

ELECTRON TRANSFER AND SINGLE MOLECULAR EVENTS

W. Schmickler

Department of Theoretical Chemistry, University of Ulm, D-89069 Ulm, Germany

Keywords: solvent reorganization, adiabatic, electronic levels, Fermi level

Contents

1. Introduction
 2. The Theories of Marcus and Hush
 3. Gerischer's Formulation
 4. Energy of Reorganization
 5. Quantum Theory
 6. Beyond First Order Perturbation
 7. From Non-adiabatic to Adiabatic Reactions
 8. Electron Transfer through Single Molecules
 9. Conclusions
- Glossary
Bibliography
Biographical Sketch

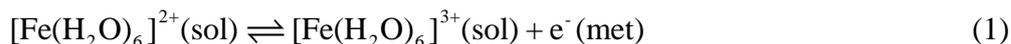
Summary

Electrochemical electron transfer reactions are reviewed, starting with the works of Marcus and Hush, who evolved the concept of solvent reorganization. The resulting equations for the electrochemical rate constants are derived, and interpreted within the Gerischer formulation. A quantum mechanical version points out the importance of the electronic interaction between reactant and electrode, and allows an investigation into adiabatic and non-adiabatic reactions. The transitions between these two regimes, the effects of the solvent friction, and of the electronic overlap are discussed in detail. The introduction of the tip of a scanning tunneling microscope into the electrochemical systems makes it possible to observe electron transfer through single molecules.

1. Introduction

Electron transfer reactions play an important role in physics, chemistry, and biology in general, but for electrochemistry they are particularly important: Every electrochemical reaction contains at least one electron transfer step. That this is so can be easily seen by considering the fact that in an electrochemical circuit electrons flow towards one of the electrodes, and out of the other. Hence they must be consumed at one electrode, and produced at the other.

Let us consider this in greater detail. An electrode is the interface between an electronic conductor (metal or semiconductor) and an ionic conductor (electrolyte). Thus, current through the interface can either be carried by electrons or by ions. An example of the former process is:



occurring at the interface between a metal and an aqueous solution; ‘sol’ and ‘met’ indicate that the particle is in the solution or in the metal. Obviously, in this example only an electron is transferred from the solution to the metal, or vice versa. This is what happens in a proper electron transfer reaction, and in this article we will be concerned with these processes, taking place on metal electrodes.

Even when an ion is exchanged between electrode and solution, as in the reaction:



an electron has been transferred to the ion. However, such ion-transfer reactions involve crystallographic aspect and desolvation, and are not treated here.

The rate constants of chemical reactions typically have the form:

$$k = A \exp\left(-\frac{E_{\text{act}}}{k_{\text{B}}T}\right) \quad (3)$$

where A is nearly independent of temperature, E_{act} is the activation energy, and k_{B} is the Boltzmann constant. E_{act} can be thought of as the height of the energy barrier, which the system has to overcome in order to react.

The rate of an electron transfer reaction depends on the electrode potential: a high potential attracts electrons and thus favors the oxidation, while a low potential will favor reduction. The rate can be expressed through the deviation from the equilibrium potential, which is denoted as the overpotential η .

Phenomenologically, the rate constant for the oxidation is described by the Butler-Volmer law:

$$k_{\text{ox}} = k_0 \exp\left(\frac{\alpha e_0 \eta}{k_{\text{B}}T}\right) \quad (4)$$

where k_0 is the rate at equilibrium, and e_0 the unit of charge. α is a phenomenological constant known as the transfer coefficient. It signifies to what extent the overpotential affects the activation energy, and for simple electron transfer it is of the order of $\alpha \approx 1/2$. A corresponding relation holds for the reduction reaction.

