

### Assignment 6

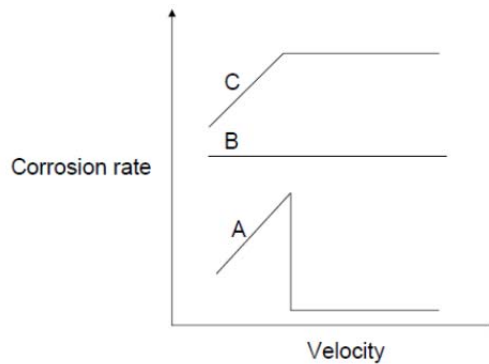
1. A metal wire (M) coated with MCl is immersed in a dilute HCl solution.  $E_{\text{MCl/M}}^0 = 0.224\text{V}$ ; Find out the electrode potential ( $E_{\text{MCl/M}}$ ) if pH of the acid is 1. ( $\text{pH} = -\log[\text{H}^+]$ )
2.  $\mu_{\text{H}_2\text{O}}^0 = -238.1\text{ kJ/mol}$ ,  $\mu_{\text{H}_2}^0 = 0\text{ J/mol}$ ,  $\mu_{\text{O}_2}^0 = 0\text{ J/mol}$ ; what will be the value of potential in volts of oxygen reduction when the solution pH becomes 1.
3. A metal wire (M) coated with MCl is immersed in a dilute HCl solution.  $E_{\text{MCl/M}}^0 = 0.224\text{V}$ ; If the electrode potential ( $E_{\text{MCl/M}}$ ) is  $0.34\text{V}$ , then find out pH of the acid. ( $\text{pH} = -\log[\text{H}^+]$ ).
4.  $\mu_{\text{H}_2\text{O}}^0 = -238.1\text{ kJ/mol}$ ,  $\mu_{\text{H}_2}^0 = 0\text{ J/mol}$ ,  $\mu_{\text{O}_2}^0 = 0\text{ J/mol}$ ; what will be the value of potential in volts of oxygen reduction when the solution pH becomes zero.
5. In the cell at atmospheric pressure (Cd-CdSO<sub>4</sub> (soln)//Hg<sub>2</sub>SO<sub>4</sub> (soln)-Hg) the EMF at T°C is  $E_T = 0.6708 - 1.02 \times 10^{-4}(T - 25)$  volts. Calculate  $\Delta G$  and  $\Delta H$  at 45°C.
6. Standard electrode potentials for Cu<sup>++</sup>/Cu and Cu<sup>+</sup>/Cu are 0.337 volts and 0.530 volts, respectively. The cell structure is (Cu<sup>+</sup>/Cu//Cu/Cu<sup>++</sup>). (a) Find out the equilibrium cell reactions. (b) Find out the standard cell voltage with the help of Nernst relations. (c) Find out the equilibrium constant of the cell reaction at 25°C.
7. Explain the followings from corrosion perspective:
  - (a) If mild steel rivets are used to fasten Cu plates in sea water application.
  - (b) Gas welding of very low carbon 18-8 austenitic stainless steel leads to sensitization.
  - (c) Graphitization of gray cast iron is a misnomer.
  - (d) Galvanic corrosion of alloys does not depend on the standard electrode potential.
  - (e) Sample area plays a major role in pitting corrosion.

8.  $\mu_{\text{Ni}^{2+}}^0 = -11.1 \text{ kcal/mol}$ ;  $\mu_{\text{Ni}}^0 = 0 \text{ kcal/mol}$ ;  $\mu_{\text{Ni(OH)}_2}^0 = -108.3 \text{ kcal/mol}$ ;  $\mu_{\text{H}_2\text{O}}^0 = -56.69 \text{ kcal/mol}$ ;  $\mu_{\text{H}^+}^0 = 0 \text{ kcal/mol}$ . Possible equilibrium reactions in Ni-H<sub>2</sub>O system are:

