CET IIA

Materials and Corrosion
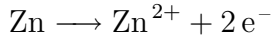## Corrosion and Material Selection: Part I

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Worksheet 1 Solutions
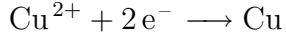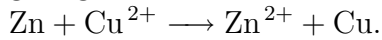
Question 1

Part (a)

Zinc is the anode and Copper the cathode. The anodic reaction will be
$Zn \longrightarrow Zn^{2+} + 2e^{-}$
and the cathodic reaction will be
$Cu^{2+} + 2e^{-} \longrightarrow Cu$
giving an overall reaction of
$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$.

Part (b)

The Gibbs free energy for this reaction is given by

$$\Delta G = -nFE_{cell} = -nF\left(E_{cathode} - E_{anode}\right) . \tag{1}$$

Substitute the following values in;

$$
\begin{aligned}
n &= 2 \\
F &= 9.648 \times 10^4 \text{ C mol}^{-1} \\
E_{cathode} &= +0.34 \text{ V} \\
E_{anode} &= -0.76 \text{ V} .
\end{aligned}
$$

Giving $\Delta G = -212$ kJ mol^{-1}.

Part (c)

The Nernst equation is one that should be memorised and is

$$E = E_{cell}^o - \frac{RT}{nF} \ln \left[\prod a_j^{\nu_j} \right] . \tag{2}$$

For this reaction;

$$
\begin{aligned}
\prod a_j^{\nu_j} &= \frac{a_{Zn^{2+}} \; a_{Cu}}{a_{Zn} \; a_{Cu^{2+}}} \\
&= \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}
\end{aligned}
$$

Substitute the following values into the Nernst equation;

$$
\begin{aligned}
E_{cell}^o &= +1.1 \text{ V} \\
R &= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \\
T &= 298 \text{ K} \\
n &= 2 \\
F &= 9.648 \times 10^4 \text{ C mol}^{-1} \\
\left[Zn^{2+}\right] &= 0.4 \text{ M} \\
\left[Cu^{2+}\right] &= 0.2 \text{ M} .
\end{aligned}
$$

Giving $E = +1.091$ V.

Part (d)

Say the cell potential decreases by 1% so $E_{cell} = +1.08009$ V. Find the change in the number of moles of each species:

$$E_{cell} = -\frac{RT}{nF} \ln\left(\frac{[\text{Zn}^{2+}] + x}{[\text{Cu}^{2+}] - x}\right) . \tag{3}$$

Giving $x = 0.095$ moles. The thickness gained or lost is given by:

$$\text{Thickness Gained/Lost} = \frac{xM_R}{\rho A_{electrode}} . \tag{4}$$

Substitute the following values in;

$$
\begin{aligned}
\rho_{Cu} &= 8920 \text{ kg m}^{-3} \\
\rho_{Zn} &= 7140 \text{ kg m}^{-3} \\
M_R^{Cu} &= 63.54 \text{ kg kmol}^{-1} \\
M_R^{Zn} &= 65.38 \text{ kg kmol}^{-1} \\
A_{electrode} &= 0.01 \text{ m}^2 \\
x &= 9.5 \times 10^{-5} .
\end{aligned}
$$

So Cu gains 68 μm and Zn loses 87 μm.

Question 2

Part (a)

$$E = E^o - \frac{RT}{nF} \ln \left[\frac{1}{[\text{Zn}^{2+}]} \right] . \tag{5}$$

$E = -0.937$ V.

Part (b)

$$E = E^o - \frac{RT}{nF} \ln \left[\frac{1}{[\text{H}^+]^2} \right] . \tag{6}$$

Recall that $\text{pH} = -\log_{10}[\text{H}^+]$, so $\frac{1}{[\text{H}^+]} = 10^{pH}$. Substituting this into the Nernst equation gives:

$$E = -0.439 - 0.059 \text{ pH} \tag{7}$$

Part (c)

$$
\begin{aligned}
K &= \frac{\text{conc. of products}}{\text{conc. of reactants}} \\
&= \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \\
&= \frac{10^{-6}}{10^{-2pH}}
\end{aligned}
$$

After some rearrangement pH = 8.44.

Alternatively, use the two equations derived in parts (a) and (b) to find the pH. This can be done because all three lines in this question intersect at the same point.

Part (d)

Potential-pH diagrams are useful for telling us what change in E or pH is required to stop corrosion occurring.

The limitations are that they;

• Only apply to the specified conditions.

