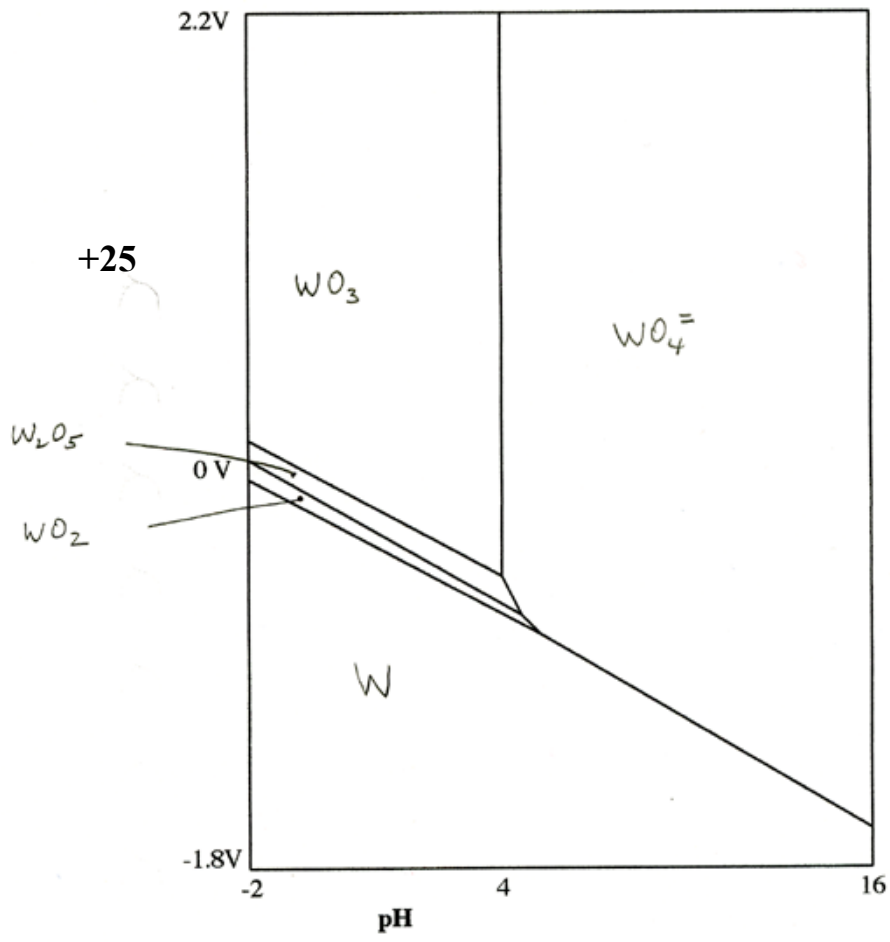
1. (a) Using the seven equilibrium formulae listed below, label the regions of thermodynamic stability of the following species in tungsten's Pourbaix diagram, which is sketched on the next page: W, WO₂, W₂O₅, WO₃, and WO₄²⁻. (Note: W, WO₂, W₂O₅, WO₃ are all solids; WO₄²⁻ is an aqueous species)



(b) The addition of 2 atomic percent (a/o) of tungsten (W) to commercially pure aluminum is found to increase the resistance of aluminum to pitting corrosion in sea water. Specifically, 2 a/o of W is found to increase the resistance of aluminum to the propagation of pitting corrosion (i.e., 2 a/o W inhibits the propagation of pits). Using the Pourbaix diagram of tungsten, provide an explanation for how 2 a/o of tungsten is able to increase the resistance of aluminum to the propagation of pits in sea water.

The Pourbaix diagram indicates WO₃ is stable in low pH solutions. The stability of WO₃ in acidic solutions suggests that W inhibits growth of pits in Aluminum in the same way that Mo inhibits growth of pits in stainless steel. In the acidic solution inside pits, aluminum is preferentially corroded, as Al₂O₃ is soluble in low pH. The preferential corrosion of Al results in enrichment of W on the surface of the pit. Eventually, the surface of the pit is covered by WO₃ and further pit growth stops.

