

Problem Set 2

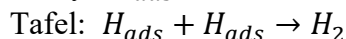
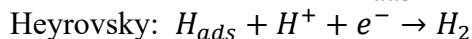
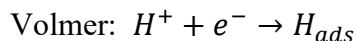
Due: Wednesday 10/15/25 at the start of class

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. Tafel Derivation

- a. You have a mechanism that involves $n+q$ electron transfers to convert from reactant to product. For simplicity, let us assume that your reactant is an aqueous species $A^{(n+q)+}$ and your product is A ($A^{(n+q)+}$ is reduced during this process). This process will take place through n single electron transfers, with the final rate-determining step (RDS) being a transfer of q electrons (in practice, q will be either 1 or 0, representing an electron transfer RDS or a thermochemical RDS). **Write out the reaction equations as reductions for first electron transfer, the i^{th} electron transfer ($1 \leq i \leq n$), the n^{th} electron transfer, and the RDS with q electrons transferred.**
- b. Following our derivation of the Butler-Volmer equation in class (with the same assumptions), **write an expression for the current density given the RDS from part (a).** In this expression, leave the exchange current density (i_0) explicit in terms of the concentration of A^{q+} . Assume that the reductive direction of the RDS has a rate constant of $k_R = k_{0,R} e^{-\frac{E_{a,R}}{RT}}$ and the oxidative direction of the RDS has a rate constant of $k_O = k_{0,Ox} e^{-\frac{E_{a,Ox}}{RT}}$ at zero applied potential. Your answer should be in terms of F , $[A^{q+}]$, $k_{0,R}$, $E_{a,R}$, q , R , T , ϕ_{eq} , β , and ϕ_{app} . Hint: define your current density as $i = i_O - i_R$ and remember that by definition, a reductive current is negative. Ignore any surface adsorbate or surface coverage effects. **What is the current density in the limit of large reductive overpotentials?** Use the expression for current density in the large overpotential limit for the rest of this problem.
- c. Assuming all non-rate determining steps are at equilibrium and ignoring surface adsorbate or surface coverage effects, write out an expression for the equilibrium constant in terms of chemical species, the applied potential, and additional constants (F , R , T) for the i^{th} chemical reaction. Use K_i to represent the equilibrium constant. Note that $1 \leq i \leq n$.
- d. Combine the equilibrium expressions from part (c) with the RDS from part (b) to derive an expression that does not contain any concentrations except $[A^{(n+q)+}]$. Hint: begin by writing $[A^{q+}]$ in terms of $[A^{(n+q)+}]$.
- e. Derive an expression for the Tafel slope, $\left| \frac{\partial \phi_{app}}{\partial \log_{10}|i|} \right|$, in terms of the number of electron transfers before the RDS (n) and the number of electrons transferred during the RDS (q). You may assume that $\beta = \frac{1}{2}$.
- f. What is the maximum possible Tafel slope given the above derivation? What would such a Tafel slope tell you about the mechanism?

- g. For the hydrogen evolution reaction in acidic media, there are three relevant reactions:



One can imagine hydrogen evolution occurring via a combination of the above steps. For each of the following reaction pathways and rate-determining steps, what is the Tafel slope?

Pathway 1: Volmer-Heyrovsky (Volmer limiting)

Pathway 2: Volmer-Heyrovsky (Heyrovsky limiting)

Pathway 3: Volmer-Tafel (Volmer limiting)

Pathway 4: Volmer-Tafel (Tafel limiting)

Problem 2. Tafel Practicalities

Instead of using the Butler-Volmer equation, it is also possible to use simplified forms in certain potential regimes. At room temperature, for $\alpha_a = 0.5$ and $\alpha_c = 0.5$, as well as $\alpha_a = 0.1$ and $\alpha_c = 0.9$, calculate the error in using the following approximations for the Butler-Volmer equation, as both an explicit equation and a numerical value at the given overpotentials.

- The linear i vs. η characteristic of small overpotentials, for overpotentials of 10, 20, and 50 mV.
- the Tafel (totally irreversible) relationship which is used for large overpotentials, for overpotentials of 50, 100, and 200 mV.

Also, describe qualitatively how the value of the apparent transfer coefficient influences the error in the approximations, and how one should select values of the overpotential for collecting data on Tafel slopes in an experimental system.