Electrochemical electron transfer belongs to the wider class of electron transfer in solutions. The theory of these reactions started with the works of Marcus and Hush, who were faced with the following problem: The exchange of an electron between two reactants in a solution, a distance of the order of one nanometer apart, should occur by tunneling, i.e. a rapid, classically forbidden transition in which the electron passes through any intervening barrier. Hence the exchange was expected to be very fast and to

not require an energy of activation. In reality, such electron transfer reactions do require an energy of activation, and are not as fast as a simple tunneling mechanism would suggest. The answer to this puzzle is, that the change of the charge that accompanies the electron transfer, entails a change in the solvation, a reorganization of the solvent. While the transfer of an electron is fast and occurs on the time-scale of 10^{-16} – 10^{-15} s, the solvent reorganization requires a reorientation of the molecules, which takes about one thousand times longer. If an electron were to pass from a reactant A to a reactant B without prior solvent reorganization, the products A^+ and B^- would find themselves in a solvent environment that would not correspond to their charges. Consequently, the system would have a high energy, and the electron would immediately return. Therefore, electron transfer is preceded by a partial reorganization of the solvent to an intermediate state, and this process requires an activation energy and slows the reaction down.

These ideas, whose quantitative aspects will be treated below, were immediately transferred to electrochemical electron transfer. There is, however, an important difference: electrodes are either metals or semiconductors, and both have a continuum of electronic levels; in contrast, molecules have discrete levels. As was realized by Levich and Dogonadze, and a little later by Gerischer, this entails some important differences, especially for reactions with a large free energy.

The theories of Marcus and Hush apply only to so-called outer sphere reactions, in which no chemical bonds are formed or broken, and we shall limit ourselves to this class of reactions here. Also, we shall only consider reactions at metal electrodes. Reactions on semiconductors, while certainly of interest, are mainly governed by the occupation of the conduction and valence band, and less by the dynamics of electron transfer.

2. The Theories of Marcus and Hush

These theories were originally formulated for homogenous outer-sphere electron transfer reactions in polar solvents, which do not involve the breaking or formation of a bond. They are based on the idea that the electron transfer is accompanied by the reorganization of the reactants' solvation spheres. For a quantitative description, the response of the solvent is divided into a slow part, which is the response of the nuclei, and a fast part due to electronic interactions. The fast part is supposed to follow the motion of the transferring electron instantaneously; therefore it affects, or renormalizes, the energy of the system, but does not require an energy of activation. In contrast, the motion of the nuclei is much slower, and determines the energy of activation. In addition to the reorganization of the solvent, electron transfer may also be accompanied by a reorganization of the reactant's ligands, the inner sphere.

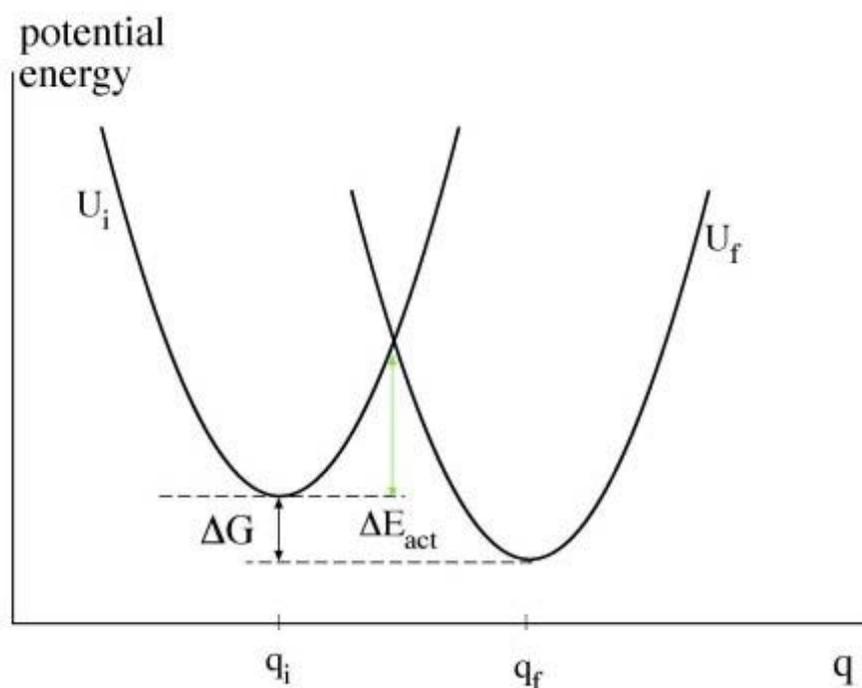


Figure 1. Simplified, one-dimensional potential energy surfaces for electron transfer.

