

Fermi Golden Rule Approach to Evaluating Outer-Sphere Electron-Transfer Rate Constants at Semiconductor/Liquid Interfaces

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Fermi's golden rule is used to formulate rate expressions for charge transfer of delocalized carriers in a nondegenerately doped semiconducting electrode to localized, outer-sphere redox acceptors in an electrolyte phase. If the charge-transfer rate constant is known experimentally, these rate expressions allow computation of the value of the electronic coupling matrix element between the semiconducting electrode and the redox species. This treatment also facilitates comparison between charge-transfer kinetic data at metallic and semiconducting electrodes in terms of parameters such as the electronic coupling to the electrode, the attenuation of coupling with distance into the electrolyte, and the reorganization energy of the charge-transfer event. Within this framework, rate constant values expected at representative semiconducting electrodes have been evaluated from experimental data for charge transfer from Au electrodes to ferrocene-terminated thiols, to Ru(NH₃)₅^{3+/2+}-terminated thiols, and through blocking layers to dissolved [Fe(2,2'-bipyridine)₂(CN)₂]⁺⁰. Based on the experimental parameters determined for these systems, the maximum rate constant (i.e. at optimal exoergicity) for outer-sphere processes at semiconducting electrodes is computed to be in the range 10⁻¹⁷–10⁻¹⁶ cm⁴ s⁻¹. These values are in excellent agreement with prior theoretical models and experimental results for charge-transfer kinetics at semiconductor/liquid interfaces and thus serve to unify the theoretical and experimental descriptions of electrochemical processes at semiconducting and metallic electrodes.

I. Introduction

Rate constants for heterogeneous charge transfer at metallic and semiconducting electrodes have received increasing attention in recent years.^{1–7} Measurements of rate constants at metallic electrodes have been possible due to the development of pinhole-free, insulating organic layers³ and the use of redox reagents incorporated into self-assembled monolayers,^{1,2,4,8} both of which allow for precise measurements of rate constant vs distance relationships. In addition, the preparation of nearly defect-free semiconductor electrodes that obey the expected second-order rate law for interfacial charge transfer has permitted measurements of rate constants by straightforward experimental techniques.^{6,7,9,10} At both semiconducting and metallic electrodes, measurements of the dependence of the interfacial rate constant on the driving force for charge transfer are consistent with the predictions of electron-transfer theory with respect to the contribution of nuclear terms.^{1,2,4,7,11–13}

To date, a comparison between the absolute magnitude of the rate constants at metallic and semiconducting electrodes has been unavailable. Such a comparison is not straightforward, since the charge-transfer processes in these systems, as measured using common laboratory techniques, obey different rate laws.¹³ The purpose of this paper is to present a framework that readily facilitates such a comparison on a common basis, specifically, the electronic coupling of the redox species to an electronic state of the electrode.

A brief review of the rate laws that describe charge-transfer processes at four types of interfaces is first presented. The rate-constant relationships for these four systems are then derived using a common theoretical framework. Finally, this framework is used to establish analytical formulas that allow comparison between these rate constants based on reference to readily measured observables. The four systems are (a) a metallic

electrode with redox acceptor species located at a known, fixed distance from the electrode surface, (b) a metallic electrode with a random distribution of redox acceptors dissolved in the solution phase, (c) a semiconducting electrode with redox acceptor species located at a known, fixed distance from the electrode surface, and (d) a semiconducting electrode with a random distribution of redox acceptors dissolved in the solution phase. Although the equations given herein have been derived for electron transfer from the electrode to the solution (cathodic current flow), analogous expressions are readily obtained for electron transfer from the solution to the electrode (anodic current flow).

II. Basic Kinetic Equations for Heterogeneous Charge-Transfer Reactions

For a metal electrode with redox acceptors located at a distance r from the electrode surface, the electron flux that defines the charge-transfer rate, $\text{rate}_m(r, E)$, at a specific electrode potential, E , is given by

$$\text{rate}_m(r, E) = k_m(r, E) C(r) \quad (1)$$

where $C(r)$ is the acceptor coverage, in cm⁻², that is present at a distance r from the electrode surface. The rate constant $k_m(r, E)$ has units of s⁻¹ so that a flux is obtained from this rate expression. For a set of redox acceptors affixed to the electrode, eq 1 is a potential-dependent function that must be evaluated at the particular distance of interest.

