Lecture 23 - Heterogeneous Charge Transfer

5/9/2014

Notes by MIT Student (and MZB)

The rate R of a general reaction in any particular direction is dictated by the difference in excess chemical potential[1] between the transition state and starting state i:

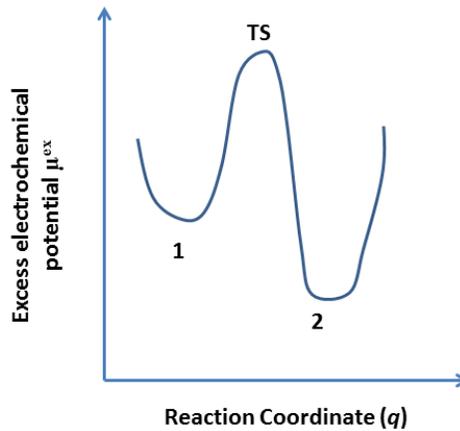$$R = \tau_{i \to final} e^{-\left(\frac{\mu_{TS}^{ex} - \mu_i^{ex}}{kT}\right)} \quad (1)$$

Figure 1 Schematic showing excess chemical potential landscape for a general reaction with transition state

where $\tau_{i \to final}$ is the frequency of hop attempts and $e^{-\left(\frac{\mu_{TS}^{ex} - \mu_i^{ex}}{kT}\right)}$ effectively represents the probability of a successful hop. Applying this equation to the general reaction $A \leftrightarrow B$, and multiplying each reaction rate by the concentration of reacting species available, the *net* rate going from A to B [1] is:

$$R_{A \to B} = \tau_{A \to B} \tilde{c}_A e^{-\left(\frac{\mu_{TS}^{ex} - \mu_A^{ex}}{kT}\right)} - \tau_{B \to A} \tilde{c}_B e^{-\left(\frac{\mu_{TS}^{ex} - \mu_B^{ex}}{kT}\right)} \quad (2)[2]$$

Now, let us consider the electrochemical reaction

$$O + ne^- \leftrightarrow R \quad (3)$$

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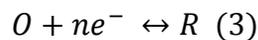
[1] Recall that excess chemical potential μ^{ex} is defined such that $\mu = \mu^o + kT \ln a + ze\varphi = kT \ln c + \mu^{ex}$. We use excess electrochemical potential in the limit where the concentrations of reactants and products are equal

[2] Note that all concentrations henceforth are non-dimensionalized by a reference concentration c_{ref}

occurring at an electrode, where O and R are the participant oxidized and reduced species. Given our definition of μ^{ex} and assuming $\tau_{A\to B} = \tau_{B\to A} = \tau$, we may re-express eq 3 as

$$R_{A\to B} = \tau e^{-\frac{\mu_{TS}^{ex}}{kT}}\left[e^{\left(\frac{\mu_1}{kT}\right)} - e^{\left(\frac{\mu_2}{kT}\right)}\right] \quad (4)$$

Note that this equation is applicable to any general chemical reaction for which a suitable model of excess chemical potential can be found. As we have seen in class, such a formulation describes the Langmuir model of surface adsorption as well as the Butler-Volmer model of Faradaic reactions at electrodes.[3]

In Marcus theory-type [2], [3] models of Faradaic reactions, μ^{ex} has a harmonic oscillator-type dependence on the reaction coordinate x such that $\mu^{ex} = \frac{k}{2}(x - x_o)^2$, where x_o is the reaction coordinate[4] at lowest excess chemical potential and k is the force constant associated with the normal modes of the solvation shell vibration around reactant molecules/ions.[5] The application of the model implied by eq 4 in homogeneous chemical reactions has resulted in a successful prediction of reaction rates[4], and motivates an extension to heterogeneous electron transfer reactions. We may write the excess electrochemical potential of the reactants and products as:
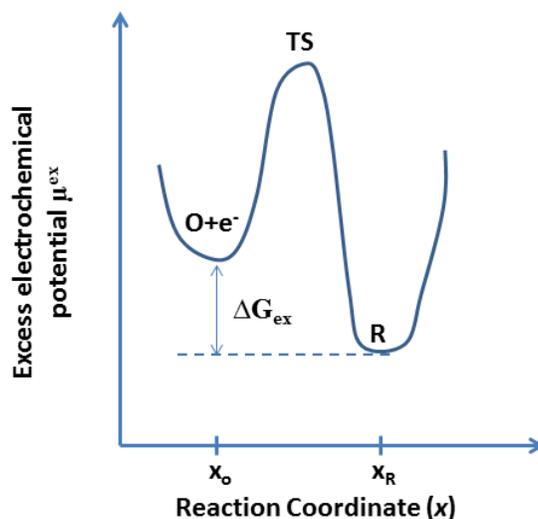

Figure 2 Schematic showing excess chemical potential landscape for an electrode reaction with transition state and driving force ΔG_{ex}.