The basic idea can be understood in terms of a simple, one-dimensional picture (see Fig. 1). To be specific, we consider electron transfer from a reactant with charge q_i to a metal electrode, resulting in a reactant with charge $q_f = q_i + 1$. The state of the slow part of the solvent can be characterized by a single generalized solvent coordinate q , which upon proper normalization has the following meaning: A solvent in the state q would be in equilibrium with a reactant of charge q . In the initial state i , the system is in equilibrium for $q = q_i$, so that the potential energy $U_i(q)$ has its minimum there. Correspondingly, the potential energy $U_f(q)$ for the final state has its minimum at q_f . To a first approximation, both potential energy curves can be approximated by harmonic oscillator potentials, i.e. two parabolas with their minima at different positions:

$$U_i(q) = \frac{1}{2} m \omega^2 (q - q_i)^2 \quad U_f(q) = \frac{1}{2} m \omega^2 (q - q_f)^2 + \Delta G \quad (5)$$

where m is the effective mass, ω the frequency, and ΔG is the energy change, which can be identified with the change in the free energy, since a one-dimensional picture implies an average over all other degrees of freedom. Notice that it has been assumed, that the frequency does not change between initial and final state. The energy of activation E_{act} is the difference in energy between the crossing point of the two parabolas, which corresponds to the activated state, and the energy of the initial state. A simple calculation gives:

$$E_{\text{act}} = \frac{(\lambda + \Delta G)^2}{4\lambda} \quad \text{where} \quad \lambda = \frac{1}{2} m\omega^2 (q_i - q_f)^2 \quad (6)$$

Here, λ is the energy of reorganization associated with the electron transfer; it is the most important parameter of this theory. The same equation can be derived in a multi-dimensional model, in which a large number of modes are reorganized. The energy of reorganization contains then a sum over all contributing modes ν :

$$\lambda = \sum_{\nu} = \frac{1}{2} m\omega^2 (q_{i,\nu} - q_{f,\nu})^2 \quad (7)$$

Electron transfer can thus be visualized in the following way (see Fig. 1): Initially, the system is in the well $U_i(q)$. A thermal fluctuation of the solvent brings it to the crossing point between the two surfaces U_i and U_f . At this point, electron transfer can take place without change of energy, and the system then relaxes towards its new equilibrium position q_f . If electron transfer takes place every time that the system is on the saddle point, the reaction is said to occur adiabatically; otherwise it is non-adiabatic. An adiabatic reaction implies a strong electronic interaction between reactant and electrode.

The theories of Marcus and Hush assume an adiabatic transfer. Originally, the pre-exponential factor of the reaction rate was identified with the collision frequency between the reactants. However, later it was realized that the fluctuation required for the transfer is better considered as the result of a random or Brownian motion of the solvent, which is governed by its viscosity or, equivalently, by its internal friction. The resulting expression for the reaction rate is:

$$k = \gamma \exp\left(-\frac{(\lambda + \Delta G)^2}{4\lambda k_B T}\right) \quad (8)$$

where k_B is the Boltzmann constant, T the temperature, and γ is the friction coefficient.

In electrochemical reactions, the reaction free energy can be expressed through the overpotential η ; for electron transfer to the electrode (anodic reaction) this reads: $\Delta G = -e_0\eta$. So, to a first approximation, we can apply Eq. (8) to electrochemical reactions by identifying ΔG with $-e_0\eta$, and this works quite well near equilibrium. Indeed, for $|e_0\eta| \ll \lambda$, the terms of order $(e_0\eta)^2$ can be neglected, and the rate equation attains the same form as the Butler-Volmer law with a transfer coefficient $\alpha = 1/2$, where $\alpha = -k_B T \partial \ln k / \partial (e_0\eta)$ (c.f. Eq. (4)).