In the case of a metal electrode with redox acceptors randomly distributed in solution, the rate expression is

$$\text{rate}_m(E) = k_m(E)[A] \quad (2)$$

where $[A]$ is the concentration, in cm⁻³, of the redox species in the interfacial region, and $k_m(E)$ is the conventional charge-

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transfer rate constant at a metal electrode.¹⁴ The units of $k_m(E)$ are therefore cm s^{-1} .

For a semiconducting electrode with redox acceptors located at a distance r from the electrode surface, the appropriate expression is

$$\text{rate}_{\text{sc}}(r, E) = k_{\text{sc}}(r) n_s(E) C(r) \quad (3)$$

where $\text{rate}_{\text{sc}}(r, E)$ and $k_{\text{sc}}(r)$ are the rate (flux) and the distance-dependent heterogeneous rate constant, respectively. In this expression, the electron concentration at the surface of the semiconductor, $n_s(E)$, is explicitly written in the rate law. This occurs because, unlike at a metal electrode, the value of $n_s(E)$ for a semiconductor electrode is a quantity that can be varied experimentally.^{13–15} Since the observed flux is linearly proportional to the value of $n_s(E)$, the flux must be divided by $n_s(E)$ in order to obtain the rate constant for this electrochemical process. As a result, the value of $k_{\text{sc}}(r)$ has units of $\text{cm}^3 \text{s}^{-1}$.

In the case of a semiconducting electrode with redox acceptors randomly distributed in solution, the rate expression is

$$\text{rate}_{\text{sc}}(E) = k_{\text{sc}} n_s(E) [A] \quad (4)$$

where $\text{rate}_{\text{sc}}(E)$ is the rate (flux) and k_{sc} is the heterogeneous rate constant. Following the same reasoning as above, k_{sc} has units of $\text{cm}^4 \text{s}^{-1}$ for charge transfer from a semiconductor electrode to a random distribution of redox acceptor species dissolved in solution.¹³

III. Fundamental Expressions for Interfacial Electron-Transfer Rate Constants

To unify the rate expressions for these four different systems, we refer to a theoretical treatment, based on Fermi's golden rule, which describes the rate of a kinetic process in terms of fundamental, quantum-mechanical parameters.^{16–18} Specifically, Fermi's golden rule relates the rate of a state crossing to the electronic coupling matrix element for the process and to the Franck–Condon density of states for an isoenergetic electron-transfer event at each energy of concern. This approach is valid only for nonadiabatic electron-transfer events, and modifications will be introduced where appropriate to account for situations in which adiabatic effects arise.^{11,12,17,19}

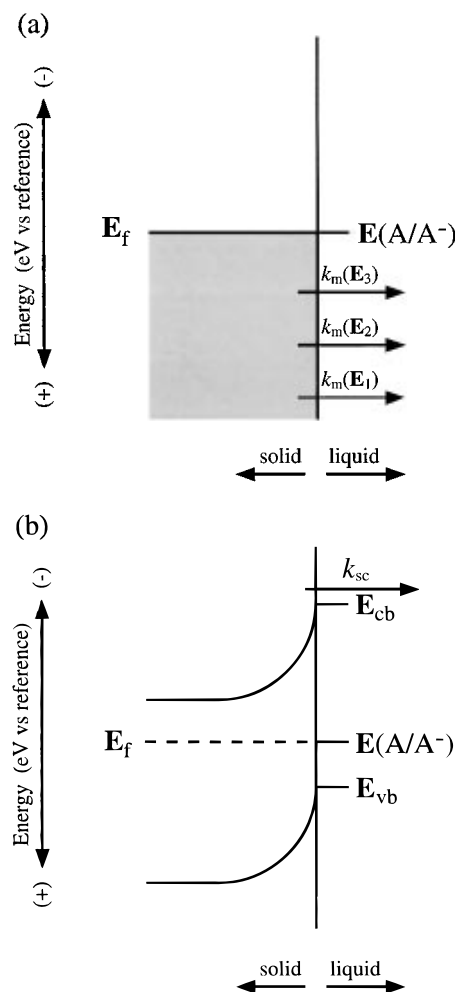
A. Metallic Electrodes: Fixed-Distance Redox Species.

