Assignment 7

1. Draw the plots of following reactions in the Pourbaix diagram for Cu-H₂O system when $[Cu^{2+}] = 1$. Use following data:

$Cu^{2+} + 2e = Cu$	$E = 0.337 + 0.0295 \log[Cu^{2+}]$
$Cu^{2+} + H_2O = CuO + 2H^+$	$\log[Cu^{2+}] = 7.89 - 2pH$
$2Cu^{2+} + H_2O + 2e = Cu_2O + 2H^+$	E = 0.203 + 0.0591 pH + 0.0591 log[Cu2+]
$2Cu + H_2O = Cu_2O + 2H^+ + 2e$	E = 0.471 - 0.0591 pH
$Cu_2O + H_2O = 2CuO + 2H^+ + 2e$	E = 0.669 - 0.0591 pH

You need to show the values of pH and potential at all the junction points in the schematic plot.

2. Draw the complete Pourbaix diagram of a metal (Me) with the following data. Clearly show the regions of different species. (assume all the ionic activities to be unity).

$Me^{3+} + 3e = Me$	$E^0 = -1.662$ volts (SHE)
$Me_2O_3 + 6H^+ + 6e = 2Me + 3H_2O$	$E^0 = -1.55$ volts (SHE)
$MeO_{2}^{-} + 4H^{+} + 3e = Me + 2H_{2}O$	$E^0 = -1.262$ volts (SHE)
$Me_2O_3 + 6H^+ = 2Me^{3+} + 3H_2O$	$K=(a_{M3+})^2/(a_{H+})^6=10^{11.4}$
$2MeO_2^- + 2H^+ = Me_2O_3 + H_2O$	$K=1/(a_{MeO2})^2(a_{H^+})^2=10^{29.2}$

3. (a) Prove that the potential must increase from equilibrium potential during anodic polarization.

(b)
$$O_2 + 4H^+ + 4e = 2H_2O$$
 (E⁰=1.227 volts (SHE))
 $O_2 + 2H_2O + 4e = 4OH^-$ (E⁰=0.401 volts (SHE)).

Show that these two reactions meet at pH=7 with the same slope in the Pourbaix diagram.

- 4. A metal (Me) plate shows pitting tendency in sea water. Total weight loss after 180 days was measured to be 5 gm. The overall plate area exposed to sea water is 100 cm² and density of the plate is 7.86 gm/cm³. Find out the corrosion rate in mpy and SI unit. Do you think that this metal can be useful in sea water application from corrosion perspective and why?
- 5. (a) A Nickel electrode is corroding in a deaerated solution with the evolution of hydrogen at 25° C. Determine the i_{corr} and E_{corr} of nickel. Given : $E^{0}_{Ni++/Ni} = -0.250$ V (SHE); $E^{0}_{H+/0.5H2} = 0$ V (SHE); Tafel slope for anodic and cathodic reaction is 0.1 V/decade; i₀ (hydrogen) on Ni = 10⁻⁵ amp/cm²; i₀ (Ni) on Ni = 10⁻⁵ amp/cm².

(b) The linear polarization slope $\Delta E/\Delta i$ at low current densities for iron in a given corrosive is 4 mv/µ amp/cm². Calculate the corrosion rate in mdd. Given Tafel slope for anodic and cathodic reaction is 0.1 V/decade; atomic wt of Fe = 55.85.

- 6. (a) Schematically show on overpotential (η) vs. current density (i) plot (η vs i) that if exchange current density increases only for cathodic reaction, both the corrosion rate and corrosion potential increase.
 - (b) The weight gain vs. time data for oxidation of Ni at 700 and 800° C are given below:

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Time(min)	Weight gain (mg/cm ²)	
	700^{0} C	800 ⁰ C
10	0.527	3.000

Table

Assuming the oxidation kinetics to obey the parabolic law, calculate the activation energy for the oxidation of the metal in the range of $700-800^{\circ}$ C.

- 7. Schematically show with the help of mixed potential theory that galvanization does minimize the corrosion rate of Fe to a great extend in deaerated acid medium, however, it does not completely stop corrosion of Fe. E⁰_{Fe++/Fe} > E⁰_{Zn++/Zn}; i₀ (Hydrogen) on Fe > i₀ (Hydrogen) on Zn and i₀ (Fe⁺⁺/Fe) on Fe > i₀ (Zn⁺⁺/Zn) on Zn (Only schematic with proper level).
- (a) Show that anodic protection is possible with much less current requirement compared to impressed current cathodic protection in case of active passive metals. (With proper schematic).
 - (b) What is cathodic over-protection?
 - (c) What is sheathing?