Problem Set 6

Due: Wednesday 11/12/25 at the start of class

Feel free to use any resource to work these problems, including books, websites, and your classmates. However, your problem set submission must be your own work.

Problem 1: Mass transport and kinetics

We have individually discussed diffusion and kinetics, but what do they look like together? One example is the Koutecky-Levich equation, which we discussed in class with regards to rotating disk electrodes. In this problem, you will derive a similar equation and show that the measured current can be related to the diffusion-limiting current and the kinetic current through simple diffusion boundary layer analysis.

a. Let's assume that a cathodic reaction $A + e^{-} \rightarrow B$. In the bulk, the concentration of A is c_A^0. What is the diffusion limited current, i_{MT}, if the diffusion constant is *D* and the boundary layer thickness is δ?

b. Let's assume that the reaction kinetics obey the Tafel equation:

$$i = Fkc_A e^{-\frac{\alpha FE}{RT}}$$

Normally, we treat the concentration term, c_A as a constant representing bulk concentration. However, a more accurate representation would be where c_A is actually the concentration at the electrode surface. In this situation, $c_A(x = 0) \neq 0$. Instead, $c_A(x = 0)$ takes the value that satisfies the boundary conditions for Fick's laws of diffusion. Write out the diffusion equation you must solve for the steady state concentration profile and the two boundary conditions needed.

c. Solve for the concentration profile.

d. Using your results from above and taking $i_k = Fkc_A^0 e^{-\frac{\alpha FE}{RT}}$ is the kinetic current in terms of the bulk concentration, derive an equation for i in terms of i_k and i_{MT}.

e. Instead of the current, we can rewrite your result from (d) in terms of resistance. Show that the total resistance can be expressed as the sum of a mass transport resistance and a kinetic resistance. That is, given Ohm's law where both the mass transport and kinetic processes can be represented as currents and resistances with the same applied voltage, E:

$$E = i_i R_i$$

Show that:

$$R = R_k + R_{MT}$$