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[3] The Butler-Volmer model results from the assumption that the chemical potential of the transition state is split between the initial and final states, together with an extra 'chemical energy' at the transition state such that $\mu^{ex} = \alpha\mu_1 + (1 - \alpha)\mu_2 + kT\ln\gamma_{TS}$.

[4] The reaction coordinate refers to the variation in the total configuration of bonds and distances between the reactant/product species and solvent environment, and not inter-nuclear distances.

[5] For solids, k is related to the vibrations between the reactant and surrounding ions in the lattice.

$$\mu_o^{ex} = \mu_o^\theta + n\mu_e^\theta + kT \ln(\gamma_o \gamma_e^n) + z_o e\varphi - ne\varphi_e + \frac{k_o}{2}(x - x_o)^2 \quad (5)$$

$$\mu_R^{ex} = \mu_R^\theta + kT \ln(\gamma_R) + z_R e\varphi + \frac{k_R}{2}(x - x_R)^2 \quad (6)$$

where γ represents the activity coefficient of the species of interest, φ is the solution potential and φ_e is the electrode potential.

Given that at the transition state, $\mu_o^{ex} = \mu_R^{ex}$, we can find ΔG_{ex}, which represents the free energy change for the reduction of O:

$$\Delta G_{ex} = \frac{k_o}{2}(x_\Pi - x_o)^2 - \frac{k_R}{2}(x_\Pi - x_R)^2 \quad (7)$$

Note, however, that this definition of free energy does not include any concentration effects, since we originally defined the general reaction such that reactions are dictated by the landscape of excess chemical potential. This assumption is valid for homogeneous reactions where concentrations do not vary significantly in bulk solution, however for interfacial electron transfer reactions, the concentrations of reactant and product phases may be vastly different. We thus introduce a correction based on our initial definition of overpotential η, where

$$ne\eta = \Delta G = \Delta G_{ex} + kT \ln \frac{c_R}{c_o c_R^n} \quad (8)$$

Eq 8 is what results if the full definition of chemical potential is used in eqs 5 and 6, and the logarithm terms include the non-dimensional reactant and product concentrations as well as the activity coefficients. By solving for x_Π in eq 7 and assuming $k_o = k_R$, we can find the barriers for reduction and oxidation independently:

$$\Delta G_{red}^{ex} = \mu_\Pi^{ex} - \mu_o^{ex}(x_o) = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{ex}}{\lambda}\right)^2 \quad (9)$$

$$\Delta G_{ox}^{ex} = \mu_\Pi^{ex} - \mu_R^{ex}(x_R) = \frac{\lambda}{4}\left(1 - \frac{\Delta G^{ex}}{\lambda}\right)^2 \quad (10)$$

where $\lambda = \frac{k}{2}(x_O - x_R)^2$, defined as the solvent reorganization energy. By substituting the definition of excess chemical potential at the transition state from eqs 9 and 10 into eq 2, we can find the net reaction rate for the reduction of O:

$$R = k_o e^{-\left(\frac{\lambda}{4kT}\right)} e^{-\frac{(\Delta G^{ex})^2}{4kT\lambda}} \left(c_o c_e^n e^{-\frac{\Delta G^{ex}}{2kT}} - c_R e^{\frac{\Delta G^{ex}}{2kT}}\right) \quad (11)$$

Based on the definition of overpotential used in eq 8, and that $I = neR$, we can write a current-overpotential relationship:

$$I = I_0 e^{-\frac{(ne\eta)^2}{4kT\lambda}} \left(e^{\left(\frac{-\alpha ne\eta}{kT}\right)} - e^{\left(\frac{(1-\alpha)ne\eta}{kT}\right)} \right) \quad (12)$$
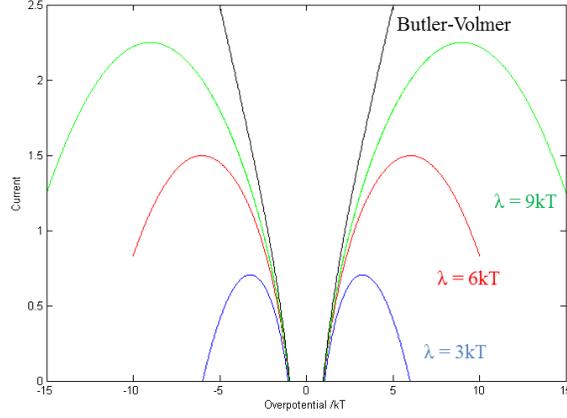

Figure 3 Figure showing current-voltage relationship for reorganization energies of 3, 6 and 9 kT. The overpotential is scaled to kT and the current I is scaled to the exchange current. The peak of each parabola occurs at the reorganization energy.

where $I_o = nek_o e^{-\left(\frac{\lambda}{4kT}\right)}(c_O c_e^n)^{3-2\alpha/4}(c_R)^{1+2\alpha/4}$ and $\alpha = \frac{1}{2}\left(1 + \frac{kT}{\lambda}\ln\frac{c_O c_e^n}{c_R}\right)$. Notice that at small overpotentials $|\eta| \ll \lambda$ and reorganization energies $\lambda \ll kT$, and provided $c_o c_e^n$ does not vary too much from c_R, eq 12 reduces to the symmetric Butler-Volmer equation, as shown in the figure above.

