Corrosion Examples Paper 1 – Sample Solutions (2019 Youtube version, revision 2).

1. (a) $Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$ (A1)

   Which is a displacement reaction (electrochemical).

   (b) $\Delta G_{reaction} = -zFE_{reversible\ cell}$, with $z = 2$ considering one mole of Mg. (A2)

   $E^0_{reversible\ cell} = E^0_{cathode} - E^0_{anode} = 0.799\ V_{SHE} - (-2.363\ V_{SHE}) = +3.162\ V$ (A3)

   The superscript circle in the above equation means 'standard', i.e. at unit activities.

   $\Delta G^\circ_{reaction} = -610\ kJ\ mol^{-1}$ of magnesium (A4)

   (c) $E_{0,cathode} = E^0_{cathode} + \frac{RT}{zF} \ln\left(\frac{a(Ag^+)}{a(Ag)}\right) = +0.758\ V_{SHE}$ (A5)

   ... using $z = 1$ for the silver electrode, $(Ag|Ag^+)$.

   [Note that if you wanted to use $z = 2$ so that the silver equation has the same z-value as the magnesium equation, then the activity of Ag+ inside the log term would need to be squared and you would get the same numerical result. Clearly, the equilibrium potential for the silver anode reaction is a property of the Ag+ concentration, and not affected by rescaling.]

   Nernst Equation: unit activity for solid; activity = molar concentration for solutions.

   $E_{0,anode} = E^0_{anode} + \frac{RT}{zF} \ln\left(\frac{a(Mg^{2+})}{a(Mg)}\right) = -2.374\ V_{SHE}$ (A6)

   (using $z = 2$ for the magnesium)

   $E_{0,reversible\ cell} = E_{0,cathode} - E_{0,anode} = +3.132\ V$ (A7)

   (d) Note the liquid volume is 1 dm³ for each electrode.

   When x moles of magnesium have reacted,

   $a(Mg^{2+}) = 0.4 + x$ (A8)

   $a(Ag^+)\ = 0.2 - 2x$ (A9)

   Note that the cell voltage will decrease as the reaction proceeds towards equilibrium. (Le Chatelier principle: the change in concentrations will oppose the driving force of the reaction, which is the positive $E_{0\ reversible\ cell}$). So we are looking for when the cell voltage drops to 0.99×3.132 V.

   $E_{0\ reversible\ cell} = E^0_{reversible\ cell} + \frac{RT}{zF} \ln\left(\frac{(0.2-2x)^2(1)}{(0.4+x)(1)^2}\right) = (3.132\ V) * 0.99$ (A10)

   (with $z = 2$)

   One side of this is the Nernst Equation for a complete cell, combining the equations above with unit activities for the solid metals. The right hand side of the equation is 99% of the initial driving force, which will have decreased as spontaneous reaction proceeds. Solving:

$$\frac{(0.2-2x)^2}{0.4+x} = \exp(-4.753) = 0.0682 \tag{A11}$$

$$x = 0.0682 \tag{A12}$$

(the other solution to the quadratic equation, $x = 0.133$, is unphysical as it implies negative silver ion concentration.)

So 0.0682 moles of Mg dissolve, and 0.1364 moles of silver plate out.

Check: new Ag^+ activity is 0.0636 and new Mg^{2+} activity is 0.4682, and when put into the Nernst equation, these produce the required EMF.

Convert moles, N, to thickness, d, given area A, density ρ, and atomic weight (in g/mol).

$$d(\text{Mg}) = N_{\text{Mg}} \times (m_{\text{Mg}} = 24.3 \text{ g mol}^{-1}) \div (\rho_{\text{Mg}} * A) = -95 \text{ μm} \tag{A13}$$

(thickness dissolved)

$$d(\text{Ag}) = N_{\text{Ag}} \times (m_{\text{Ag}} = 107.87 \text{ g mol}^{-1}) \div (\rho_{\text{Ag}} * A) = 140 \text{ μm} \tag{A14}$$

(thickness gained)