For this scenario we follow the basic equations, outlined by Levich²⁰ and restated more recently by Chidsey and co-workers,^{1,4} that describe the situation in the classical Marcus limit of interfacial electron transfer.¹⁶ In this formalism, the electron-transfer rate at a metal electrode as a function of r is given by

$$\text{rate}_m(r, E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_m)^{-1/2} \} \{ C(r) \} \int_{-\infty}^{\infty} \overline{H_{\text{AB},m}^2(r, \mathbf{E})} \times \mathcal{F}(\mathbf{E}, E) \{ \rho_{\text{m,eff}}(\mathbf{E}) \} e^{\{-[q(\mathbf{E}-qE^\circ) + \lambda_m]^2 / 4\lambda_m k T\}} d\mathbf{E} \quad (5)$$

In this equation, h is Planck's constant, $\rho_{\text{m,eff}}(\mathbf{E})$ is the effective density of states in the metal (in units of states eV^{-1}) at the energy \mathbf{E} that couples in the charge-transfer event, k is Boltzmann's constant, T is the temperature, λ_m is the reorganization energy of the acceptor at the electrode surface, $\mathcal{F}(\mathbf{E}, E)$ is the Fermi occupancy function as a function of energy at the electrode potential E ,²¹ q is the charge of an electron, and E° is the formal potential of the redox species.²² The quantity $\overline{H_{\text{AB},m}^2(r, \mathbf{E})}$ represents the square of the matrix element that couples reactant and product states at \mathbf{E} , averaged over all degenerate states in the metal having an energy \mathbf{E} in a plane

SCHEME 1: Energetics of a Metal/Liquid Interface (a) and of a Semiconductor/Liquid Interface (b)^a



^a (a) The quantity $E(A/A^-)$ is the electrochemical potential of the solution, $k_m(E_n)$ is the charge-transfer rate constant at energy E_n , and E_f is the Fermi level of the electrode. The shaded region represents the occupied states in the metal. (b) The energy of the conduction band at the surface of the semiconductor is given by E_{cb} , the energy of the valence band at the surface of the semiconductor is given by E_{vb} , and the rate constant at energies $E \approx E_{cb}$ is k_{sc} .

parallel to the solid/liquid interface. The value of $\overline{H_{\text{AB},m}^2(r, \mathbf{E})}$ has units of $\text{eV}^2 \text{state}^{-1}$.

Assuming the effective density of states²³ and the matrix coupling elements¹ are independent of energy, eq 5 can be recast as follows:

$$\text{rate}_m(r, E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_m)^{-1/2} \} \{ C(r) \} \{ \overline{H_{\text{AB},m}^2(r)} \} \{ \rho_{\text{m,eff}} \} \times \int_{-\infty}^{\infty} \mathcal{F}(\mathbf{E}, E) e^{\{-[q(\mathbf{E}-qE^\circ) + \lambda_m]^2 / 4\lambda_m k T\}} d\mathbf{E} \quad (6)$$

The definite integral in eq 6 defines the energy range over which the charge-transfer process occurs and properly weights the rate constant at each energy according to the appropriate Franck–Condon density of states for the reaction (Scheme 1a). This density of states arises from the nuclear reorganization required by the reactants and products to achieve an isoenergetic electron-transfer event. If λ and E are known, then the value of the definite integral can be computed by numerical integration.

The only remaining quantity required to compute the rate constant is therefore the number of states eV^{-1} that participate in the charge-transfer process, $\rho_{\text{m,eff}}$. The density of states, D_m ,

is known for most metals from application of the Drude free-electron gas model.²³ Taking the electron concentration, N_m (in electrons cm^{-3}), at the Fermi level of the metal and dividing by the Fermi energy, E_f , yields

$$D_m = \frac{3}{2} \left(\frac{N_m(E_f)}{E_f} \right) \quad (7)$$

Here D_m is assumed to be approximately independent of energy.²³ The number of states per atom per eV in the metal, ρ_m , can then be obtained by dividing D_m by the atomic density of the solid, d_m . For gold, $\rho_m = 0.27$ states $\text{atom}^{-1} \text{eV}^{-1}$.