The following figure is a SKETCH of tungsten's Pourbaix Diagram (i.e., the locations of the lines on the diagram are approximately correct)



2. From the last equation on pg. 2

$$\left. \frac{di_{net}}{d\eta} \right|_{\eta=0} = i_{corr} [b_{ox} + b_{red}]$$

Three estimates of $\left. \frac{di_{net}}{d\eta} \right|_{\eta=0}$:

$$(1) \left. \frac{di_{net}}{d\eta} \right|_{\eta=0} \approx \frac{4.0650 \text{ mA}/10 \text{ cm}^2}{0.001 \text{ V}} = 0.0407 \frac{\text{A}}{\text{ohm}\cdot\text{cm}^2}$$

$$(2) \left. \frac{di_{net}}{d\eta} \right|_{\eta=0} \approx \frac{4.2734 \text{ mA}/10 \text{ cm}^2}{0.001 \text{ V}} = 0.0427 \frac{\text{A}}{\text{ohm}\cdot\text{cm}^2}$$

$$(3) \text{ "Average value" } \left\langle \left. \frac{di_{net}}{d\eta} \right|_{\eta=0} \right\rangle = \frac{0.0407 + 0.0427}{2} \frac{\text{A}}{\text{ohm}\cdot\text{cm}^2} \\ = 0.0417 \frac{\text{A}}{\text{ohm}\cdot\text{cm}^2}$$

$$\therefore i_{corr} \approx \left(0.0417 \frac{\text{A}}{\text{ohm}\cdot\text{cm}^2} \right) \frac{1}{(66.67 + 16.67) \text{ V}^{-1}} = 0.5 \frac{\text{mA}}{\text{cm}^2}$$

+25

3. A titanium tank, which is part of a plastic's manufacturing plant, is used to store 0.1M sulfuric acid. The sulfuric acid is commercial grade and is of relatively low purity. In particular, the stored acid contains 0.05M ferric chloride (FeCl_3) as an impurity. Ferric ions are oxidizers. Measurements have shown that the titanium tank is resistant to corrosion because titanium is passive in the stored acid. In high purity 0.1M sulfuric acid titanium corrodes at a rate that is greater than its corrosion rate in the low purity acid by a factor of 10^5 .

(a) The supplier offers to provide 0.1M sulfuric acid containing 0.1M FeCl_3 at a large discount because other consumers reject it on the basis of its deep orange color. Assume that the plastic's manufacturing process is not affected by the higher concentration of FeCl_3 . What are the possible effects of the new acid on the corrosion resistance of the tank? Based on corrosion considerations alone, would you accept the new acid?

See next page for two part answer (i) and (ii)

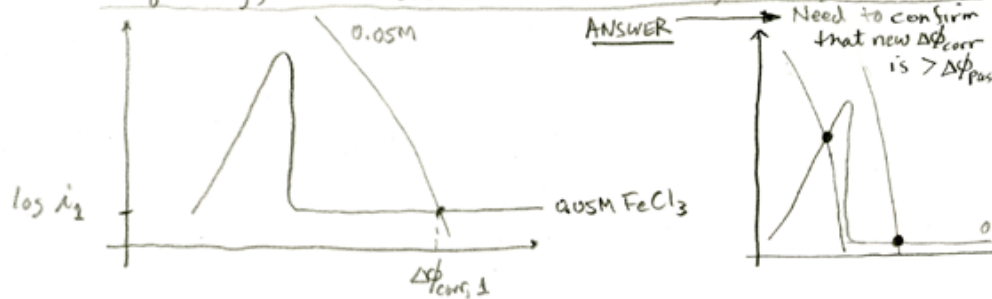
(b) An excess of pure 0.1M sulfuric acid with 0.025M FeCl_3 becomes available from another part of the plant. Can you take this acid into your storage tank without any risk of increasing corrosion?

With 0.05M FeCl_3 , titanium is passive.

with 0M FeCl_3 , titanium is active

Consequently, with 0.025M FeCl_3 Ti might be active.