2. (a) Using the Nernst equation for the equilibrium potential for $(Zn|Zn^{2+})$, or in other words for the half reaction $Zn \rightarrow Zn^{2+} + 2e^-$ at the non-unit activity, $a(Zn^{2+}) = 10^{-4}$

$$E_0(Zn|Zn^{2+}) = E°(Zn|Zn^{2+}) + \frac{RT}{zF}\ln\left(\frac{a(Zn^{2+})}{a(Zn)}\right) = -0.878 \text{ V}_{SHE} \tag{A 2.1}$$

With $z = 2$ and using $a(Zn) = 1$

This provides the horizontal equilibrium line between zinc metal stability and Zn^{2+} ion stability. If the environment exerts a more positive galvanic potential than this, a reaction will proceed with zinc dissolving at the anode, because there will be a positive $E_{reversible\ cell}$ for a process with $(Zn|Zn^{2+})$ at the anode and some environmental reagents at the cathode.

(b) For the electrochemical half reaction $Zn + 2H_2O = Zn(OH)_2 + 2H^+ + 2e^-$ we can assume unit activity of zinc, water, and zinc hydroxide. Hence the Nernst equation for the equilibrium potential of the electrode $(Zn|Zn(OH)_2)$ expands as follows

$$E_0 = E° + \frac{RT}{zF}\ln\left(\frac{[oxidised]}{[reduced]}\right) \tag{A 2.2}$$

$$E_0(Zn|Zn(OH)_2) = E°(Zn|Zn(OH)_2) + \frac{RT}{zF}\ln\left(\frac{a(Zn(OH)_2)a(H^+)^2}{a(Zn)a(H_2O)^2}\right) \quad \text{with } z = 2 \tag{A 2.3}$$

$$= -0.439 \text{ V}_{SHE} + 0.0257\ln(a(H^+)) \tag{A 2.4}$$

Recalling the definition of pH

$$pH = -\log_{10}(a(H^+)) = -\log_{10}(e)\ln(a(H^+)) \approx -(1/2.3)\ln(a(H^+)) \tag{A 2.5}$$

$$\ln(a(H^+)) \approx -2.3 \text{ pH} \tag{A 2.6}$$

Substituting from (A 2.6) into (A 2.4),

$$E_0 = -0.439 - 0.059 \text{ pH} \qquad \text{(with } E_0 \text{ having units of V}_{SHE}.) \tag{A 2.7}$$

As required.

(c) The equilibrium constant is given for the reaction $Zn(OH)_2 + 2H^+ \leftrightarrow Zn^{2+} + 2H_2O$

$$K = \frac{a(Zn^{2+})a(H_2O)^2}{a(Zn(OH)_2)a(H^+)^2} = 7.58 * 10^{10} \tag{A 2.8}$$

Given unit activity for liquid water and solid zinc hydroxide, and 10^{-4} for the zinc ions, it is easy to solve for the pH at equilibrium (which means, on the pH-potential diagram, the pH of the vertical line at the phase boundary).

$$a(H^+) = 3.63 \times 10^{-8} \tag{A 2.9}$$

$$pH = -\log_{10}(a(H^+)) = 7.43 \tag{A 2.10}$$

(d) Refer to page 24 of handout 1 (as of 2016). Uses of the equilibrium phase diagram: pH and local oxidation potential are both easily measured and provide a sufficiently good description of many environments to predict corrosion behaviour. Limitations: does not predict rates or say whether a solid oxide phase is impermeable enough to cause passivation; neglects chloride role unless more complicated diagrams are constructed; equilibrium lines are constructed for a single, arbitrary ion activity.

3. (a) (i) The position of a metal in the electrochemical series is determined by the standard electrode potential of its key oxidation reaction, like Cu|Cu²⁺, for which $E°(\text{Cu}|\text{Cu}^{2+}) = +0.337\ V_{SHE}$. This is a property of one single electrochemical half reaction.