Of these states, however, only a certain fraction will be effective in facilitating the interfacial charge-transfer event. This fraction is l_m/δ_m , where l_m (in cm) is the effective coupling length of the redox acceptor wave function into the metal and δ_m is the average diameter of an atom in the metal lattice (in units of cm atom^{-1}). Thus, the effective density of states for the charge-transfer process is

$$\rho_{m,\text{eff}} = \rho_m \frac{l_m}{\delta_m} \approx D_m \frac{l_m}{d_m^{2/3} (6/\pi)^{1/3}} \quad (8)$$

Assuming an effective coupling length, l_m , taken by Chidsey to be 1×10^{-8} cm into the electrode,¹ therefore allows calculation of the total number of effective states eV^{-1} that participate in the charge-transfer process. With $l_m \approx 3 \times 10^{-8}$ cm, approximately one atom is effective in the coupling process, yielding a total effective density of states of approximately 0.27 states eV^{-1} .

Since the rate is measured as a flux of charge through the electrode surface, comparison of the rate law of eq 1 and the rate expression of eq 6 shows that

$$k_m(r, E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_m)^{-1/2} \} \overline{\{ H_{AB,m}^2(r) \} \{ \rho_{m,\text{eff}} \} I(\lambda_m, E)} \quad (9)$$

where $I(\lambda_m, E)$ is the definite integral in eq 6. For a redox species located at a specific, fixed distance r_A from the electrode, the rate constant, $k_{m,r_A}(E)$, is given by

$$k_{m,r_A}(E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_m)^{-1/2} \} \overline{\{ H_{AB,m,r_A}^2 \} \{ \rho_{m,\text{eff}} \} I(\lambda_m, E)} \quad (10)$$

where $\overline{H_{AB,m,r_A}^2}$ is the value of $\overline{H_{AB,m}^2(r)}$ at $r = r_A$. Measurement of the rate constant $k_{m,r_A}(E)$ thus allows calculation of the coupling per state from eq 10, assuming that the reorganization energy is known or has been determined experimentally for the process of concern.

B. Metallic Electrodes: Random Distribution of Dissolved Redox Acceptors. Equation 2 serves as the basis for an expression to obtain the rate constant, $k_m(E)$, that describes charge transfer from a metal electrode to a random distribution of dissolved redox species. In its simplest form, the nuclear coupling terms are taken to be independent of distance (see refs 4, 24, and 25 for restrictions on this approximation), and the electronic coupling in the nonadiabatic regime decays approximately exponentially with distance from the electrode.^{4,17,26} Thus, the expected rate expression is

$$\text{rate}_m(E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_m)^{-1/2} \} [A] \int_{r_0}^{\infty} \int_{-\infty}^{\infty} \overline{\{ H_{AB,m}^2(\mathbf{E}) \} e^{-\beta_m(r-r_0)}} \times \mathcal{F}(\mathbf{E}, E) \{ \rho_{m,\text{eff}}(\mathbf{E}) \} e^{-[q(\mathbf{E}-qE^\circ) + \lambda_m]^2/4\lambda_m k T} d\mathbf{E} dr \quad (11)$$

where $\overline{H_{AB,m}^2(\mathbf{E})}$ is the square of the electronic coupling matrix element observed at r_0 , the distance of closest approach of the redox species to the electrode surface, averaged over all degenerate states at each \mathbf{E} and averaged over the plane that lies parallel to the electrode surface, and β_m is the coupling attenuation factor. If $\rho_{m,\text{eff}}(\mathbf{E})$ and $\overline{H_{AB,m}^2(\mathbf{E})}$ are taken to be independent of energy, eq 11 reduces to

$$\text{rate}_m(E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_m)^{-1/2} \} [A] \overline{\{ H_{AB,m}^2 \} \{ \beta_m^{-1} \} \{ \rho_{m,\text{eff}} \} I(\lambda_m, E)} \quad (12)$$

where $\overline{H_{AB,m}^2}$ is the square of the electronic coupling matrix at r_0 , averaged over all degenerate states in a plane parallel to the solid/liquid contact for each \mathbf{E} . Comparison of this expression with eq 2 indicates that the rate constant for this process is

$$k_m(E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_m)^{-1/2} \} \overline{\{ H_{AB,m}^2 \} \{ \beta_m^{-1} \} \{ \rho_{m,\text{eff}} \} I(\lambda_m, E)} \quad (13)$$