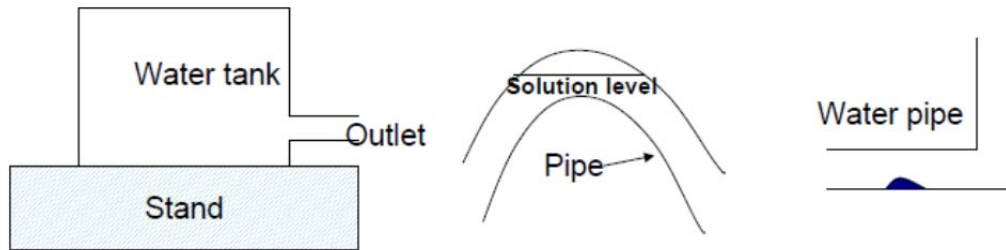
- (a)  $\text{Ni}^{+2} + 2\text{e} = \text{Ni}$
- (b)  $\text{Ni(OH)}_2 + 2\text{H}^+ + 2\text{e} = \text{Ni} + 2\text{H}_2\text{O}$
- (c)  $\text{Ni}^{2+} + 2\text{H}_2\text{O} = \text{Ni(OH)}_2 + 2\text{H}^+$
- (d)  $\text{O}_2 + 4\text{H}^+ + 4\text{e} = 2\text{H}_2\text{O}$  ( $E^0 = 1.223 \text{ volts}$ )
- (e)  $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} = 4\text{OH}^-$
- (g)  $\text{H}^+ + \text{e} = 0.5\text{H}_2$  ( $E^0 = 0 \text{ volts}$ )
- (h)  $2\text{H}_2\text{O} + 2\text{e} = 2\text{OH}^- + \text{H}_2$

Draw the Pourbaix diagram for Ni at 25<sup>0</sup>C and 1 atm pressure (assume that the concentration of Ni ion is unity). 1cal=4.18J; R=8.314 J/mol/K; 1 Faraday=96485 Coulomb.

- 9. Find out the relation between corrosion rate and current density if the metal is pitting prone.
- 10. Sand blasting improves stress corrosion cracking resistance of metals and alloys. Why? How do you find out the critical stress below which stress corrosion cracking does not happen?
- 11. Three metals (A, B and C) show corrosion behavior as a function of solution velocity of the solution (Fig). Oxygen reduction is the cathodic reaction. A is an active passive metal; and B and C are active metals in the respective solutions. With the help of mixed potential theory (only schematic with proper leveling) explain the above corrosion rates for three metals as a function of velocity.



12. (a) The corrosion current of a steel specimen in deaerated pure HCl acid is  $1.6 \times 10^{-5}$  amp/cm<sup>2</sup>. Calculate the corrosion potential of iron vs saturated calomel electrode (SCE) in the acid of pH 3.  $\beta_c$  is assumed to be 0.1 v/decade and  $i_0$  is  $10^{-7}$  amp/cm<sup>2</sup> for iron. ( $E_{SCE}=0.241$ v and  $T=25^{\circ}C$ ).
- (b) Suggest proper design recommendation for the following three cases (Fig. 2) in order to minimize corrosion.



13. (a) Show with proper illustration (mixed potential theory) that anodic protection mechanism is much better than impressed current cathodic protection in terms of economic standpoint in case of active passive metals. (Write as minimum as possible).
- (b) Hydrogen poisons can lead to hydrogen embrittlement. Why?
14. (a) Metal M is corroding in deaerated pure HCl solution. Show the overvoltage vs current density (absolute scale) plot for all the cathodic and anodic reactions. Level  $E_{corr}$ ,  $i_{corr}$  and  $i_0$  for all the cathodic and anodic reactions.
- (b) The linear polarization slop  $\Delta E/\Delta i$  at low current densities for iron in a given corrosion solution is  $2\text{mv}/\mu\text{Acm}^2$ . Calculate the corrosion current. (assume  $\beta_c=\beta_a=0.1$  v/decade).

15. (a) A n-type oxide (MO) is doped with aluminium. What would be the oxidation resistance of the metal after doping?

(b) The weight gain vs. time data for oxidation of Ni at 700 and 800°C are given below:

Table

Time(min)	Weight gain (mg/cm <sup>2</sup> )	
	700°C	800°C
10	0.527	0.755
30	0.857	1.307
100	1.526	2.387

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°C.