(ii) The galvanic potential of a metal is the potential measured on the metal's surface under some conditions (e.g. in neutral groundwater). This is the potential which is reached spontaneously when several half-reactions take place – the mixture of reactions achieves charge balance (no net accumulation or loss of electrons) at the galvanic potential (at any other potential, the imbalanced charge flow would alter the surface potential towards the galvanic potential until it is reached). Since this galvanic potential is a weighted average of the equilibrium potentials of all the half-reactions happening on the metal surface (not just metal dissolution; also dissolved oxygen reaction etc.), and the metal dissolution reaction is generally not (in fact, almost never) at equilibrium with its dissolved ions in unit activity, therefore the galvanic potential is rarely equal to the metal's E^0. The hydrogen and oxygen reactions may have a strong influence on the galvanic potential of metals like platinum which are strong electrocatalysts for these reactions, and proportionally less influence on other metals (e.g. magnesium).

TLDR: Galvanic potential is an average potential on a metal's surface, as a result of several half reactions. Depending on the concentration of the species present, and how good a catalyst the metal is for each reaction, the galvanic potential may be far from the standard equilibrium potential of the metal itself.

(b) Corrosion generally happens at the anode of a cell. Electrochemical corrosion of a metal proceeds if the electromotive force of the cell is positive with a metal at the anode, i.e. if

$$E_{\text{reversible cell}} = E_{0,\text{cathode}} - E_{0,\text{anode}} > 0 \tag{A 3.1}$$

For the corrosion of gold in sulphuric acid, we might have $E_{\text{anode}} \sim E^0(\text{Au}|\text{Au}^{3+}) = +1.40 V_{SHE}$, and $E_{\text{cathode}} \sim E^0(\text{H}_2|\text{H}^+) = 0.0\ V_{SHE}$. So, at unit activity (or even with extremely dilute gold ions) $E_{\text{reversible cell}} \ll 0$ and corrosion would not proceed.

In the mixture of concentrated nitric and hydrochloric acid, we have: (i) a high value of the cathode potential, because nitrate ions are powerful oxidising agents, **and** (ii) a lower value of the possible anode reaction, because the formation of the gold chloride complex (which is more stable than lone gold ions) has a less positive equilibrium potential that the formation of Au³⁺. The exact reactions are not examinable, but they may be similar to the following:

$$\text{Au} + 4\text{Cl}^- \rightarrow \text{AuCl}_4^- + 3\text{e}^- \tag{A 3.2}$$

$$\text{with } E_{0,\text{anode}} \sim E^0(\text{Au}, 4\text{Cl}^-|\text{AuCl}_4^-) = +1.002\ V_{SHE}$$

$$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O} \tag{A 3.3}$$

$$\text{with } E_{0,\text{cathode}} \sim E^0(\text{NO}, 2\text{H}_2\text{O}|\text{NO}_3^-, \text{H}^+) = +0.96\ V_{SHE}$$

There would be a small negative driving force at unit ion activity, but given high nitrate concentration and/or a dissolved gold complex concentration below ~0.1 molar, dissolution would occur. Note there are several possibilities for the cathode reaction when nitrate ions are present, and this is just one of them.

Cf. use of aqua regia by Georgy de Hevesy to dissolve Max von Laue's and James Franck's Nobel prize medals in 1940 (in Denmark).

4.   (a)   Faraday equation. Consider the corrosion current density,

i = 1 mA / 0.002 m² = 0.5 A/m²   (A 4.1)

Current density $= i = \dfrac{zF}{A}\dfrac{dN}{dt} = \dfrac{zF}{A} * \dfrac{\rho A * dl/m}{dt}$ (A 4.2)

0.5 A/m² $= \dfrac{zF\rho}{m\,dt} * dl$ (A 4.3)

With z = 2 for magnesium, and z = 1 for silver. Density is ρ, area is A but it is not needed because it cancels out, and a depth dl corrodes in time dt, where i is constant and ∫dt = 1 year here. Atomic mass is m. Putting in the values for a time of 1 year, we see the speed of corrosion is 1.14 mm/year for magnesium (1.985 kg/m².yr), and 1.68 mm/year for silver, (17.628 kg/m².yr).

