

Supplemental Information: Nernst Equation calculations

The Nernst equation is used to calculate half reduction potentials and is presented in a general form below.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{\prod a_p}{\prod a_r}$$

where

E° = standard potential

R = universal gas constant

T = Temperature

n = electrons transferred

F = Faraday's constant

a_p = activity of products

a_r = activity of reactants

Because the potential changes as a function of reactant and product chemical activities, the potentials tabulated in literature should be adjusted to represent experimental conditions.

For example, we set out initial conditions in the fumarate reducing cathode to be 4 mM fumarate at pH of 7. We also take succinate concentration to be 1 μ M to give a non-infinite logarithm calculation. A review of the half reactions in Table 2 shows that reaction potential will depend on fumarate, succinate, and proton activities. We assume that the solution is ideal and dilute, so that concentrations are equivalent to activities. Thus, the theoretical potential for the initial conditions in the cathode can be calculated as follows.

$$\begin{aligned} E &= E^{\circ} - \frac{RT}{nF} \ln \frac{\prod a_p}{\prod a_r} \\ &= (+0.031 \text{ V}) - \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2)(96485.3 \text{ C mol}^{-1})} \ln \frac{(10^{-6} \text{ M})}{(4 \times 10^{-3} \text{ M})} \\ &= +0.137 \text{ V} \end{aligned}$$

Potentials for other relevant half reactions are calculated in a similar way and presented in Table 2.