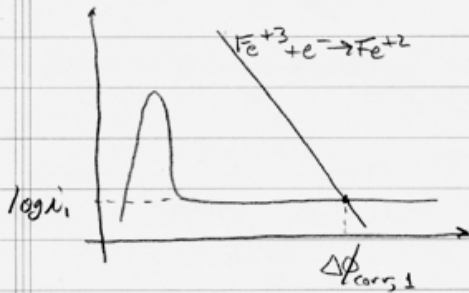
+10



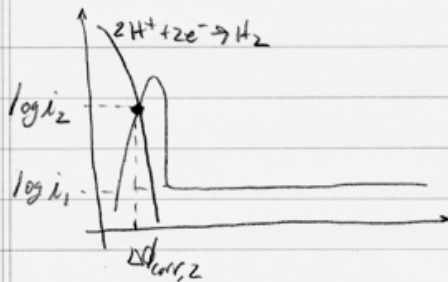
3.

From the information provided we can represent the kinetics of oxidation and reduction as follows:

In $0.1\text{M H}_2\text{SO}_4 + 0.05\text{M FeCl}_3$:



In $0.1\text{M H}_2\text{SO}_4$:

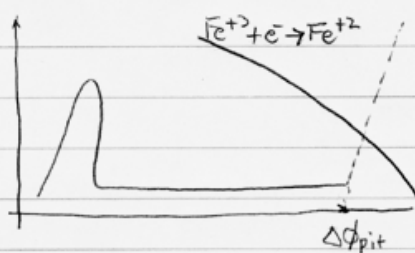


$$\log i_2 - \log i_1 = 5$$

(a) In $0.1\text{M H}_2\text{SO}_4 + 0.1\text{M FeCl}_3$,

+6 (i) $\Delta\phi_{\text{corr}}$ will be $> \Delta\phi_{\text{corr},1}$, so Ti will be passive.

+7 (ii) However, because of the higher concentration of chloride, it is possible that $\Delta\phi_{\text{corr}}$ will be greater than $\Delta\phi_{\text{pit}}$.



$\Delta\phi_{\text{corr}}$ might be $> \Delta\phi_{\text{pit}}$.

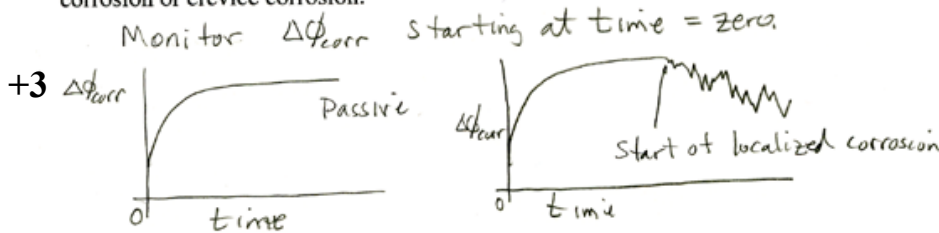
Before accepting new acid, need to confirm that new $\Delta\phi_{\text{corr}}$ is $< \Delta\phi_{\text{pit}}$.

+2

4.(a) List the conditions that must be met for crevice corrosion of a metal in an aqueous solution.

- +4
- (1) crevice
 - (2) oxidizer
 - (3) susceptible metal (i.e., $\Delta\phi_{\text{passive}}$ and i_{passive} increase with increasing concentration of H^+ and/or anion concentration)
 - (4) Anion other than OH^-

(b) Briefly describe a non-invasive method for determining whether or not a metallic component that is immersed in sea water is undergoing pitting corrosion or crevice corrosion.



(c) Briefly explain why tests of crevice corrosion typically exhibit a large amount of scatter. i.e., at the end of the test period, presumably identical samples exhibit a wide range of crevice corrosion: some samples might be completely free of crevice corrosion and other samples might have a small amount or an extensive amount of crevice corrosion.

- +4
- Severity of crevice corrosion depends on the ratio of surface area to volume of the crevice. The ratio of surface area to volume is difficult to reproduce.
- The higher the ratio of surface area to volume, the more likely is crevice corrosion.

(d) Based on the mechanism of pitting corrosion, suggest reasons why measurements of an alloy's pitting potential also exhibits a fair amount of scatter.

- +4
- (i) Initiation of pitting corrosion occurs at passive film's defects, such as insoluble and soluble inclusions in the alloy. The sizes and shapes of the inclusions are highly variable (as are other defects such as grain boundaries, dislocations).
- (ii) The propagation of pitting corrosion depends on the size and shape of the pit nucleus that forms from the pit initiation process. The geometry of the pit nuclei are highly variable.