• Do not tell us if the passive state actually prevents corrosion. The passive layer may be a loose deposit offering little or no protection.

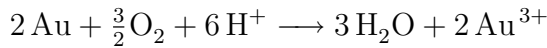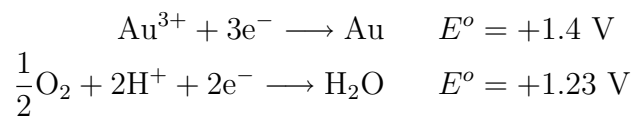• Do not give any information on the corrosion rate.

Question 3

Part (a)

A galvanic series is a list of the reactivity of metallic compounds for SPECIFIED CONDITIONS. Electrochemical series do not take into account the nature of oxides formed on metals or the influence that the environment might have on breaking down the oxides.

Part (b) (i)

It is not thermodynamically possible for gold to corrode in strong acid. For a reaction to take place, remember that there has to be a net release of Gibbs energy; $\Delta G < 0$.

$$Au^{3+} + 3e^- \longrightarrow Au \quad E^o = +1.4 \text{ V}$$
$$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O \quad E^o = +1.23 \text{ V}$$

$$2\,Au + \tfrac{3}{2}O_2 + 6\,H^+ \longrightarrow 3\,H_2O + 2\,Au^{3+}$$

$$E = E^o_{cell} - \frac{RT}{nF} \ln \left[\frac{\left[Au^{3+}\right]^2}{\left[H^+\right]^6 P^{1.5}_{O_2}} \right] . \tag{8}$$

Part (b) (ii)

The formation of complexes reduces the number of $\left[Au^{3+}\right]$ ions which can make $\Delta G < 0$.

Question 4

Another equation that needs to be memorised is Faraday's equation;

$$i = \frac{nF}{A} \left(-\frac{dN}{dt} \right) \tag{9}$$

Variables given;

$$\begin{aligned}
\rho_{Cu} &= 8920 \text{ kg m}^{-3} \\
\rho_{Al} &= 2700 \text{ kg m}^{-3} \\
M_R^{Cu} &= 63.54 \text{ kg kmol}^{-1} \\
M_R^{Al} &= 26.98 \text{ kg kmol}^{-1} \\
A_{anode} &= 0.005 \text{ m}^2 \\
I &= 0.001 \text{ A} .
\end{aligned}$$

The current density for both Cu and Al is

$$i = \frac{\text{current}}{\text{anode area}} = \frac{0.001}{0.001} = 0.2 \text{ A m}^{-2} = 0.2 \text{ C m}^{-2} \text{ s}^{-1} . \tag{10}$$

Part (a)

The mass wastage rate is given by $\frac{1}{A}\left(-\frac{dM}{dt}\right)$. Rearranging Faraday's equation gives;

$$
\begin{aligned}
\frac{1}{A}\left(-\frac{dM}{dt}\right) &= \frac{i\ M_R^{Cu}}{nF} \\
&= \frac{6,307,200 \times 63.54}{2 \times 9.648 \times 10^7} \\
&= 2.08 \text{ kg m}^{-2} \text{ yr}^{-1}\ .
\end{aligned}
$$

To get the corrosion rate just divide the mass wastage rate by the density;

$$
\begin{aligned}
\frac{1}{A}\left(-\frac{dM}{dt} \times \frac{1}{\rho_{Cu}}\right) &= \frac{2.08}{8920} \\
&= 2.33 \times 10^{-4} \text{ m yr}^{-1} \\
&= 0.233 \text{ mm yr}^{-1}\ .
\end{aligned}
$$

Part (b)

Exactly the same procedure as for Cu. The mass wastage rate is

$$
\begin{aligned}
\frac{1}{A}\left(-\frac{dM}{dt}\right) &= \frac{i\ M_R^{Al}}{nF} \\
&= \frac{6,307,200 \times 26.98}{3 \times 9.648 \times 10^7} \\
&= 0.588 \text{ kg m}^{-2} \text{ yr}^{-1}\ .
\end{aligned}
$$

The corrosion rate is

$$
\begin{aligned}
\frac{1}{A}\left(-\frac{dM}{dt} \times \frac{1}{\rho_{Al}}\right) &= \frac{0.588}{2700} \\
&= 2.18 \times 10^{-4} \text{ m yr}^{-1} \\
&= 0.218 \text{ mm yr}^{-1}\ .
\end{aligned}
$$

