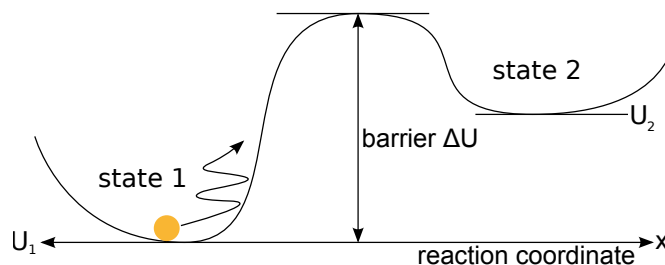


# Faradaic Reactions in Dilute Solutions

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  $U_{TS} - U_{1,2} \gg k_B T$  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:

$$\begin{aligned} \langle \tau_{1 \rightarrow 2} \rangle &= \text{mean first passage time} \\ &= \tau_0 e^{\frac{U_{TS} - U_1}{k_B T}} \end{aligned}$$

Or the mean escape rate per particle:

$$r_{1 \rightarrow 2} = r_0 e^{-\frac{U_{TS}}{k_B T}}$$

Where  $R_0 \propto \frac{D_0}{L_{\min} L_{\max}}$  with:  
 $D_0$  = a microscopic diffusivity (measuring thermal noise).  
 $L_{\min}$  = width of the energy minimum.  
 $L_{\max}$  = width of the saddle along transition path.  
The net reaction rate for reversible reaction  $1 \leftrightarrow 2$  is:

$$r = r_{1 \leftrightarrow 2} - r_{2 \leftrightarrow 1}$$

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):

$$R = R_{1 \rightarrow 2} - R_{2 \rightarrow 1}$$

$$R = R_0 \left[ \prod_i c_{i,1}^{s_{i,1}} e^{-\frac{U_{TS} - U_1}{k_B T}} - \prod_i c_{j,2}^{s_{j,2}} e^{-\frac{U_{TS} - U_2}{k_B T}} \right]$$

Note we can shift energy of state 2 to pull out a constant “exchange” rate  $R_0$ . Also we have:

$$\frac{R_{1 \rightarrow 2}}{R_{2 \rightarrow 1}} = \frac{\prod_i c_{i,1}^{s_{i,1}}}{\prod_j c_{j,2}^{s_{j,2}}} e^{\frac{U_1 - U_2}{kT}} \text{ another de Donder Relation}$$

In equilibrium:

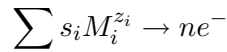
$$\Delta U^{\text{eq.}} = (U_1 - U_2)^{\text{eq.}} = k_B T \ln \left( \frac{\prod_j c_{j,2}^{s_{j,2}}}{\prod_i c_{i,1}^{s_{i,1}}} \right)$$

This looks like the Nernst Equation!

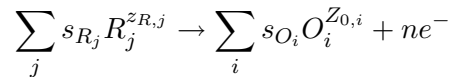
### 3 Faradaic Reactions in Dilute Solutions

#### 3.1 Standard form of initial and final states

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



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.



By charge conservation, we have

$$\sum s_{O_i} z_{O_i} - n = \sum s_{R_j} z_{R_j}$$

where  $q_o = \sum s_{O_i} z_{O_i}$  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

$$\begin{aligned} U_1 = U_R &= \sum s_{R,j} [U_{R,j}^0 + z_{R,j} e \Phi] \text{ total energy of reduced state} \\ &= U_R^0 + q_0 \Phi \\ U_2 + n e \Phi_e &= U_O = \sum s_{O,i} [U_{O,i}^0 + z_{O,i} e \Phi] \text{ total energy of oxidized state} \\ &= U_O^0 + q_0 \Phi \text{ separate electrostatic energy} \end{aligned}$$

### 3.2 Butler-Volmer Model for the transition state

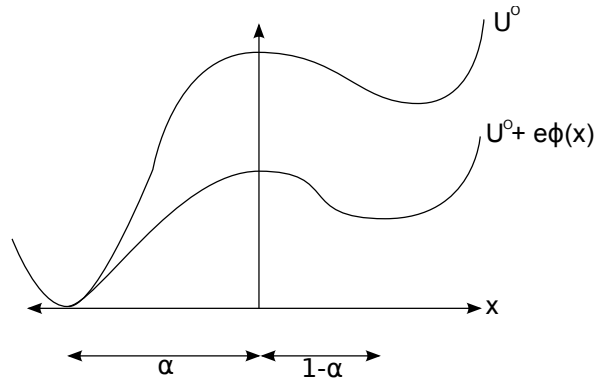
The Butler-Volmer hypothesis asserts that *the electrostatic energy of the transition state is a weighted average of electrostatic energies of the oxidized and reduced states:*

$$U_{TS} = U_{TS}^0 + \alpha q_R \Phi + (1 - \alpha) [q_O \Phi - ne\Phi_e] \text{ where } \Phi_0 \text{ is electrode potential}$$

where

- $\alpha =$  transfer coefficient
- $=$  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

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

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

$$R = k_a \prod_i c_{i,R}^{s_{i,R}} e^{(1-\alpha)ne\Delta\Phi/(k_B T)} - k_c \prod_i c_{i,O}^{s_{i,O}} e^{-\alpha ne\Delta\Phi/(k_B T)}$$

$\Delta\Phi = \Phi_e - \Phi$  = electrode potential – solution potential

$R = \frac{\text{number of reactions}}{\text{time}}$  per reaction site

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

Source: [http://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2011/lecture-notes/MIT10\\_626S11\\_lec12.pdf](http://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2011/lecture-notes/MIT10_626S11_lec12.pdf)