

III. Reaction Kinetics

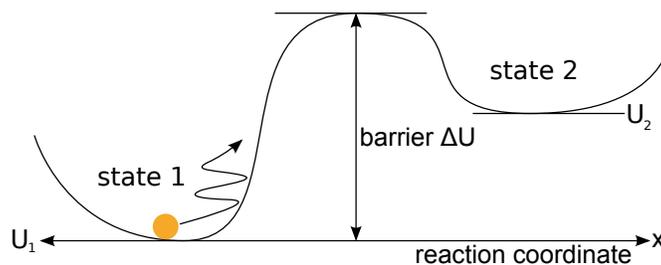
Lecture 12: Reaction Kinetics in Dilute Solutions

Notes by MIT Student, re-written by MZB 2014

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As we begin to study electrochemical energy systems out of equilibrium, we are first concerned with reaction kinetics. We begin by considering general transition state theory and then applying it to Faradaic charge-transfer reactions at electrodes.

1 Stochastic Theory of Reaction Rates



The classical Transition State Theory of reaction kinetics is based on stochastic processes biased by intermolecular forces. The reaction complex diffuses by thermal excitations through an energy landscape $U(\vec{x})$ (as a function of various reaction coordinates) to occasionally cross over an energy barrier U_{TS} at the “transition state” separating two energy minima, representing the initial and final states, U_1 and U_2 . The barrier energy must be larger than the thermal voltage,

$$\Delta U_{1,2} = U_{TS} - U_{1,2} \gg k_B T \quad (1)$$

in order to ensure that transitions are “rare events” compared to thermal fluctuations, so that the reactants and products spend most of the time in

well-defined, long-lived “states” corresponding to energy wells around the minima.

The model problem of “escape” over an energy barrier from one well to another can be analyzed in great detail in the *dilute solution limit*, where the reactants follow independent stochastic processes (random walks) and do not alter the energy landscape.¹ The fundamental result is that the mean reaction rate r per molecule (events/time), equal to the inverse of the mean first passage time τ from the minimum to the transition state, is given by

$$r = \frac{1}{\tau} \sim \nu e^{-\Delta U/k_B T} \quad (2)$$

in the asymptotic limit $\Delta U \gg k_B T$. This is the familiar Arrhenius temperature dependence of any thermally activated process. It can also be derived by arguing that the rate is proportional to the probability of finding the system at the transition state in a Boltzmann distribution, $p \propto e^{-\Delta U/k_B T}$. This assumes local thermodynamic equilibrium, which is justified for a large barrier, $\Delta U \gg k_B T$, since the system spends most of its time trapped in the potential well, relative to the time scale of thermal vibrations.

The prefactor ν depends on the curvatures of the energy landscape at the minimum, $K_{min} = U''_{min} > 0$ and transition state (saddle point), $K_{max} = -U''_{TS} > 0$. For example, for escape from a symmetric well, the prefactor is

$$\nu = \frac{2D_0 \sqrt{K_{min} K_{TS}}}{\pi k_B T} \left(1 + a \sqrt{\frac{k_B T}{\Delta U}} + b \frac{k_B T}{\Delta U} + \dots \right) \quad (3)$$

where D_0 is a diffusivity characterizing thermal noise at the molecular scale. The constants a and b depend on higher derivatives of the energy landscape.² We can also define length scales L_{min} and L_{TS} characterizing the width of the potential well and the transition-state saddle region, respectively, via $K_{min} = (\pi/2)\Delta U/L_{min}^2$ and $K_{TS} = -(\pi/2)\Delta U/L_{TS}^2$ and express the prefactor as

$$\nu = \frac{D_0}{\sqrt{L_{min} L_{TS}}} \left[\frac{\Delta U}{k_B T} + a \left(\frac{\Delta U}{k_B T} \right)^{3/2} + b \left(\frac{\Delta U}{k_B T} \right)^2 + \dots \right] \quad (4)$$

The rate is enhanced for narrow potential wells (small L_{min}) due to the larger spring constant and higher vibrational frequency, leading to more

¹ See lectures 10-12 from 2009.

² a and b are derived in a homework solution online from 2009 for the Kramers escape problem.

frequent escape attempts for the same ΔU . The rate is also enhanced by a narrow saddle around the transition state, since the escape process will waste fewer attempted escapes by exploring the saddle region and falling back into the original well. These are typically small corrections, however, as long as $\Delta U \gg k_B T$, and the primary implication of transition state theory is the dominant Arrhenius temperature dependence.

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 (or backward) reaction, the number of such transitions (per volume) is proportional to $c_1 = \prod c_{i,1}^{s_{i,1}}$ (or $c_2 = \prod c_{i,2}^{s_{i,2}}$) assuming a dilute solution. So we can calculate the net reaction rate (number/time per reaction site) as:

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

$$R = \nu_1 c_1 e^{-\frac{U_{TS} - U_1}{kT}} - \nu_2 c_2 e^{-\frac{U_{TS} - U_2}{kT}}$$

The ratio of the forward and backward rates is given by

$$\frac{R_{1 \rightarrow 2}}{R_{2 \rightarrow 1}} = \frac{\nu_1 c_1}{\nu_2 c_2} e^{\frac{U_1 - U_2}{kT}}$$

In equilibrium, this ratio is unity (detailed balance), and we have

$$\Delta U^{\text{eq.}} = (U_1 - U_2)^{\text{eq.}} = \Delta U^0 + k_B T \ln \frac{c_2}{c_1}$$

where $\Delta U^0 = k_B T \ln \frac{\nu_2}{\nu_1}$. This looks like the Nernst Equation!

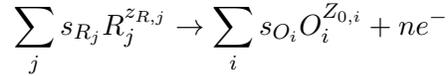
3 Faradaic Reactions in Dilute Solutions

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

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

3.2 Butler-Volmer Model for the transition state

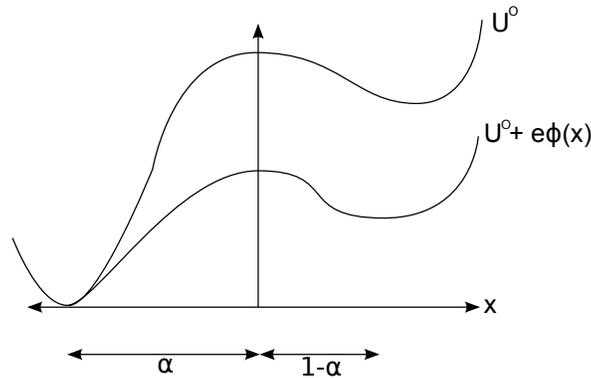
The Butler-Volmer hypothesis asserts that *the electrostatic energy of the transition state is a weighted average of electrostatic energies of the oxidized and reduced states*:

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

where

$$\begin{aligned} \alpha &= \text{transfer coefficient} \\ &= \text{weight of reduced state electrostatic energy at transition state} \end{aligned}$$

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

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

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

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