Question 5

The oxidation of Pb occurs at the anode, the reduction of H occurs at the cathode. The equations for the two lines can be written as;

$$
\begin{aligned}
E_{0,c} - E_{corr} &= -\beta_c \left[\log_{10}\left(i_{corr}\right) - \log_{10}\left(i_{0,c}\right)\right] \\
E_{corr} - E_{0,a} &= \beta_a \left[\log_{10}\left(i_{corr}\right) - \log_{10}\left(i_{0,a}\right)\right]\ .
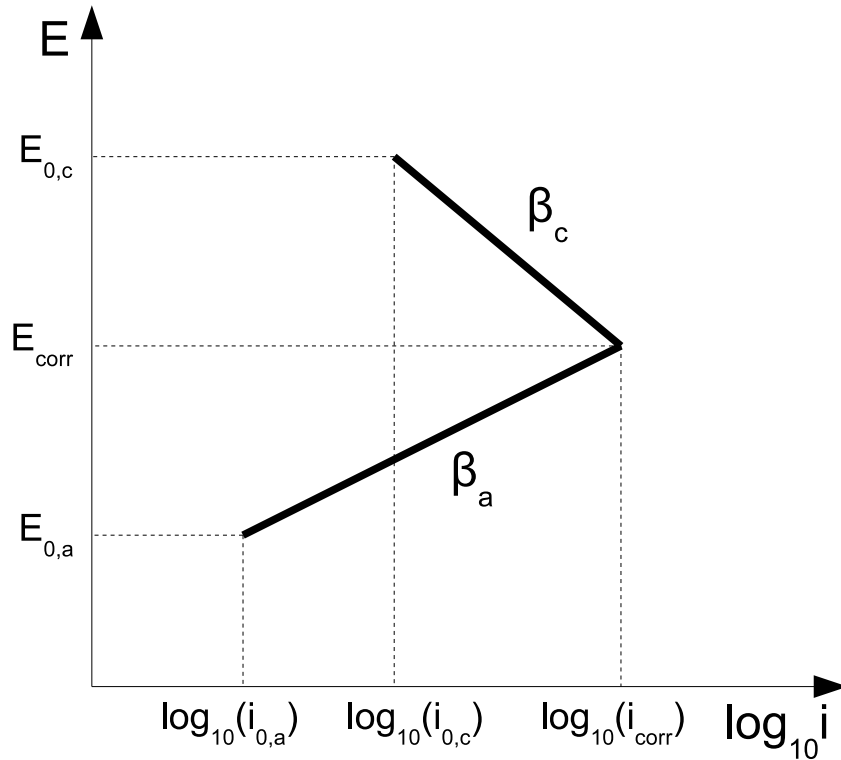\end{aligned}
$$

Adding results in;

Figure 1: *Evans Diagram for Q5.*

$$E_{0,c} - E_{0,a} = -\beta_c \log_{10}\left(\frac{i_{corr}}{i_{0,c}}\right) + \beta_a \log_{10}\left(\frac{i_{corr}}{i_{0,a}}\right)$$

Substituting the given values in leaves;

$$
\begin{aligned}
0.126 &= 0.1 \log_{10}\left(\frac{i_{corr}}{1 \times 10^{-8}}\right) + 0.12 \log_{10}\left(\frac{i_{corr}}{2 \times 10^{-9}}\right) \\
0.126 &= \log_{10}\left(\frac{i_{corr}^{0.1}}{0.16}\right) + \log_{10}\left(\frac{i_{corr}^{0.12}}{0.09}\right) \\
0.126 &= \log_{10}\left(\frac{i_{corr}^{0.22}}{0.014}\right) .
\end{aligned}
$$

Therefore $i_{corr} = 1.55 \times 10^{-8}$ A cm^{-2}. Substitution also gives $E = -0.019$ V. Be careful with the number of significant figures used during calculations in these questions, as they can affect your answer a great deal.

The rate of oxidation is requested in mol cm^{-2} s^{-1}. The quantity we are looking for is (look at the Faraday equation):

$$
\begin{aligned}
-\frac{1}{A}\frac{dN}{dt} &= \frac{i}{nF} \\
&= \frac{1.55 \times 10^{-8}}{2 \times 9.648 \times 10^4} \\
&= 8 \times 10^{-14} \text{ mol cm}^{-2}\text{s}^{-1} .
\end{aligned}
$$

7

Question 6

Part (a)

Again consider Figure 1. At the anode;

$$\eta_a = E_{corr} - E_a^o = \beta_a \log_{10}\left(\frac{i_{corr}}{i_{0,a}}\right) .$$

At the cathode;

$$\eta_c = E_{corr} - E_c^o = \beta_c \log_{10}\left(\frac{i_{corr}}{i_{0,c}}\right) .$$

Follow exactly the same process as for Q(5) to get $E_{corr} = -0.35$ V and $i_{corr} = 0.052$ Am^{-2}.