Another approach to determining the electronic coupling to a random distribution of redox acceptors is to perform a series of kinetic measurements on electrodes having blocking layers of different thicknesses.³ Extrapolation to zero thickness of the blocking layer then allows determination of the electronic coupling matrix element that would be present with no barrier layer present.

C. Semiconducting Electrodes: Fixed-Distance Redox Species. The same formalisms can be used to obtain an expression for the rate constant at a semiconducting electrode. For acceptor ions located at any distance r from the electrode surface, the fundamental integral that relates the electronic coupling to the observed rate is exactly the same as that given in eq 5:

$$\text{rate}_{sc}(r, E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_{sc})^{-1/2} \} \{ C(r) \} \frac{l_{sc}}{d_{sc}^{2/3} (6/\pi)^{1/3}} \int_{-\infty}^{\infty} \overline{\{ H_{AB,sc}^2(r, \mathbf{E}) \} \times \mathcal{F}(\mathbf{E}, E) \{ D_{sc}(\mathbf{E}) \} e^{-[q(\mathbf{E}-qE^\circ) + \lambda_{sc}]^2/4\lambda_{sc} k T}} d\mathbf{E} \quad (14)$$

where the subscripts sc denote the appropriate values of quantities for the semiconductor electrode and a relationship analogous to that of eq 8 has been used to express the effective density of states that couples in the charge-transfer event.

A significant difference between a semiconducting and a metallic electrode is in the form of the density of states, $D_{sc}(\mathbf{E})$, and in the occupancy of these states at room temperature. For a semiconductor, electron transfer occurs only through a narrow distribution of energies near the bottom of the conduction band edge at the semiconductor/liquid interface (Scheme 1b). Thus, the nuclear terms are essentially constant over the region where the integrand in eq 14 is nonnegligible, and one obtains

$$\text{rate}_{sc}(r, E) = \frac{4\pi^2}{h} \{ (4\pi k T \lambda_{sc})^{-1/2} \} \{ C(r) \} \overline{\{ H_{AB,sc}^2(r) \}} \frac{l_{sc}}{d_{sc}^{2/3} (6/\pi)^{1/3}} \times e^{-[(\mathbf{E}_{cb} - qE^\circ) + \lambda_{sc}]^2/4\lambda_{sc} k T} \int_{-\infty}^{\mathbf{E}_{cb}} \mathcal{F}(\mathbf{E}, E) \{ D_{sc}(\mathbf{E}) \} d\mathbf{E} \quad (15)$$

where \mathbf{E}_{cb} represents the energy of the conduction band edge at the surface of the semiconductor. In eq 15, the electronic

coupling represented by $\overline{H_{AB,sc}^2(r)}$ has been averaged over all degenerate states at \mathbf{E} in a plane parallel to the electrode surface and has been assumed to be independent of energy over the range of interest, as was done for the situation at a metallic electrode in eqs 6 and 12.

The integral in eq 15 is well-known to equal the effective density of states in the conduction band of the semiconductor, N_c (in units of states cm^{-3}), multiplied by the value of the Fermi function evaluated at the potential of interest.^{27–29} For a nondegenerately doped semiconductor, Boltzmann statistics can be used to describe accurately the value of the Fermi function for a semiconductor electrode under depletion conditions, and the integral in eq 15 reduces to^{27–29}

$$\int_{-\infty}^{\mathbf{E}_{cb}} \mathcal{F}(\mathbf{E}, E) \{D_{sc}(\mathbf{E})\} d\mathbf{E} = N_c e^{\{(\mathbf{E}_{cb} - qE(A/A^-) - qE)/kT\}} \equiv n_s(E) \quad (16)$$