Note that the reorganization energy is dictated by the force constant of normal modes between reactant ions/molecules and the surrounding solvent along the excess chemical potential landscape. In making the assumption that $k_o = k_R$, we have supposed that these modes are similar for both reactant and product. This is valid for so-called *outer sphere* reactions where electron transfer mainly induces a relaxation of solvent molecules around the reacting species, leaving inner bond environment relatively unperturbed, as is the case for one-electron redox reactions involving oxygen [5] and aqueous self-exchange reactions such as $Fe^{2+} + Fe^{3+} \leftrightarrow Fe^{3+} + Fe^{2+}$.[2] In *inner sphere* reactions, electron transfer is accompanied by a significant change in the inner bond configuration between reacting ions and the solvent – a process that may involve bond breaking/surface adsorption of reacting species - resulting in different force constants and $k_o \neq k_R$.

For electron transfer in real experiments, the total reorganization energy is thus a sum of inner sphere, outer sphere and extra thermal contributions:

$$\lambda = \lambda_{inner} + \lambda_{outer} + \lambda_{therm} \quad (13)$$

Since inner sphere electron transfer processes are characterized by a strong electron coupling between the initial and final states [6], there will be a separation between low energy "bonding"

higher energy "antibonding" states that can be estimated by considering the secular equation from quantum mechanics:

$$\begin{vmatrix} E_{OO} - E & E_{OR} \\ E_{OR} & E_{RR} - E \end{vmatrix} = 0 \quad (14)$$

where $E_{OO} = <\psi^O|H|\psi^O>$ is the energy of the initial state, $E_{RR} = <\psi^R|H|\psi^R>$ is the energy of reduced state and E_{OR} is the coupling matrix element between the two states. Solving the equation results in two states separated by $E = \frac{1}{2}(E_{oo} + E_{RR}) \pm \Delta$ where

$\Delta = \frac{1}{2}\sqrt{(E_{RR} - E_{OO}) \pm 4E_{OR}{}^2}$. The implication of this result is that as the energy of overlap E_{OR} increases, the lower energy bonding state is favored during electron transfer. Note that if E_{OR} and $E_{RR} - E_{OO}$ are both zero, we recover the outer sphere condition where non-adiabatic electron tunneling occurs without coupling between initial and final states.
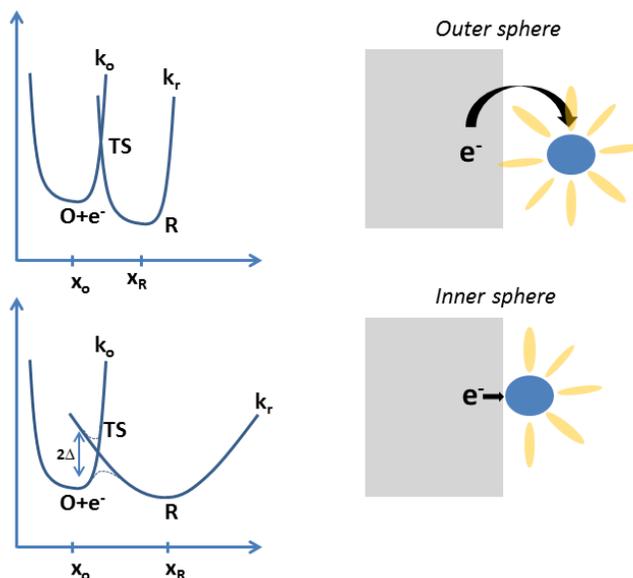

Figure 4 Schematic diagrams showing the difference between outer and inner sphere electron transfer reactions and corresponding excess chemical potential energy curves.

For outer sphere electron transfer, since there is no significant rearrangement of bonds, the reorganization energy consists mainly in the energy required to polarize solvent molecules around reacting species and is well approximated by the continuum generalized Born model of solvation such that:

$$\lambda_{outer} = \frac{(ne)^2}{8\pi\varepsilon_o}\left(\frac{1}{a} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \quad (15)$$

where ε_s is the static dielectric constant; ε_{op} is the optical dielectric constant; a, the effective Born radius, is the distance between the ion/molecule and the solvation shell; and d is the

distance over which electron transfer occurs. As expected, a small difference between ε_{op} and ε_s – representing minimal change in solvent polarizability induced by electron transfer – results in a small reorganization energy. Note also that $\lambda_{outer} \sim n^2$. This imposes an energetic

barrier that scales as $\sim \frac{n^2}{4}$ for concerted multi-electron transfer (see eqs 9 and 10). Thus a small number of electrons (ideally, 1) is likely to be transferred at any one time. This explains the step-by-step nature of most multi-electron transfer reactions at electrodes, such as those involved in 4-electron water splitting, oxygen reduction and other complex reactions of interest today.[7]

References

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