The mass wastage rate will be

$$
\begin{aligned}
-\frac{1}{A}\frac{dM}{dt} &= -\frac{M_R^{Zn}}{A}\frac{dN}{dt} \\
&= \frac{iM_R^{Zn}}{nF} \\
&= \frac{0.052 * 65.4}{2 * 9.648 \times 10^7} \\
&= 1.76 \times 10^{-8} \text{ kg m}^2 \text{ s}^{-1} \\
&= 0.56 \text{ kg m}^2 \text{ year}^{-1} .
\end{aligned}
$$

Part (b)

Increasing the area of the cathode increase the exchange current, because corrosion rate/current density is proportional to current and area.

Charge conservation tells us that

$$
\begin{aligned}
A_a i_a &= A_c i_c \\
\therefore i_a &= 100 i_c .
\end{aligned}
$$

So simply substitute this into the Tafel equation for the cathodic reaction to get $E_{corr} = -0.2$ V and $i_{corr} = 0.93$ Am^{-2}.

The mass wastage rate will be

$$
\begin{aligned}
-\frac{1}{A}\frac{dM}{dt} &= -\frac{M_R^{Zn}}{A}\frac{dN}{dt} \\
&= \frac{iM_R^{Zn}}{nF} \\
&= \frac{0.93 * 65.4}{2 * 9.648 \times 10^7} \\
&= 3.14 \times 10^{-7} \text{ kg m}^2 \text{ s}^{-1} \\
&= 9.9 \text{ kg m}^2 \text{ year}^{-1} .
\end{aligned}
$$

Question 7

Part (a)

In aqueous systems with dissolved O_2, diffusion becomes the corrosion limiting step as opposed to the kinetics of the reaction. Therefore chemical composition of the metal has less influence (composition affects the slope of the anodic line).
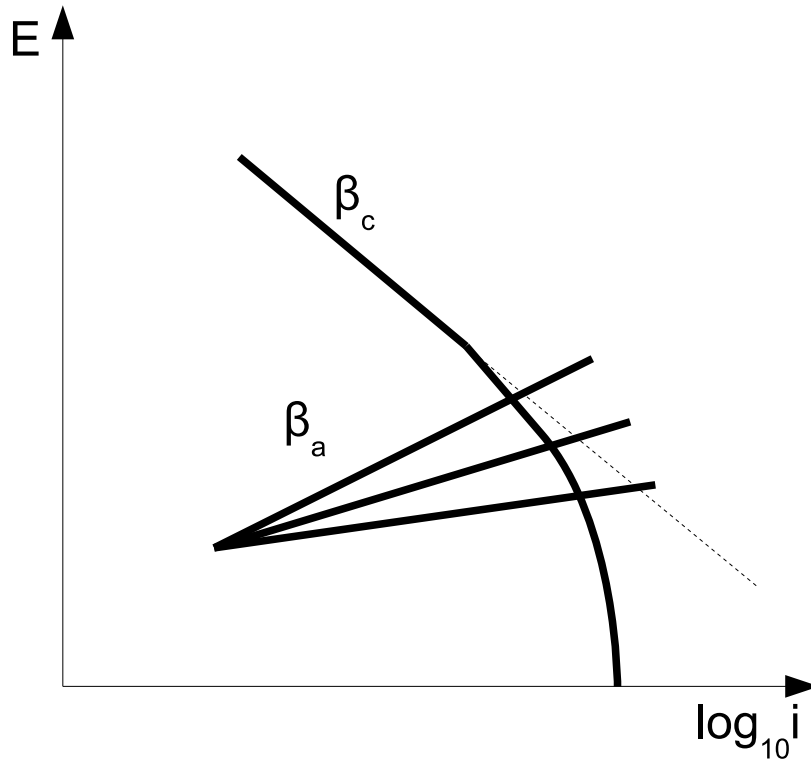

Figure 2: *Evans Diagram for Q7(a).*

Part (b)

At potential E_1 (unaerated acid), the steel corrodes. Adding oxygen to the acid raises the potential between the anode and cathode to E_2. This reduces corrosion as passivation then occurs.

