III. Reaction Kinetics

Lecture 14: Faradaic Reactions in Concentrated Solutions

MIT Student

1 Reactions in Concentrated Solutions

Note: Please see the course notes from 2009 for a detailed stochastic theory and formal derivations of reaction rates.

Until now, we have assumed that forward and backward reaction rates are proportional to concentrations, which is appropriate for chemical kinetics in a dilute solution. From our discussion of thermodynamics, we might expect to simply "replace concentrations with activities" to describe concentrated solutions in equilibrium, but this not sufficient to describe the dynamics of reactions out of equilibrium, since we also need to include describe concentrated-solution effects on the transition pathway.

As a starting point, it is useful to introduce the concept of the excess chemical potential of state i defined by

$$\mu_i = k_B T \ln C_i + \mu_i^{ex} \tag{1}$$

which is related to the activity coefficient γ_i via

$$\mu_i^{ex} = k_B T \ln \gamma_i \tag{2}$$

where C_i is the concentration of state i (equal to the product of component concentrations, if there is more than one chemical species, as before). For concreteness, we could consider a lattice gas, where the chemical potentials are defined per lattice site, but the derivation is more general. From our lattice gas theory, we recognize $k_B T \ln C_i$ as the (entropic) chemical potential of a dilute, *non-interacting gas*. Therefore, μ^{ex} contains all interaction free

energies, between the reactants and each other (for example, contributions from excluded volumes) and the external system (for example, contributions from applied potentials). We conclude that $\mu^{ex}(x)$ acts like the energy $U(x)$ in a dilute solution, by providing generalized thermodynamic forces on the reactants, including entropic compositional effects.

In this interpretation, it is important to note that here (and throughout the class) the thermodynamic quantities we denote by μ_i is the **diffusional chemical potential**, $\mu_i = \frac{\Delta G}{\Delta N_i}$, equal to the change in total free energy required to add the N_i particles needed to create state i *and alter the system accordingly* to accommodate those particles, given the constraints, e.g. with a fixed number of lattice sites. This is not the same as the true thermodynamic chemical potential, which is the free energy to add the particles, without any other changes to the system. For example, we derived the diffusional chemical potential per particle per site in a lattice gas

$$\mu_i = k_B T \ln c - k_B T \ln 1 - c = \mu_{particle} - \mu_{vacancy},$$

where the first term describes theΔ G required to create a particle and the second term describes theΔ G associated with generating a vacancy.

Now consider the general situation of a transition between two quasi-equilibrium states (free energy wells, whose depth is $\gg k_B T$), via a transition state, as illustrated in Figure 1. As argued above, we view the reaction complex (all species involved in the reaction) as performing a random walk in a *landscape of excess chemical potential* and employ the statistical theory of first passage over the barrier.

The conditional probability of a forward reaction per unit time, given that the reactants are found in state 1, is

$$\frac{1}{\tau_{1\to 2}} = r_{1\to 2} \tag{3}$$

$$\propto e^{-\left(\mu^{ex}_{TS} - \mu^{ex}_1\right)/k_B T}, \tag{4}$$

assuming $\mu^{ex}_{TS} - \mu^{ex}_1 \ll k_B T$ so that μ_1 is a long-lived stable state at temperature T. Here $\tau_{1\to 2}$ is the mean first passage time to the transition state. The net mean rate of the forward reaction is

$$\mathcal{R}_{1\to 2} = \mathcal{R}^0_{1\to 2} C_1 e^{-\left(\mu^{ex}_{TS} - \mu^{ex}_1\right)/k_B T} \tag{5}$$

$$= \mathcal{R}^0_{1\to 2} e^{-\left(\mu^{ex}_{TS} - \mu_1\right)/k_B T} \tag{6}$$

$$\tag{7}$$

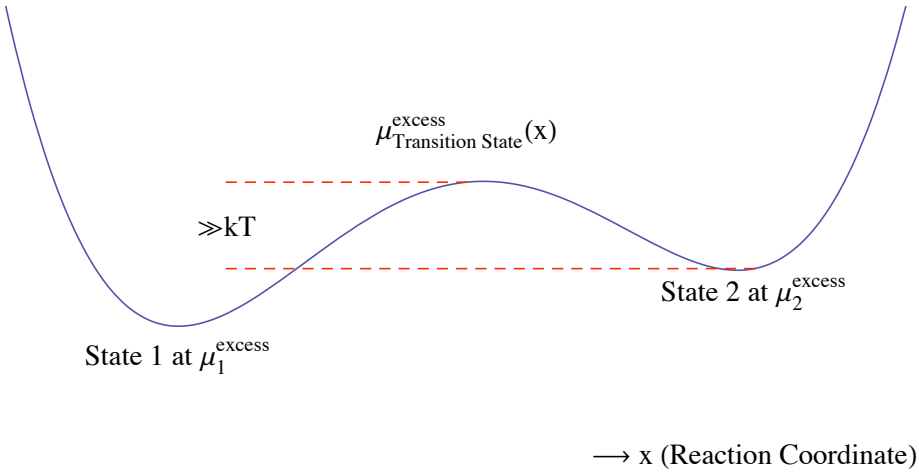

Figure 1: Conceptual reaction diagram for an out-of-equilibrium process. The schematic energy function is intended to represent a landscape of excess chemical potential, taking into account compositional effects and other contributions to the energy landscape.

where the probability (per time) of finding the reactants in state 1 is proportional to the concentration C_1 (per reaction site). The net reaction rate (per site) is

$$\mathcal{R} = \mathcal{R}_{1\to 2} - \mathcal{R}_{2\to 1} \tag{8}$$

$$= \mathcal{R}^0_{1\to 2} e^{-\left(\mu^{ex}_{TS}-\mu_1\right)/k_BT} - \mathcal{R}^0_{2\to 1} e^{-\left(\mu^{ex}_{TS}-\mu_2\right)/k_BT}. \tag{9}$$