This definition is thermodynamically rigorous at equilibrium, i.e., for $E = E(A/A^-) = \mathbf{E}_f/q$. As long as a Boltzmann-type relationship holds between the electron concentration at the surface of the solid and its value in the bulk, the definition in eq 16 is valid for any electrode potential E . Substituting eq 16 into eq 15 therefore yields

$$\text{rate}_{sc}(r, E) = \frac{4\pi^2}{h} \{ (4\pi kT \lambda_{sc})^{-1/2} \} \{ \overline{C(r)} \} \{ \overline{H_{AB,sc}^2(r)} \} \frac{l_{sc}}{d_{sc}^{2/3} (6/\pi)^{1/3}} \times e^{\{ -[(\mathbf{E}_{cb} - qE^\circ) + \lambda_{sc}]^2 / 4\lambda_{sc} kT \}} n_s(E) \quad (17)$$

The rate at optimal exoergicity occurs when $qE^\circ - \mathbf{E}_{cb} = \lambda_{sc}$. Comparing the rate expression of eq 17 when $qE^\circ - \mathbf{E}_{cb} = \lambda_{sc}$ with the rate law of eq 3, the rate constant at optimal exoergicity, $k_{sc,max}(r)$, is

$$k_{sc,max}(r) = \frac{4\pi^2}{h} \{ (4\pi kT \lambda_{sc})^{-1/2} \} \{ \overline{H_{AB,sc}^2(r)} \} \frac{l_{sc}}{d_{sc}^{2/3} (6/\pi)^{1/3}} \quad (18)$$

D. Semiconducting Electrodes: Random Distribution of Dissolved Redox Acceptors. In the case of a semiconductor electrode in contact with a random distribution of redox species dissolved in solution, the rate expression is identical to that given in eq 11:

$$\text{rate}_{sc}(E) = \frac{4\pi^2}{h} \{ (4\pi kT \lambda_{sc})^{-1/2} \} [A] \frac{l_{sc}}{d_{sc}^{2/3} (6/\pi)^{1/3}} \times \int_{r_0}^{\infty} \int_{-\infty}^{\infty} \{ \overline{H_{AB,sc}^2(\mathbf{E})} e^{\{-\beta_{sc}(r-r_0)\}} \} \times \mathcal{F}(\mathbf{E}, E) \{D_{sc}(\mathbf{E})\} e^{\{-[q(\mathbf{E} - qE^\circ) + \lambda_{sc}]^2 / 4\lambda_{sc} kT\}} d\mathbf{E} dr \quad (19)$$

where the subscript sc again denotes the parameters for a semiconductor electrode.

Applying the same treatment as above to remove the nuclear terms from the integral, analytically evaluating the remaining terms of the integral with respect to distance, and substituting eq 16 into eq 19 results in the following expression:

$$\text{rate}_{sc}(E) = \frac{4\pi^2}{h} \{ (4\pi kT \lambda_{sc})^{-1/2} \} [A] \{ \overline{H_{AB,sc}^2} \} \{ \beta_{sc}^{-1} \} \frac{l_{sc}}{d_{sc}^{2/3} (6/\pi)^{1/3}} \times e^{\{ -[(\mathbf{E}_{cb} - qE^\circ) + \lambda_{sc}]^2 / 4\lambda_{sc} kT \}} n_s(E) \quad (20)$$

where $\overline{H_{AB,sc}^2}$ has again been assumed to be independent of energy.

The rate constant at optimal exoergicity is thus readily obtained by relating the rate expressions of eqs 4 and 20 when $qE^\circ - \mathbf{E}_{cb} = \lambda_{sc}$:

$$k_{sc,max} = \frac{4\pi^2}{h} \{ (4\pi kT \lambda_{sc})^{-1/2} \} \{ \overline{H_{AB,sc}^2} \} \{ \beta_{sc}^{-1} \} \frac{l_{sc}}{d_{sc}^{2/3} (6/\pi)^{1/3}} \quad (21)$$

