Problem V.S ... Electrochemistry 5—transfer of mass and RDE 10 points

1. *In the Levich equation, physical quantities on the right-hand side appear with non-integer exponents. Verify that both sides of the equation have the same units. – 1 point*
2. *In a beaker intended for a rotating disc electrode, we dissolved* $0.63\,\mathrm{g}$ *of seventy percent perchloric acid in* $750\,\mathrm{ml}$ *of pure water and mixed everything thouroughly. Then, on a platinum working electrode with a circular shape and a diameter of* $5.0\,\mathrm{mm}$*, we varied the voltage for the hydrogen formation reaction until we reached the limiting current of* $0.29\,\mathrm{mA}$*. After measuring it, we started spinning the electrode at a frequency of* $3\,600\,\mathrm{rpm}$*, where the limiting current was* $11.5\,\mathrm{mA}$*. Determine the diffusion coefficient and the thickness of the diffusion layer before spinning. The kinematic viscosity of water is* $\nu = 0.9\,\mathrm{mm^2{\cdot}s^{-1}}$*. – 3 points*
3. *Find the highest power that a galvanic cell with the following parameters can provide and determine the corresponding load. For simplicity, consider the Tafel regime with a Tafel slope of* $100\,\mathrm{mV/dec}$ *and a parameter* $I_0 = 2\cdot 10^{-8}\,\mathrm{A}$*. The ohmic resistance is* $R_\Omega = 55\,\mathrm{m\Omega}$*. The open-circuit voltage is* $1.18\,\mathrm{V}$*. Neglect the diffusion regime. – 3 points*
4. *Derive the Koutecký-Levich equation as presented in the serial text. Start from the derivative of the Levich equation in the case where* $c(z=0) = c^s \neq 0$*. – 3 points*

Jarda wanted to include hydrodynamics, but even he didn't understand the inner workings.

Problem 1

We take the Levich equation[1]

$$I_\mathrm{lim} = 0.62 nFAD^{2/3}\nu^{-1/6}\omega^{1/2}c_\mathrm{b}$$

and gradually write out the SI units of all the quantities:

$$\begin{aligned}
[i_\mathrm{lim}] &= \mathrm{C{\cdot}s^{-1}}\,,\\
[0.62] &= 1\,,\\
[n] &= 1\,,\\
[F] &= \mathrm{C{\cdot}mol^{-1}}\,,\\
[A] &= \mathrm{m^2}\,,\\
[D] &= \mathrm{m^2{\cdot}s^{-1}}\,,\\
[\nu] &= \mathrm{m^2{\cdot}s^{-1}}\,,\\
[\omega] &= \mathrm{s^{-1}}\,,\\
[c_\mathrm{b}] &= \mathrm{mol{\cdot}m^{-3}}\,,
\end{aligned}$$

where, to recap, i_lim is the limiting current at the electrode, 0.62 is a dimensionless constant, n is the number of electrons in the reaction, F is Faraday constant, A is the electrode surface

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[1] `https://en.wikipedia.org/wiki/Levich_equation`

area, D is the diffusion coefficient, ν is the kinematic viscosity of the solution, ω is the angular rotation rate of the electrode, and finally, c_b is the bulk concentration of the reactants in the solution.

Let us now rewrite the equation in terms of units:

$$\begin{aligned}\mathrm{A} = \mathrm{C{\cdot}s^{-1}} &= 1 \cdot 1 \cdot \mathrm{C{\cdot}mol^{-1}m^2} \cdot \left(\mathrm{m^2{\cdot}s^{-1}}\right)^{2/3} \cdot \left(\mathrm{m^2{\cdot}s^{-1}}\right)^{-1/6} \cdot \left(\mathrm{s^{-1}}\right)^{1/2} \cdot \mathrm{mol{\cdot}m^{-3}} = \\ &= \mathrm{C} \cdot \mathrm{mol^{-1}} \cdot \mathrm{m^2} \cdot \mathrm{m^{4/3}} \cdot \mathrm{s^{-2/3}} \cdot \mathrm{m^{-2/6}} \cdot \mathrm{s^{1/6}} \cdot \mathrm{s^{-1/2}} \cdot \mathrm{mol} \cdot \mathrm{m^{-3}} = \\ &= \mathrm{C} \cdot \mathrm{mol^{1-1}} \cdot \mathrm{m^{2-3+4/3-2/6}} \cdot \mathrm{s^{1/6-1/2-2/3}} = \\ &= \mathrm{C} \cdot \mathrm{mol^0} \cdot \mathrm{m^0} \cdot \mathrm{s^{-1}} = \mathrm{C{\cdot}s^{-1}} = \mathrm{A}\,.\end{aligned}$$

Thus, the equality is confirmed.