By definition of thermal equilibrium, we must have $\mu_1 = \mu_2$ if and only if $\mathcal{R} = 0$. Therefore, $\mathcal{R}^0_{1\to 2} = \mathcal{R}^0_{2\to 1}$ if we have properly defined μ_1 and μ_2. Thus we arrive at a general expression for the reaction rate (per site) in a concentrated solution:

$$\mathcal{R} = \mathcal{R}_0 \left[e^{-\left(\mu^{ex}_{TS}-\mu_1\right)/k_BT} - e^{-\left(\mu^{ex}_{TS}-\mu_2\right)/k_BT} \right]. \tag{10}$$

Note that C_{TS}, the concentration in the transition state, is effectively a very small constant, since that state is short-lived. By changing $\mathcal{R}_0$ we could write μ_{TS} in place of μ^{ex}_{TS}.

We also have the *de Donder Relation*:

$$\frac{\mathcal{R}_{1\to 2}}{\mathcal{R}_{2\to 1}} = e^{\frac{(\mu_1-\mu_2)}{k_B T}}, \tag{11}$$

which relates reaction kinetics (left side) to equilibrium thermodynamics (right side).

2 Nernst Equation

When the mean transition rates between the two quasi-equilibrium states are equal ("*detailed balance*"), then the system is in equilibrium. We now show that detailed balance provides a kinetic derivation of the general form of the Nernst equation in terms of chemical activities, rather than concentrations (which are suitable only for a dilute solution), which we previously derived from equilibrium considerations alone.

Consider the general Faradaic half-cell reaction

$$\sum_i s_i M_i^{z_i} \to n e^-, \tag{12}$$

which we write as

$$R \to n e^- + O, \tag{13}$$

where the left and right sides are derived from states 1 and 2, respectively, while $R = \sum_i s_{iR} M_{iR}^{z_{iR}}$ and $O = \sum_i s_{iO} M_{iO}^{z_{iO}}$. We can separate the electrostatic contributions to the chemical potential as follows:

$$\mu_1 = \mu_R + q_R \phi, \tag{14}$$

where $\mu_R = k_B T \ln a_R$ is the chemical part and $\phi q_R = \phi \sum_i s_{iR} z_{iR} e$ is the electrostatic part, with ϕ denoting the solution potential. Similarly,

$$\mu_2 = \mu_O + q_O \phi - n e \phi_e, \tag{15}$$

where $\mu_O = k_B T \ln a_O$, $q_O = \sum_i s_{iO} z_{iO} e$, and ϕ_e denotes the electrode potential. The de Donder relation then implies that in equilibrium,

$$1 = \frac{\mathcal{R}_{1\to 2}}{\mathcal{R}_{2\to 1}} \tag{16}$$

$$= e^{(\mu_1-\mu_2)/k_BT} \tag{17}$$

$$= \frac{a_R}{a_O} e^{\frac{q_R\phi - q_O\phi + ne\phi_e}{k_BT}}. \tag{18}$$

Using charge conservation, $q_R = q_O - ne$, we obtain the *Nernst Equation* for a concentrated solution:

$$\Delta\phi_{eq} = \frac{k_BT}{ne} \ln \frac{a_O}{a_R}, \tag{19}$$

where$\Delta\ \phi = \phi_e - \phi$, which we can write as

$$\Delta\phi_{eq} = V^0 - \frac{k_BT}{ne} \ln \frac{a_R/a_R^0}{a_O/a_O^0}, \tag{20}$$

where $V^0 = \frac{k_BT}{ne} \ln \frac{a_R^0}{a_O^0}$. Here a_O^0 and a_R^0 denote the activities in the reference states.

3 Butler-Volmer Equation

In order to derive reaction rates as well as the kinetic anddynamic behaviors of a system (out of equilibrium), we require a model of the transition state. To that end, we make the Butler-Volmer hypothesis for the electrostatic energy of the transition state:

$$\mu_{TS}^{ex} = \mu_A + \alpha q_A \phi + (1-\alpha)\left[q_0\phi - ne\phi_e\right], \tag{21}$$

where the first term on the right, $\mu_A = k_BT \ln \gamma_A$, denotes the excess chemical activity of the transition or activated state, and the second term on the right denotes the electrostatic energy of the transition state and is an α-weighted average of contributions from states 1 and 2.

Following a derivation similar to the one previously given, we substitute μ_{TS}^{ex}, μ_1, and μ_2 into $\mathcal{R}$ and use$\Delta\ \phi_{eq}$ to exprress $\mathcal{R}$ in terms of the activation overpotential, $\eta_{act} = \Delta\phi - \Delta\phi_{eq}$, to obtain

$$\mathcal{R} = \frac{\mathcal{R}_O}{\gamma_A}\left(a_R^\alpha a_O^{1-\alpha}\right)\left[e^{(1-\alpha)ne\eta/k_BT} - e^{-\alpha ne\eta/k_BT}\right]. \tag{22}$$

Let $I = neA\mathcal{R}$ denote the current, where A denotes the dimensionless area or number of reaction sites. Then

$$I = I_0\left[e^{(1-\alpha)ne\eta/k_BT} - e^{-\alpha ne\eta/k_BT}\right], \tag{23}$$

where

$$I_0 = neAC_R^\alpha C_O^{1-\alpha}\left(\frac{\gamma_R^\alpha \gamma_O^{1-\alpha}}{\gamma_A}\right), \tag{24}$$

with the term out of the parentheses representing the exchange current, while the term in parentheses is a correction factor for the activity coefficients.

10.626 Electrochemical Energy Systems

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