

# Corrosion Examples Paper 1

(Numerical answers are given at the end of this examples paper.)

1. (a) What is the overall reaction for the electrochemical cell  $\text{Mg} | \text{Mg}^{2+} || \text{Ag}^+ | \text{Ag}$  ?
- (b) What is the change in standard Gibbs free energy for this reaction?
- (c) What would be the cell potential if the solution concentrations of each half-cell are 0.4 M for  $\text{Mg}^{2+}$  and 0.2 M for  $\text{Ag}^+$  ? Take the temperature to be 298 K for both half-cells. You may assume that ion activities are approximately equal to concentrations in  $\text{mol dm}^{-3}$ .
- (d) If the electrodes both have area  $100 \text{ cm}^2$  and are in  $1000 \text{ cm}^3$  solutions, calculate the thickness lost/gained of metal on each electrode when the cell potential of the batch system in part (c) has changed by 1%.

## Data:

Standard electrode potentials:

$$E^\circ(\text{Ag}|\text{Ag}^+) = +0.799 \text{ V}_{\text{SHE}} ; E^\circ(\text{Mg}|\text{Mg}^{2+}) = -2.363 \text{ V}_{\text{SHE}}$$

Densities: Ag  $10490 \text{ kg/m}^3$  ; Mg  $1738 \text{ kg/m}^3$

Atomic weights:  $m(\text{Ag}) = 107.8682$ ;  $m(\text{Mg}) = 24.304$  (or see data book)

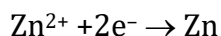
Faraday constant  $F = 96485.3 \dots \text{ C/mol}$

2. A schematic potential-pH diagram for zinc at 298 K was given to you in lectures. In this question you are to derive where three of the lines on it appear using the data below. The criterion for the corroding condition is that the concentration of metal ions exceeds  $10^{-4} \text{ M}$ .

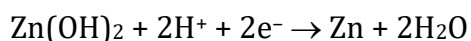
- (a) Consider the line between the Zn (immune) and  $\text{Zn}^{2+}$  (corrosion) regions. Show that this line occurs at  $E = -0.878 \text{ V}_{\text{SHE}}$ .
- (b) Consider the line between the Zn (immune) and  $\text{Zn}(\text{OH})_2$  (passive) regions. Show that this line obeys  $E = -0.439 - 0.059 \text{ pH}$ , where  $E$  is in  $\text{V}_{\text{SHE}}$ .
- (c) Consider the line between the  $\text{Zn}^{2+}$  (corrosion) and  $\text{Zn}(\text{OH})_2$  (passive) regions. Show that the line occurs at pH 7.43.
- (d) Discuss the uses and limitations of potential-pH diagrams.

## Data:

Standard electrode potentials:



$$E^\circ(\text{Zn}|\text{Zn}^{2+}) = -0.760 \text{ V}_{\text{SHE}}$$



$$E^\circ(\text{Zn}|\text{Zn}(\text{OH})_2) = -0.439 \text{ V}_{\text{SHE}}$$

Equilibrium constant:  $\text{Zn}(\text{OH})_2 + 2\text{H}^+ \leftrightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O}$   $K = 7.58 \times 10^{10}$

3. (a) Why is the ordering of metals in a galvanic series usually different from that in the electrochemical series?

(b) (i) Why does gold not normally corrode even in strong acid?

(ii) Why does gold corrode in a mixture of concentrated nitric and hydrochloric acids? (Hint: consider what happens when complexes such as  $[\text{AuCl}_4]^-$  (aq) are formed)

4. The current in an electrochemical cell with an anode area of  $20 \text{ cm}^2$  is measured using an ammeter as 1 mA. Calculate the current density, the mass wastage rate ( $\text{kg/m}^2\cdot\text{yr}$ ) and the corrosion rate ( $\text{mm/year}$ ) if the metal is:

(a) magnesium

(b) silver

You may assume that the magnesium is oxidised to  $\text{Mg}^{2+}$  ions, and silver to  $\text{Ag}^+$  ions.

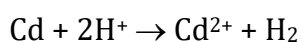
**Data:**

Standard atomic weights are given in question 1 (or refer to data book).

Density of magnesium =  $1738 \text{ kg/m}^3$

Density of silver =  $10490 \text{ kg/m}^3$

5. Cadmium experiences active corrosion in an acidic solution according to the reaction



Assuming that all the reagents have unit activity, the temperature is 298 K, and that the rates of both oxidation and reduction half-reactions are controlled by activation polarisation, calculate the corrosion potential  $E_{\text{corr}}$  and the rate of oxidation of the cadmium (in  $\text{mol/cm}^2 \text{ s}$ ) using the data below.

**Data:**

For cadmium ( $\text{Cd}|\text{Cd}^{2+}$ ):

$$E^\circ = -0.403 \text{ V}_{\text{SHE}}$$

$$i_0 = 2 \times 10^{-8} \text{ A/cm}^2$$

$$\beta_a = +0.12 \text{ V}$$

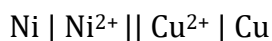
For hydrogen ( $\text{H}_2|2\text{H}^+$ )

$$E^\circ = 0.000 \text{ V}_{\text{SHE}}$$

$$i_0 = 2.5 \times 10^{-6} \text{ A/cm}^2 \text{ (on cadmium)}$$

$$\beta_c = -0.20 \text{ V}$$

6. A nickel/copper corrosion cell, at 298 K, is described as follows. The  $\text{Ni}^{2+}$  ions have a concentration of 5 mM, and the  $\text{Cu}^{2+}$  ions have a concentration of 250 mM.

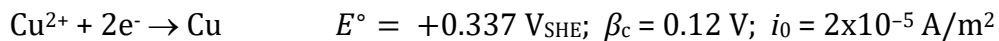


Assuming that the solutions are of high conductivity, use the data below to estimate the mixed corrosion potential and the rate of magnesium loss ( $\text{kg/m}^2\text{yr}$ ) during the corrosion process if:

(a) the electrodes have equal exposed areas

(b) the area of exposed nickel is 75 times smaller than that of the copper.

**Data:**



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**Numerical answers**

1. (b) -610 kJ/mol ; (c) +3.132 V ; (d) Mg -95  $\mu\text{m}$ , Ag +140  $\mu\text{m}$

4.  $i = 0.5 \text{ A/m}^2$  ; (a) 1.985 kg/m<sup>2</sup>.yr, 1.14 mm/year ; (b) 17.628 kg/m<sup>2</sup>.yr, 1.68 mm/year

5. -0.095 V<sub>SHE</sub>;  $3.8 \times 10^{-11} \text{ mol/cm}^2.\text{s}$

6. (a) +0.030 V<sub>SHE</sub>, 0.57 kg/m<sup>2</sup>yr ; (b) +0.132 V<sub>SHE</sub>, 5.93 kg/m<sup>2</sup>yr