Problem 2

In the case when the electrolyte is not moving, we can derive the expression for the limiting current[2] as

$$I_\mathrm{static} = nAF\frac{D}{\delta}c_\mathrm{b}\,.$$

There are currently two unknowns: the diffusion coefficient D and the diffusion layer thickness δ. The electrode area is $A = \pi d^2/4$, F is the Faraday constant, and n is the number of electrons per reaction. In our case, $n = 2$ because the hydrogen evolution reaction occurs at the platinum electrode as

$$2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}\,.$$

We also need to calculate the concentration of reactants (i.e., protons) in the solution volume. The solution was prepared using $m_\mathrm{acid} = 0.63\,\mathrm{g}$ of 70% perchloric acid, which means the actual mass of $\mathrm{HClO_4}$ is $m_{\mathrm{HClO_4}} = 0.7 m_\mathrm{acid} = 0.44\,\mathrm{g}$. Perchloric acid is considered a strong acid, so we can assume that all its molecules dissociate in water into $\mathrm{H^+}$ and $(\mathrm{ClO_4})^-$. The number of released $\mathrm{H^+}$ ions (in moles) is therefore the same as the original number of acid molecules, i.e.

$$n_{\mathrm{H+}} = n_{\mathrm{HClO_4}} = \frac{m_{\mathrm{HClO_4}}}{M_{\mathrm{HClO_4}}} = 0.004\,4\,\mathrm{mol}\,,$$

where $M_{\mathrm{HClO_4}} = 100.46\,\mathrm{g{\cdot}mol^{-1}}$ is the molar mass of the acid (not to be confused with the number of electrons per reaction $n = 2$). For simplicity, let us assume that the volume of the electrolyte did not change upon adding the acid since we added only a small amount relative to the initial volume (the density of pure acid is $1.67\,\mathrm{g{\cdot}cm^{-3}}$, which is close to the density of water, justifying our assumption of a negligible volume change). The molar concentration of $\mathrm{H^+}$ added by the acid is therefore

$$c_{\mathrm{H+}} = \frac{n_{\mathrm{H+}}}{V} = 0.0059\,\mathrm{M} = 0.0059\,\mathrm{mol{\cdot}l^{-1}}\,.$$

Let us note that even pure water always contains some dissolved amount of $\mathrm{H^+}$ and $(\mathrm{OH})^-$ ions. At room temperature, however, this is several orders of magnitude lower than the concentration created by dissolving the acid[3]. Thus, we can neglect the inherent proton concentration.

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[2] `https://link.springer.com/content/pdf/10.1007/BF02701653.pdf`

[3] All of these considerations are related to pH, which will be discussed in part 6 of the series.

We have successfully found the concentration of reactants, but we still need to calculate D and δ. Let us check whether the Levich equation for a rotating disk electrode measurement can help us solve the problem. For the limiting current, the equation gives

$$I_{\mathrm{RDE}} = 0.62 nFA\; D^{2/3} \nu^{-1/6} \omega^{1/2} c_{\mathrm{b}} \,,$$

where $\omega = 2\pi f$ is the angular velocity of rotation with frequency $f = 3\,600\,\mathrm{rpm} = 60\,\mathrm{Hz}$. The kinematic viscosity of water is given as $\nu = 0.9\,\mathrm{mm^2{\cdot}s^{-1}}$. In this equation, the only unknown is the diffusion coefficient

$$D = \left(\frac{I_{\mathrm{RDE}}}{0.62 nFA\; \nu^{-1/6}\omega^{1/2} c_{\mathrm{H^+}}}\right)^{3/2} \doteq 8.6 \cdot 10^{-9}\,\mathrm{m^2{\cdot}s^{-1}} \,.$$

We have thus obtained the value of the diffusion coefficient, which we now use to determine the diffusion length δ:

$$\delta = nAF \frac{D}{I_{\mathrm{static}}} c_{\mathrm{b}} = 0.66\,\mathrm{mm} \,.$$

This result is relatively high; typically, the diffusion length is on the order of micrometers or tens of µm. This shows that the simple model presented here does not fully capture all the processes occurring at the electrode surface.

