

Problem 3.1 A. (5 points) Reducing the potential raises the energy of electrons in the electrode. To reduce their energy, electrons leave the electrode, so the reaction proceeds faster in the forward direction.

B. (5 points) Increasing the potential lowers the energy of electrons in the electrode, so the reaction is biased in the forward direction.

C. (5 points) We want to increase both reaction rates in the forward direction. At the anode ($H_2 \rightleftharpoons H^+ + 2e^-$) you want to draw electrons to the electrode, so increase the potential. At the cathode ($2H^+ + 2e^- + \frac{1}{2}O_2 \rightleftharpoons H_2O$) you want electrons to leave the electrode, so reduce this potential. The overall voltage output falls from both effects.

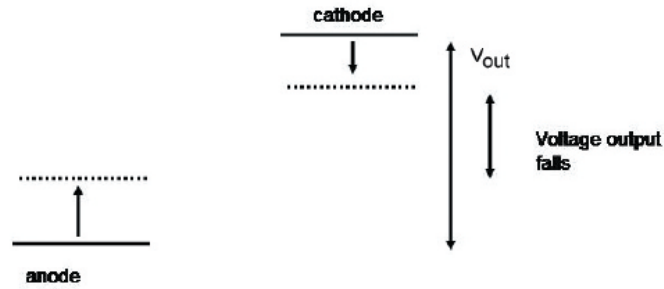


Figure 2: Schematic of activation voltage losses for problem 3.1

Problem 3.3 (10 points) Alpha is the charge transfer coefficient, it describes whether the “center of the reaction”, or peak of the reaction activation barrier, falls nearer to one side of the reaction or the other. In this figure, note that alpha does not change the final electrochemical energy

change, only the height of the peak in electrochemical energy.

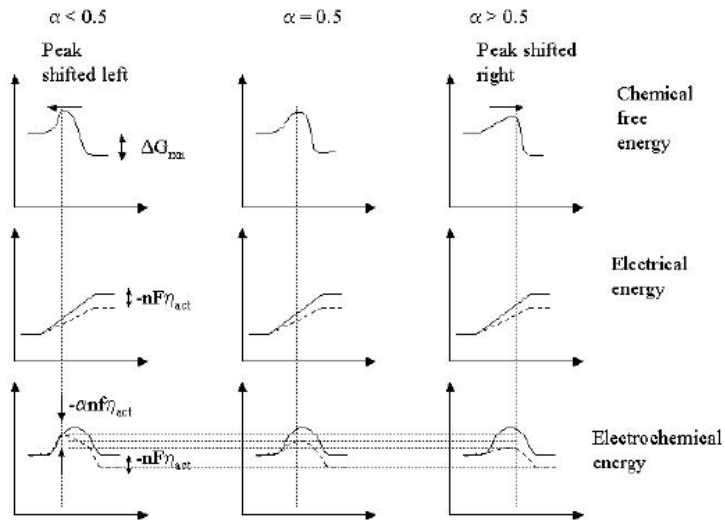


Figure 4: Effect of α on the electrochemical energy pathway for problem 3.3.

Problem 3.9 (10 points) At equilibrium, $j = 0$. The Butler-Volmer equation is

$$j = j_o \left(\frac{C_R^*}{C_R^{o*}} \exp\left[\frac{\alpha n F \eta}{RT}\right] - \frac{C_P^*}{C_P^{o*}} \exp\left[-\frac{(1-\alpha)n F \eta}{RT}\right] \right) = 0 \quad (30)$$

After canceling the j_o term and rearranging, the equation reads

$$\frac{C_R^*/C_R^{o*}}{C_P^*/C_P^{o*}} = \frac{\exp\left[-\frac{(1-\alpha)n F \eta}{RT}\right]}{\exp\left[\frac{\alpha n F \eta}{RT}\right]} = \exp\left[\frac{(\alpha-1)n F \eta}{RT} - \frac{\alpha n F \eta}{RT}\right] = \exp\left[-\frac{n F \eta}{RT}\right] \quad (31)$$

Solving for η ,

$$-\eta = \frac{RT}{nF} \ln\left[\frac{C_R^*/C_R^{o*}}{C_P^*/C_P^{o*}}\right] \quad (32)$$

Moving the negative sign to the right and inverting the argument of the logarithm,

$$\eta = \frac{RT}{nF} \ln\left[\frac{C_P^*/C_P^{o*}}{C_R^*/C_R^{o*}}\right] \quad (33)$$

The overvoltage, η , is the amount by which the actual voltage is less than the standard state voltage

$$E_T - E = \eta \quad (34)$$

For an ideal gas, the concentration is the activity, so we have

$$E = E_T - \frac{RT}{nF} \ln\left[\frac{a_P}{a_R}\right] \quad (35)$$

which is almost the Nernst equation

$$E = E_T - \frac{RT}{nF} \ln\left[\frac{\prod a_P^{\nu_P}}{\prod a_R^{\nu_R}}\right] \quad (36)$$

The difference lies in the \ln term, which does not account for a multiplicity of products and reactants. This arises from the fact that the Butler-Volmer

equation only accounts for the concentration of the *limiting* products and reactants. If you inspect the derivation of the BV equation in the text, you'll find that it is only for one electrode reaction. Since one fuel cell reaction is usually orders of magnitude slower than the other reactions, we typically neglect the sluggishness of "fast" reactions and only employ the BV equation to find the loss at one electrode. A more rigorous form of the BV equation would include all of the products and reactants (and you'd have to write one equation for the anode and one for the cathode) and would reduce exactly to the Nernst equation.