

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

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

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

$$\Delta G_{\text{reaction}}^0 = -610 \text{ kJ mol}^{-1} \text{ of magnesium}$$

(c)  $E_{0,\text{cathode}} = E_{\text{cathode}}^0 + \frac{RT}{zF} \ln \left( \frac{a(\text{Ag}^+)}{a(\text{Ag})} \right) = +0.758 \text{ V}_{\text{SHE}}$  (using  $z = 1$  for the silver).

[Note that if you wanted to use  $z = 2$  so that the silver equation has the same  $z$  as the magnesium equation, then the activity of  $\text{Ag}^+$  would need to be squared and you would get the same numerical result. However, the equilibrium potential for the silver anode is a property of this electrode alone, and does not need to be considered with  $z = 2$ .]

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

$$E_{0,\text{anode}} = E_{\text{anode}}^0 + \frac{RT}{zF} \ln \left( \frac{a(\text{Mg}^{2+})}{a(\text{Mg})} \right) = -2.374 \text{ V}_{\text{SHE}}$$
 (using  $z = 2$  for the magnesium)

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

(d) Note the liquid volume is  $1 \text{ dm}^3$  for each electrode.

When  $x$  moles of magnesium have reacted,  $a(\text{Mg}^{2+}) = 0.4 + x$ ,  $a(\text{Ag}^+) = 0.2 - 2x$

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

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

$x = 0.0682$  (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  $\text{Ag}^+$  concentration is 0.0636 and new  $\text{Mg}^{2+}$  concentration 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  $\rho$ , and atomic weight (in g/mol).

$$d(\text{Mg}) = N_{\text{Mg}} * (m_{\text{Mg}} = 24.3 \text{ g mol}^{-1}) \div (\rho_{\text{Mg}} * A) = 95 \text{ } \mu\text{m}$$
 (thickness dissolved)

$$d(\text{Ag}) = N_{\text{Ag}} * (m_{\text{Ag}} = 107.87 \text{ g mol}^{-1}) \div (\rho_{\text{Ag}} * A) = 140 \text{ } \mu\text{m}$$
 (thickness gained)

2. (a) Using the Nernst equation for the equilibrium potential of  $\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$  at non-unit activity

$$E_{0,\text{anode}} = E_{\text{anode}}^0 + \frac{RT}{zF} \ln \left( \frac{a(\text{Zn}^{2+})}{a(\text{Zn})} \right) = -0.878 \text{ V}_{\text{SHE}}$$

(b) For the reaction  $\text{Zn} + 2\text{H}_2\text{O} = \text{Zn}(\text{OH})_2 + 2\text{H}^+ + 2\text{e}^-$  with unit activity of zinc, water, and zinc hydroxide. The solids and water have unit activity.

$$E_{0,\text{anode}} = E_{\text{anode}}^0 + \frac{RT}{zF} \ln \left( \frac{a(\text{Zn}(\text{OH})_2)a(\text{H}^+)^2}{a(\text{Zn})a(\text{H}_2\text{O})^2} \right) = -0.439 \text{ V}_{\text{SHE}} + 0.0257 \ln(a(\text{H}^+))$$

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

(c) Equilibrium constant

$$K = \frac{a(\text{Zn}^{2+})a(\text{H}_2\text{O})^2}{a(\text{Zn}(\text{OH})_2)a(\text{H}^+)^2} = 7.58 * 10^{10}$$

Given unit activity for liquid water and solid zinc hydroxide, and  $10^{-6}$  for the zinc ions.

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

(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 standard electrode potential of a metal oxidation reaction,  $E^0$ , with unit ion activities, determines its position in the electrochemical series.

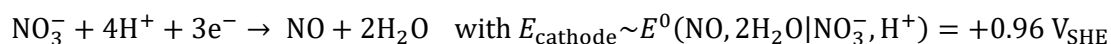
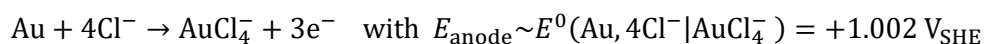
(ii) The galvanic potential of a metal is the potential measured on its surface under some conditions (e.g. in neutral groundwater). This is a weighted average of the equilibrium potentials of all the reactions happening on the metal surface (not just metal dissolution; also dissolved oxygen reaction etc.), and the metal dissolution reaction is generally not (in fact, almost never) at equilibrium with its dissolved ions in unit activity, so the galvanic potential is rarely equal to  $E^0$ . 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 little influence on other metals.