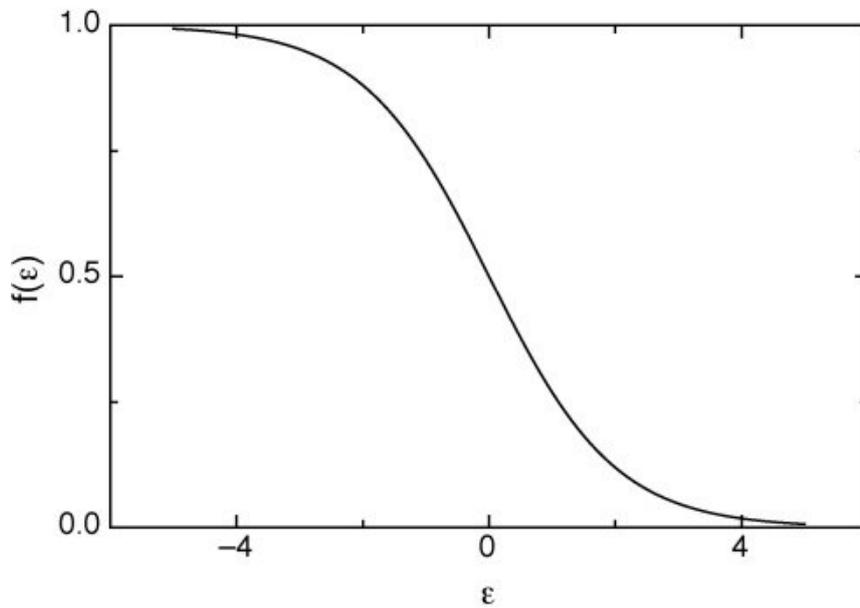


Figure 2. The Fermi-Dirac distribution; the Fermi level has been set to zero, and the energy is measured in terms of the thermal energy $k_B T$.

However, for a more exact treatment we have to consider the electronic properties of a metal electrode in greater detail. The electronic states on a metal are not discrete, but form energy bands. At $T = 0$ these bands are filled up to a highest level known as the Fermi level, whose energy is denoted as the Fermi energy E_F : all levels below the Fermi energy are filled, all levels above are empty. At finite temperatures thermal excitations may raise electrons from below the Fermi level to an empty level above, leaving an unfilled state, or hole, behind. The probability $f(\epsilon)$ that an electronic level is occupied is then given by the Fermi-Dirac distribution:

$$f(\epsilon) = \frac{1}{1 + \exp \frac{\epsilon - E_F}{k_B T}} \quad (9)$$

The shape of this distribution is shown in Fig. 2; for low temperatures it goes over into a step function, and for many applications this is a good approximation even at room temperature, where $k_B T \approx 0.025$ eV.

Near equilibrium, electron exchange occurs mainly near the Fermi level, but in general a reduced species can donate an electron to any empty level on the metal. If an electron is transferred to a level with an energy ϵ above the Fermi level, the free energy for this process is reduced by this amount, resulting in an activation energy of:

$$E_{\text{act}}(\eta, \epsilon) = \frac{(\lambda + \epsilon - e_0 \eta)^2}{4\lambda} \quad (10)$$

The probability of finding an empty level on the metal to which the electron can be transferred is: $\rho(\epsilon)[1 - f(\epsilon)]$, where $\rho(\epsilon)$ is the density of electron levels on the metal surface. The total electrochemical rate for the anodic direction is obtained by integrating:

$$k_a = \gamma \int [1 - f(\epsilon)] \rho(\epsilon) \exp\left[-\frac{(\lambda + \epsilon - e_0\eta)^2}{4\lambda k_B T}\right] d\epsilon \quad (11)$$