Problem 3

In the Tafel regime, the dependence of current on overpotential follows this formula[4]

$$I = I_0 10^{-\frac{\eta}{b}} \,,$$

where $b = 100\,\mathrm{mV/dec}$ is the Tafel slope. Thanks to the properties of exponentials, we can write

$$I = I_0 \exp\!\left(-\ln 10 \frac{\eta}{b}\right) \,,$$

from which we express the overpotential as

$$\eta = -\frac{b}{\ln 10} \ln\!\left(\frac{I}{I_0}\right) \,.$$

In a galvanic cell, the voltage decreases with increasing current due to electrode kinetic losses as

$$E_{\mathrm{kin}} = E_{\mathrm{reac}} + \eta \,,$$

where $E_{\mathrm{reac}} = 1.18\,\mathrm{V}$ is the open-circuit voltage, i.e., at zero current, and η is negative as per the previous equations. These values simulate a fuel cell where oxygen and hydrogen react to produce water and electrical energy. Additional losses are caused by the ohmic resistance of the system R_Ω, which reduces the output voltage by $R_\Omega I$. If we neglect other effects, such as mass transport, the resulting voltage of the galvanic cell as a function of current is given by

$$E = E_{\mathrm{reac}} - \frac{b}{\ln 10} \ln\!\left(\frac{I}{I_0}\right) - R_\Omega I \,.$$

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[4] `https://en.wikipedia.org/wiki/Tafel_equation`

The power then becomes

$$P = EI = E_{\mathrm{reac}} I - \frac{bI}{\ln 10} \ln\left(\frac{I}{I_0}\right) - R_{\Omega} I^2 \,.$$

To find the maximum value for power, we differentiate the expression with respect to the current and set the derivative equal to zero

$$\frac{\mathrm{d}P}{\mathrm{d}I} = E_{\mathrm{reac}} - \frac{b}{\ln 10} \ln\left(\frac{I}{I_0}\right) - \frac{b}{\ln 10} - 2R_{\Omega} I = 0 \,,$$

which leads to the relation

$$\left(E_{\mathrm{reac}} - \frac{b}{\ln 10}\right) - 2R_{\Omega} I_{\mathrm{max}} = \frac{b}{\ln 10} \ln\left(\frac{I_{\mathrm{max}}}{I_0}\right) \,,$$

which we cannot calculate analytically. The numerical value is $I_{\mathrm{max}} \doteq 2.9\,\mathrm{A}$.

From the zero-derivative condition, we can substitute into the expression for power, which simplifies to

$$P_{\mathrm{max}} = I_{\mathrm{max}} \left(\frac{b}{\ln 10} + R_{\Omega} I_{\mathrm{max}}\right) \doteq 0.59\,\mathrm{W} \,.$$

The voltage at maximum power is then simply

$$E_{\mathrm{max}} = \frac{b}{\ln 10} + I_{\mathrm{max}} R_{\Omega} = 0.2\,\mathrm{V} \,.$$

The corresponding load must draw the current I_{max} and simultaneously have the voltage E_{max} across it, so it must have the resistance

$$R_{\mathrm{max}} = \frac{E_{\mathrm{max}}}{I_{\mathrm{max}}} = \frac{b}{I_{\mathrm{max}} \ln 10} + R_{\Omega} = 0.07\,\Omega \,.$$

Under these conditions, the power is maximized, but the voltage is relatively low and unsuitable for practical applications.

Problem 4

Deriving this equation is straightforward. The right-hand side of the integrated equation remains the same, while on the left side, the difference $c^b - c^s$ appears. Here, we can write the limiting current as

$$I = 0.62 nFAD^{2/3} \nu^{-1/6} \omega^{1/2} \left(c^b - c^s\right) = I_{\mathrm{lim}} \left(1 - \frac{c^s}{c^b}\right) \,.$$

The reaction kinetics are described via

$$I = nFAkc^s = I_{\mathrm{kin}} \frac{c^s}{c^b} \,.$$

Substituting into the previous equation

$$I = I_{\mathrm{lim}} \left(1 - \frac{I}{I_{\mathrm{kin}}}\right) \quad \Rightarrow \quad \frac{1}{I} = \frac{1}{I_{\mathrm{kin}}} + \frac{1}{I_{\mathrm{lim}}} \,,$$

which completes the derivation.

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