(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

$$E_{\text{reversible cell}} = E_{\text{cathode}} - E_{\text{anode}} > 0$$

For the corrosion of gold in sulphuric acid, we might have  $E_{\text{anode}} \sim E^0(\text{Au}|\text{Au}^{3+}) = +1.40\text{V}_{\text{SHE}}$ , and  $E_{\text{cathode}} \sim E^0(\text{H}_2|\text{H}^+) = 0.0\text{V}_{\text{SHE}}$ . Hence 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 than the formation of  $\text{Au}^{3+}$ . The exact reactions are not examinable, but they may be similar to the following:



There would be a small negative driving force at unit ion activity, but given high nitrate concentration and dissolved gold complex concentration below about 0.1 molar, dissolution would occur. Note there are various possibilities for the cathode reaction with nitrate, and this is just one.

4. (a) Faraday equation. Consider the corrosion current density,  $i = 1 \text{ mA} / 0.002 \text{ m}^2 = 0.5 \text{ A/m}^2$

$$\text{Current density} = i = \frac{zF}{A} \frac{dN}{dt} = \frac{zF}{A} * \frac{\rho A * dl/m}{dt}$$

$$0.5 \text{ A/m}^2 = \frac{zF\rho}{m dt} * dl$$

With  $z = 2$  for magnesium, and  $z = 1$  for silver. Density is  $\rho$ , area is  $A$  but it is not needed because it cancels out, and a depth  $dl$  corrodes in time  $dt$ , where  $\int dt = 1 \text{ year}$  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/m<sup>2</sup>.yr), and 1.68 mm/year for silver, (17.628 kg/m<sup>2</sup>.yr).

5. (a) This question is about the speed of spontaneous corrosion of a 2-electrode system at standard concentrations.

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

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

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

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 ( $A$ ).

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

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

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

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

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

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

This can be solved for the given values:

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

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

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

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

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

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

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

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

6. (a) Mathematically, this is similar to question 5, except that the equilibrium potentials at non-unit ion activities do need to be calculated using a correction from the Nernst equation. 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,  $T=298\text{K}$ , and unit activities for the solid metal phases, the equilibrium potentials are as follows.

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

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

(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  $E$ .

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

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

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

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

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

Therefore putting this surface potential back into the Tafel equation for the zinc reaction.

$$i(\text{Ni}|\text{Ni}^{2+}) = 0.059 \text{ A m}^{-2}$$

Given area  $A$ , molecular mass of nickel (58.69) cf. zinc  $m = 65.4 \text{ g/mol}$ ,  $z=2$ :

$$\frac{1}{A} \frac{dN}{dt} m = \frac{i}{zF} m = 1.795 \times 10^{-8} \text{ kg m}^{-2} \text{ s}^{-1} = 0.566 \text{ kg m}^{-2} \text{ year}^{-1}$$

(b) The second example has non-equal electrode areas:

$$|i(\text{Ni}|\text{Ni}^{2+})| = 100 |i(\text{Cu}|\text{Cu}^{2+})|$$

$$\frac{(E-E_0(\text{Ni}|\text{Ni}^{2+}))}{\beta_a} - \frac{(E-E_0(\text{Cu}|\text{Cu}^{2+}))}{\beta_c} = 2 + \log_{10}(i_0(\text{Cu}|\text{Cu}^{2+})) - \log_{10}(i_0(\text{Ni}|\text{Ni}^{2+}))$$

$$\frac{E+0.317 \text{ V}_{\text{SHE}}}{0.12 \text{ V}} - \frac{(E-0.319 \text{ V}_{\text{SHE}})}{-0.10 \text{ V}} = 2$$

$$E = +0.139 \text{ V}_{\text{SHE}}$$

$$\text{and } 0.566 \times 10^{\frac{+0.139-0.030}{0.1}} = 6.96 \text{ giving the new mass loss rate of Ni, in kg m}^{-2} \text{ year}^{-1}.$$

Followup question for supervisions: how would the question be solved if the cathode reaction was not  $(\text{Cu}|\text{Cu}^{2+})$  but actually the more common hydrogen reaction  $(\text{H}_2|\text{H}^+)$ , 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