The integral is over all states in the conduction band, but for practical purposes it may be extended to $-\infty$ and ∞ , since the width of the conduction band is much larger than the energy of reorganization, which is typically in the range 0.5–1 eV, and also much larger than $e_0\eta$, since the applied overpotential rarely exceeds 1 V. Also, in many cases the metal density of states can be taken as constant in the vicinity of the Fermi level, and taken in front of the integral. The resulting form of the rate constant, as a function of the overpotential, is shown in Fig. 3. For high overpotentials, it attains a constant limit:

$$k_{\text{lim}} = \gamma \rho (4\pi\lambda k_B T)^{1/2} \quad (12)$$

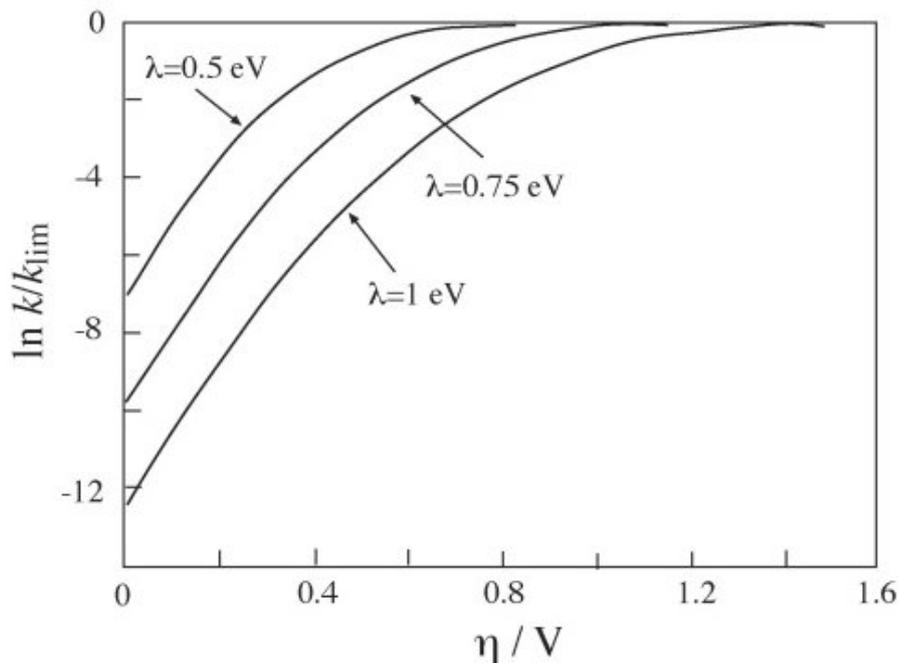


Figure 3. Normalized rate constant for the anodic direction as a function of the overpotential, for various energies of reorganization.

The corresponding equation for the cathodic direction – electron transfer from the metal to the reactant – can be obtained by changing a few signs. Electrons can only be transferred from occupied levels of the metal, and the effect of the overpotential is reversed:

$$k_c = \gamma \int f(\varepsilon) \rho(\varepsilon) \exp\left[-\frac{(\lambda - \varepsilon + e_0 \eta)^2}{4\lambda k_B T}\right] d\varepsilon \quad (13)$$

At high overpotentials, the electrochemical rates become constant. This is in contrast to the rate for homogeneous reactions as given by Eq. (8), which predicts a decrease of the rate for very high reaction free energies, when $-\Delta G > \lambda$; this is known as the inverted region. For homogenous reactions such a decrease has really been observed. For electrochemical electron transfer on metals this decrease does not occur because of the large range of electronic levels available for the exchange.