∫ dl (Mg) $= \dfrac{m}{zF\rho} \int i\, dt$ = 1.14 mm in 1 year   (A 4.4)

5. (a) The ions are at unit activity, so the equilibrium potentials are equal to the standard electrode potentials (with the Nernst equation correction being zero).

$$E_0(\text{Cd}|\text{Cd}^{2+}) = E°(\text{Cd}|\text{Cd}^{2+}) + \frac{RT}{zF}\ln(1) = -0.403 \text{ V}_{\text{SHE}} \tag{A 5.1}$$

$$E_0(\text{H}_2|\text{H}^+) = E°(\text{H}_2|\text{H}^+) + \frac{RT}{zF}\ln(1) = +0.00 \text{ V}_{\text{SHE}} \tag{A 5.2}$$

In spontaneous corrosion the rate of electron loss by lead oxidation must equal the rate of electron uptake by hydrogen evolution. (I.e. there is a charge balance with zero electron accumulation on the metal). The reaction is on a single metal surface, so the area for each process is the same (A).

$$|i(\text{Cd}|\text{Cd}^{2+})|A = |i(\text{H}_2|\text{H}^+)|A \tag{A 5.3}$$

The electrodes are on a single metal surface, so the electrode potential, E, is the same, so the polarisations are as follows.

$$\eta(\text{Cd}|\text{Cd}^{2+}) = E - E_0(\text{Cd}|\text{Cd}^{2+}) \tag{A 5.4}$$

$$\eta(\text{H}_2|\text{H}^+) = E - E_0(\text{H}_2|\text{H}^+) \tag{A 5.5}$$

The reactions are activation-limited, so the Tafel equation describes the rates.

$$i_0(\text{Cd}|\text{Cd}^{2+}) \times 10^{\frac{\left(E-E_0\left(\text{Cd}|\text{Cd}^{2+}\right)\right)}{\beta_a}} = |i_0(\text{H}_2|\text{H}^+)| \times 10^{\frac{\left(E-E_0(\text{H}_2|\text{H}^+)\right)}{\beta_c}} \tag{A 5.6}$$

This can be solved for the given values:

$$\frac{\left(E-E_0\left(\text{Cd}|\text{Cd}^{2+}\right)\right)}{\beta_a} - \frac{\left(E-E_0(\text{H}_2|\text{H}^+)\right)}{\beta_c} = \log_{10}\left(i_0(\text{H}_2|\text{H}^+)\right) - \log_{10}\left(i_0(\text{Cd}|\text{Cd}^{2+})\right) \tag{A 5.7}$$

$$\frac{E+0.403 \text{ V}_{\text{SHE}}}{0.12V} - \frac{(E-0.00 \text{ V}_{\text{SHE}})}{-0.20 \text{ V}} = 2.09 \tag{A 5.8}$$

Note the two minus signs (top and bottom) on the second term cancel. Multiply by both denominators.

$$E(0.12 \text{ V} + 0.20 \text{ V}) + 0.2V * 0.403 \text{ V}_{\text{SHE}} = 2.09 * 0.12 \text{ V} * 0.20 \text{ V} \tag{A 5.9}$$

$$E = -0.095 \text{ V}_{\text{SHE}} \tag{A 5.10}$$

So by putting this value of E into the Tafel equation, we can get the corrosion current density

$$i_{\text{corr}} = i(\text{Cd}|\text{Cd}^{2+}) = i_0(\text{Cd}|\text{Cd}^{2+})| \times 10^{\frac{\left(E-E_0\left(\text{Cd}|\text{Cd}^{2+}\right)\right)}{\beta_a}} = 7.36 \times 10^{-6} \text{ A cm}^{-2} \tag{A 5.11}$$

$$(1/A)\frac{dN}{dt} = \frac{i}{zF} = 3.81 \times 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1} \tag{A 5.12}$$

6. (a) Mathematically, this is similar to question 5, except that the equilibrium potentials at the non-unit ion activities <u>must</u> be calculated using a correction from the Nernst equation [forgetting to do the step in equations 5.1-5.2 or 6.1-6.2, and just using the standard electrode potentials directly, is the commonest error in exams!]. The equal exchange current densities in this question make the algebraic solution easier than in question 5. This calculation of a spontaneous electrochemical corrosion rate (with non-unit ion activities) is a very important example, and is worth learning.