Part (c)

Higher fluid velocities increase the corrosion rate as more oxygen reaches the pipe wall (concentration polarisation dominates). It is possible at higher velocities that a passive oxide layer forms, reducing the corrosion rate.
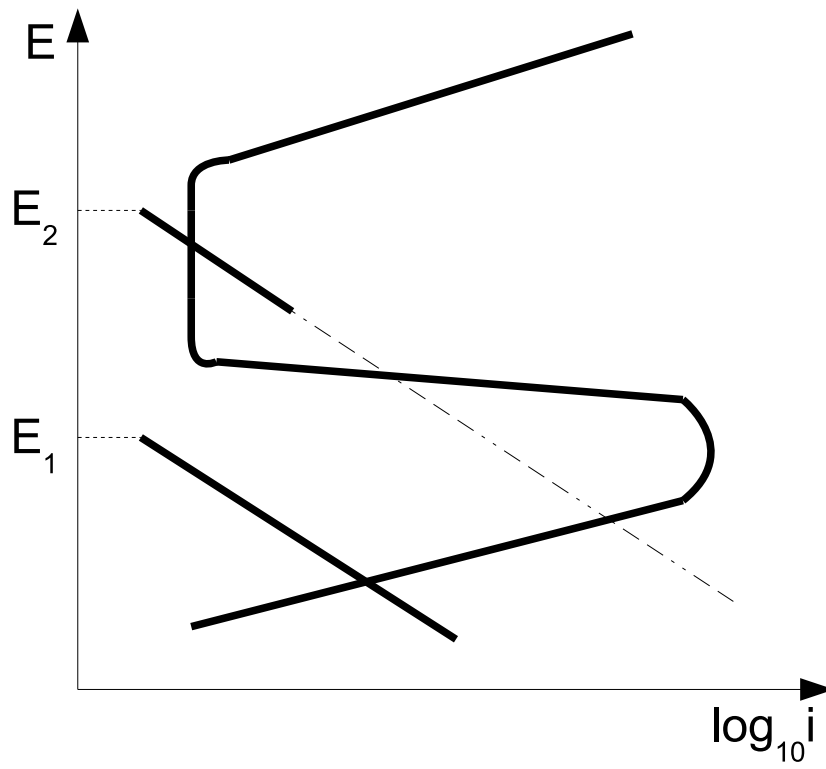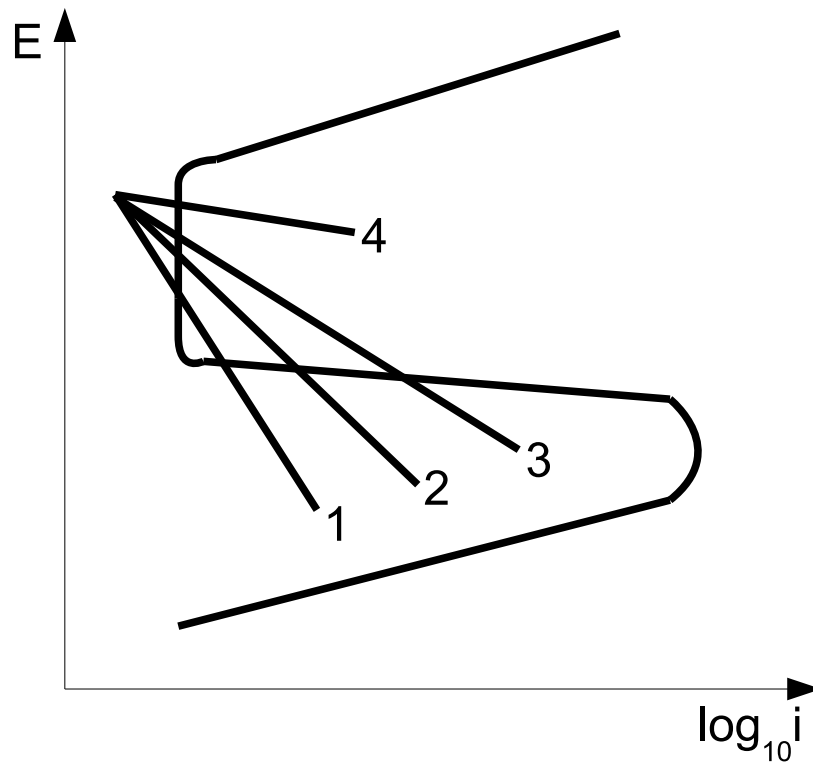
Figure 3: *Evans Diagram for Q7(b).*

Figure 4: *Evans Diagram for Q7(c).*