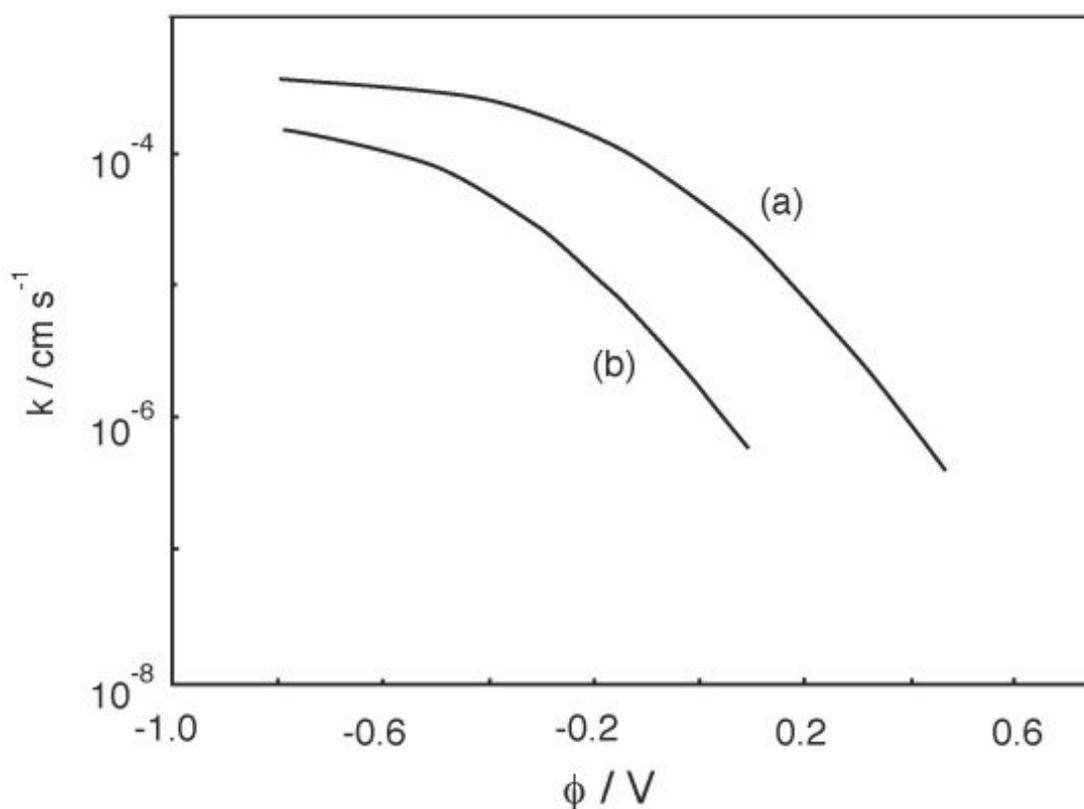


Figure 4. Rate constants for the reduction of $[\text{Mo}(\text{CN})_8]^{3-}$ (upper curve) and $[\text{W}(\text{CN})_8]^{3-}$ (lower curve) on gold electrodes derived with a monolayer of $\text{HO}(\text{CH}_2)_{16}\text{SH}$. The electrode potential is given with respect to an Ag/AgCl electrode in saturated KCl .

Classical experiments on electron transfer reactions at bare metal electrodes are usually restricted to a small range of overpotentials, because at high overpotentials mass transfer becomes rate-determining. It is therefore difficult to show that the current-potential curves have the sigmoidal shape shown in Fig. 3. The experiment is much easier to perform on electrodes coated with an insulating film, through which the transferring electron must tunnel, so that the reaction rate is decreased by several orders of magnitude. For this purpose, Miller and Grätzel investigated a series of outer-sphere electron-transfer reactions on gold electrodes coated with ω -hydroxy-thiol layers about

20 Å thick. They recorded current-potential curves over a range of 0.5 to 1 V, and found the expected curvature in all cases investigated. Figure 4 shows the data for the reduction of $[\text{Mo}(\text{CN})_6]^{3-}$ and $[\text{W}(\text{CN})_8]^{3-}$. The curves follow the theoretical equations (11) and (13) quite well. By a fitting procedure the density of states of the oxidized species can be obtained. In the case of $[\text{Mo}(\text{CN})_6]^{3-}$ one obtains an energy of reorganization of about 0.4 eV.