Identifying $z=2$ for both electrodes, $T=298$K, and unit activities for the solid metal phases, the equilibrium potentials are as follows.

$$E_0(\text{Ni}|\text{Ni}^{2+}) = E°(\text{Ni}|\text{Ni}^{2+}) + \frac{RT}{zF}\ln(0.005) = -0.317\ \text{V}_{\text{SHE}} \tag{A 6.1}$$

$$E_0(\text{Cu}|\text{Cu}^{2+}) = E°(\text{Cu}|\text{Cu}^{2+}) + \frac{RT}{zF}\ln(0.250) = +0.319\ \text{V}_{\text{SHE}} \tag{A 6.2}$$

(a) When the metal areas are equal, equate the anode and cathode current densities given that the metals are in contact and share a mixed surface potential E.

$$i_0(\text{Ni}|\text{Ni}^{2+}) \times 10^{\frac{\left(E-E_0(\text{Ni}|\text{Ni}^{2+})\right)}{\beta_a}} = |i_0(\text{Cu}|\text{Cu}^{2+})| \times 10^{\frac{\left(E-E_0(\text{Cu}|\text{Cu}^{2+})\right)}{\beta_c}} \tag{A 6.3}$$

The exchange current densities are equal, so this simplifies as follows.

$$\frac{\left(E-E_0(\text{Ni}|\text{Ni}^{2+})\right)}{\beta_a} = \frac{\left(E-E_0(\text{Cu}|\text{Cu}^{2+})\right)}{\beta_c} \tag{A 6.4}$$

$$\frac{E+0.317\ \text{V}_{\text{SHE}}}{0.12V} = \frac{(E-0.319\ \text{V}_{\text{SHE}})}{-0.10\ \text{V}} \tag{A 6.5}$$

$$E = +0.030\ \text{V}_{\text{SHE}} \tag{A 6.6}$$

Therefore putting this surface potential back into the Tafel equation for the nickel reaction. (FIXING A MATH ERROR FROM VERSION 1)

$$i(\text{Ni}|\text{Ni}^{2+}) = 0.0156\ \text{A m}^{-2} \tag{A 6.7}$$

Given area A, molecular mass of nickel (58.69) so m = 58.69 g/mol, $z=2$:

$$\frac{1}{A}\frac{dN}{dt}m = \frac{i}{zF}m = 1.795 \times 10^{-8}\ \text{kg m}^{-2}\ \text{s}^{-1} = 0.15\ \text{kg m}^{-2}\ \text{year}^{-1} \tag{A 6.8}$$

(b) The second example has non-equal electrode areas. Allowing for area:

$$|i(\text{Ni}|\text{Ni}^{2+})| = 75\ |i(\text{Cu}|\text{Cu}^{2+})| \tag{A 6.9}$$

$$\frac{\left(E - E_0(\text{Ni}|\text{Ni}^{2+})\right)}{\beta_a} - \frac{\left(E - E_0(\text{Cu}|\text{Cu}^{2+})\right)}{\beta_c} = 1.88 + \log_{10}\left(i_0(\text{Cu}|\text{Cu}^{2+})\right) - \log_{10}\left(i_0(\text{Ni}|\text{Ni}^{2+})\right) \boxed{\tag{A 6.10}}$$

$$\frac{E+0.317\ \text{V}_{\text{SHE}}}{0.12V} - \frac{(E-0.319\ \text{V}_{\text{SHE}})}{-0.10\ V} = 1.88 \tag{A 6.11}$$

$$E = +0.132\ \text{V}_{\text{SHE}} \tag{A 6.12}$$

And (inventing a short cut) $0.15 \times 10^{\frac{+0.132-0.030}{0.12}} = 5.93$ \tag{A 6.13}

giving the new mass loss rate of Ni, as 1.06 kg m^{-2} year^{-1}.

Follow-up question for supervisions: how would the question be solved if the cathode reaction was not (Cu|Cu^{2+}) but actually the more common hydrogen reaction (H_2|H^+), and you were given the pH?

Answer: you always need to use the electrode equilibrium potentials at the ion activities that are actually present. In the written versions of question 5, the unit activities mean that the equilibrium potentials are equal to the standard electrode potentials. In question 6, it is necessary to use the Nernst equation to find the equilibrium potentials for the relevant ion activities. In general, this step will always be needed, and often the pH needs to be used to obtain the hydrogen ion activity which is relevant to the cathode reaction.

EJR