Faradaic Reactions in Dilute Solutions

As we begin to study electrochemical energy systems out of equilibrium, we are first concerned with the kinetics of Faradaic (charge-transfer) reactions.

1 Stochastic Theory of Reaction Rates

Here we model a particle diffusing through a potential energy landscape on the molecular scale. We need $U_{TS} - U_{1,2} \gg k_BT$ to ensure that transitions are “rare events” and that particles are most of the time in well-defined “states” corresponding to local energy minima. See 2009 notes for analysis of the first passage time $\tau$ for a particle to “escape” from state 1 to state 2.

Here we just quote the result:

$$< \tau_{1\rightarrow2} > = \text{mean first passage time}$$

$$= \tau_0 e^{-\frac{U_{TS}-U_1}{k_BT}}$$

Or the mean escape rate per particle:

\[ r_{1\rightarrow 2} = r_0 e^{-\frac{U_{T_S} - U_{1}}{k_B T}} \]

Where \( R_0 \propto \frac{D_0}{L_{\text{min}} L_{\text{max}}} \) with:
- \( D_0 \) = a microscopic diffusivity (measuring thermal noise).
- \( L_{\text{min}} \) = width of the energy minimum.
- \( L_{\text{max}} \) = width of the saddle along transition path.

The net reaction rate for reversible reaction \( 1 \leftrightarrow 2 \) is:

\[ r = r_{1\rightarrow 2} - r_{2\rightarrow 1} \]

Where:

\[ \frac{r_{1\rightarrow 2}}{r_{2\rightarrow 1}} = e^{-\frac{U_{1} - U_{2}}{k_B T}} \]

This is a form of the de Donder Relation. The second equation does not depend on the transition state, only the local equilibrium states 1 and 2.

2 Reactions in Dilute Solutions

Consider the reaction \( \sum s_i R_i \rightarrow \sum s_j P_j \), where reactants are in state 1 and products are in state 2. For every reaction complex going from state 1 to state 2 there is a transition state with energy \( U_{TS} \). The state energies are:

\[ U_1 = \sum s_{i,1} U_{i,1} \]
\[ U_2 = \sum s_{j,2} U_{j,2} \]

For the forward reaction, the number of such transitions (per volume) is proportional to \( \prod c_{i,1}^{s_{i,1}} \) assuming a dilute solution. So we can calculate the net reaction rate (number/time per reaction site):

\[ R = R_{1\rightarrow 2} - R_{2\rightarrow 1} \]
\[ R = R_0 \left[ \prod_i c_{i,1}^{s_{i,1}} e^{-\frac{U_{T_S} - U_{1}}{k_T}} - \prod_i c_{j,2}^{s_{j,2}} e^{-\frac{U_{T_S} - U_{2}}{k_T}} \right] \]
Note we can shift energy of state 2 to pull out a constant “exchange” rate $R_0$. Also we have:

$$\frac{R_{1-2}}{R_{2-1}} = \prod_i \frac{c_{i,1}^{s_{i,1}}}{c_{i,2}^{s_{i,2}}} e^{\frac{U_{1-2}}{kT}}$$

another de Donder Relation

In equilibrium:

$$\Delta U^{eq} = (U_1 - U_2)^{eq} = k_B T \ln \left( \frac{\prod_j c_{j,2}^{s_{j,2}}}{\prod_i c_{i,1}^{s_{i,1}}} \right)$$

This looks like the Nernst Equation!

3 Faradaic Reactions in Dilute Solutions

3.1 Standard form of initial and final states

Consider the general half-cell Faradaic reaction, which we write in the standard form

$$\sum s_i M_i^{z_i} \rightarrow ne^-$$

where the reaction produces $n$ electrons (oxidation) in the forward direction.

We break this into reactants ($s_i > 0$) comprising the “reduced state” and products ($s_i < 0$) comprising the “oxidized state” of the anodic reaction.

$$\sum_j s_{R,j} R_j^{z_{R,j}} \rightarrow \sum_i s_{O,i} O_i^{z_{O,i}} + ne^-$$

By charge conservation, we have

$$\sum s_{O,i} Z_{O,i} - n = \sum s_{R,j} z_{R,j}$$

where $q_0 = \sum s_{O,i} Z_{O,i}$ and $q_R = \sum s_{R,j} z_{R,j}$.

This allows us to express the initial and final states of the reaction (“states 1 and 2” above) as

$$U_1 = U_R = \sum s_{R,j} \left[ U_{R,j}^0 + z_{R,j} e \Phi \right]$$

total energy of reduced state

$$= U_R^0 + q_0 \Phi$$

$$U_2 + ne \Phi_e = U_O = \sum s_{O,i} \left[ U_{O,i}^0 + z_{O,i} e \Phi \right]$$

total energy of oxidized state

$$= U_O^0 + q_O \Phi$$

separate electrostatic energy
3.2 Butler-Volmer Model for the transition state

The Butler-Volmer hypothesis asserts that the electrostatic energy of the transition state is a weighted average of electrostatic energies of the oxidized and reduced states:

\[ U_{TS} = U_{TS}^0 + \alpha q_R \Phi + (1 - \alpha) [q_0 \Phi - n e \Phi_e] \]

where \( U_{TS}^0 \) is electrode potential

\[ \alpha = \text{transfer coefficient} = \text{weight of reduced state electrostatic energy at transition state} \]

It is typically to assume (or infer) symmetric electron transfer, \( \alpha = (1 - \alpha) = \frac{1}{2} \).

Although the extreme values, \( \alpha = 1 \) or \( \alpha = 0 \), for asymmetric electron transfer are also possible.

Then if we focus on the electrostatic potential, we obtain

\[ R = k_a \prod_i c_{i,R} e^{-[\alpha q_R \Phi + (1-\alpha) (q_0 \Phi - n e \Phi_e) - q_R \Phi] / (kT)} - k_c \prod_i c_{i,O} e^{-[\alpha q_R \Phi + (1-\alpha) (q_0 \Phi - n e \Phi_e) - q_O \Phi] / (kT)} \]

where we absorb \( U_i^O \) into anodic (oxidation) and cathodic (reduction) reaction rate constants, \( k_a \) and \( k_c \) respectively.

Using charge conservation \( q_O - q_R = n \), we finally express the Faradaic reaction rate in a dilute solution in the following general form
\[ R = k_a \prod_i c_{i,R}^{s_{i,R}} e^{(1-\alpha)\Delta \Phi/(k_B T)} - k_c \prod_i c_{i,O}^{s_{i,O}} e^{-\alpha n\Delta \Phi/(k_B T)} \]

\[ \Delta \Phi = \Phi_e - \Phi = \text{electrode potential} - \text{solution potential} \]

For further reading, see O’Hare et al., *Fuel Cell Fundamentals* (Ch 3).