-
-
-

TO ACCESS ALL THE 20 PAGES OF THIS CHAPTER,
Visit: <http://www.eolss.net/Eolss-sampleAllChapter.aspx>

Bibliography

1. R.A. Marcus, (1965) *J. Chem. Phys.* **24** 966. [Classical paper on the theory of electron transfer in solutions].
2. N.S. Hush, (1958) *J. Chem. Phys.* **28** 962. [Classical paper on the theory of electron transfer in solutions].
3. H. Gerischer, Z. (1960) *Phys. Chem. NF* **6** 223; **27** (1961) 40, 48. [Classical paper on electrochemical electron transfer; unfortunately in German].
4. H. Gerischer, Z. (1961) *Phys. Chem.*; **27** (1961) 40, 48. [Classical paper on electrochemical electron transfer; unfortunately in German].
5. H.A. Kramers, (1940) *Physica, Amsterdam*, **7** 284. [Theory of reaction rates in condensed phases].
6. A.N. Kuznetsov, (1995) *Charge Transfer in Physics, Chemistry, and Biology*, Gordon and Breach, New York. [Good general source electron transfer in condensed phases].
7. R.R. Dogonadze, (1971) in *Reactions of Electrons at Electrodes*, edited by N.S. Hush, Interscience, London. [Review of early theory of electrochemical electron transfer].
8. W. Schmickler, (1986) *J. Electroanal. Chem. Interfacial Electrochem.* **204** 31. [Theory of adiabatic electrochemical electron transfer].
9. C. Miller and M. Grätzel, (1991) *J. Phys. Chem.* **95** 5225. [Experimental study of the relation between current and potential over a wide range].
10. T. Iwasita, W. Schmickler, and J.W. Schultze, (1985) *Ber. Bunsenges. Phys. Chem.* **89** 138. [Experimental study that examines the reaction rates in dependence on the nature of the metal].
11. D.E. Khoshitariya, T.D. Dolidze, L.D. Dolidze, L.D. Zusman, and D.H. Waldeck, (2001) *J. Phys. Chem. A.* **105** 1818. [Examines the effect of viscosity and friction on the reaction rate].
12. N. Tao, (1996) *Phys. Rev. Lett.* **76** 4066. [Classic experiment on electron transfer via single molecules].

Biographical Sketch

Prof. Dr. Wolfgang Schmickler was born in Bonn on Sept. 11, 1946. He studied physics and

mathematics at the Universities of Bonn, Heidelberg, and Imperial College, London. In 1972 he received his diploma in physics at the University of Bonn, Germany, and in 1973 he was awarded the Ph.D. in natural sciences at the same university. After graduation, he received various fellowships, the most prestigious one being the Heisenberg Fellowship of the German Research Foundation. These enabled him extended stays at the Frumkin Institute of the Soviet Academy of Sciences (1979), the Laboratoire d'Electrochimie Interfaciale du C.N.R.S. Meudon, France (1981/82), the IBM Research Laboratory, San Jose, California, USA (1983/84), and at the State University of New York at Stony Brook (1989/90). From 1985 to 1990 he was professor at the chemistry department of the University of Bonn, and 1990 to 1992 at the physics department of Utah State University (USA). Since 1992 he is professor at the chemistry department of the University of Ulm, Germany. He has published four books and more than 200 research articles, among them: (i) W. Schmickler *Interfacial Electrochemistry*, Oxford University Press, New York, 1996; (ii) M.T.M. Koper and W. Schmickler, *A Unified Model for Electron and Ion Transfer Reactions on Metal Electrodes*, *Frontiers of Electrochemistry*, ed. by J. Lipkowski and P.N. Ross, VCH Publishers, 1998; (iii) W. Schmickler, *Electrical Double Layers: Theory and Simulations*, Bard, Stratmann (eds.), *Encyclopedia of Electrochemistry*. Vol. I, Wiley-VCH, 2007. In 1985 he was awarded the Bodenstein-Award of the Deutsche Bunsengesellschaft für Physikalische Chemie. His research interest lie in theoretical electrochemistry; presently the focus is on electrocatalysis, and the formation and energetics of nanostructures.

Prof. Dr. Wolfgang Schmickler is a member of the Bunsengesellschaft für Physikalische Chemie, the Gesellschaft Deutscher Chemiker, and the International Society of Electrochemistry.