IV. Relationships between Rate Constants for Metal and Semiconductor Electrodes

A. Fixed-Distance Redox Acceptors. From eqs 8, 9, and 18, the following expression for the rate constant ratio between $k_{sc,max}(r)$ and $k_m(r, E)$ is obtained:

$$\frac{k_{sc,max}(r)}{k_m(r, E)} = D_m^{-1} \frac{\overline{H_{AB,sc}^2(r)}}{H_{AB,m}^2(r)} \left[\frac{l_{sc}}{l_m} \right] \left[\frac{d_m}{d_{sc}} \right]^{2/3} \left[\frac{\lambda_m}{\lambda_{sc}} \right]^{1/2} \Gamma^{-1}(\lambda_m, E) \quad (22)$$

The two kinetic quantities $k_m(r, E)$ and $k_{sc,max}(r)$ can be related experimentally if D_m is known and if the numerical value of the definite integral, I , in eq 6 can be determined for the specific situation of concern. Under these conditions, assuming that the average coupling per state is the same for a metal and a semiconductor electrode (i.e. $\overline{H_{AB,m}^2(r)} = \overline{H_{AB,sc}^2(r)}$), that the penetration length of the acceptor wave function into the solid is the same for a metal and a semiconductor electrode (i.e. $l_m = l_{sc}$), and that the ratio of the reorganization energies at each interface is unity, one obtains³⁰

$$k_{sc,max}(r) = k_m(r, E) D_m^{-1} \left[\frac{d_m}{d_{sc}} \right]^{2/3} \Gamma^{-1}(\lambda_m, E) \quad (23)$$

Evaluation of eq 23 at a particular distance therefore results in the desired relationship for the case of fixed-distance redox acceptors.

B. Random Distribution of Redox Acceptors. A similar analysis, but including the integration of the electronic coupling over distance, and assuming the ratio of β_m to β_{sc} is unity, allows one to relate the rate constants at metal (eq 13) and semiconductor (eq 21) electrodes for a random distribution of acceptor species. In the nonadiabatic limit

$$\frac{k_{sc,max}}{k_m(E)} = D_m^{-1} \frac{\overline{H_{AB,sc}^2}}{H_{AB,m}^2} \left[\frac{\beta_m}{\beta_{sc}} \right] \left[\frac{l_{sc}}{l_m} \right] \left[\frac{d_m}{d_{sc}} \right]^{2/3} \left[\frac{\lambda_m}{\lambda_{sc}} \right]^{1/2} \Gamma^{-1}(\lambda_m, E) \quad (24)$$

In this case, assumptions analogous to those that led to eq 23 yield

$$k_{sc,max} = k_m(E) D_m^{-1} \left[\frac{d_m}{d_{sc}} \right]^{2/3} \Gamma^{-1}(\lambda_m, E) \quad (25)$$

A simple, first-order approach to account for adiabaticity is to use eq 23 at each distance to relate $k_{sc,max}(r)$ to $k_m(r, E)$, with the constraint that $k_m(r, E) < k_{m,ad}$, where $k_{m,ad}$ is the maximum rate constant for charge transfer in the adiabatic limit.³¹ Typically $k_{m,ad} = 10^{13} \text{ s}^{-1}$ in polar solvents,¹⁶ which is the value that will be used herein. The integration over distance must then be performed numerically in order to obtain a value for $k_{sc,max}$:

$$k_{sc,max} = \{ \int_{r_0}^{\infty} k'_m(r, E) dr \} D_m^{-1} \left[\frac{d_m}{d_{sc}} \right]^{2/3} \Gamma^{-1}(\lambda_m, E) \quad (26)$$

where

$$k'_m(r,E) \equiv \begin{cases} k_{m,ad} & \text{for } k_m(r,E) > k_{m,ad} \\ k_m(r,E) & \text{for } k_m(r,E) \leq k_{m,ad} \end{cases} \quad (27)$$

C. Relation between Fixed-Distance Measurements at Metal Electrodes and Rate Constant Data for Randomly Dissolved Acceptors at Semiconductor Electrodes. The relationship between the rate constant $k_{sc,max}$ obtained for a random distribution of acceptor species at a semiconductor electrode and the distance-dependent measurements of $k_m(r,E)$ for species immobilized on a metal electrode can also be derived from the fundamental rate equations given above. If the value of $k_m(r,E)$ is known at a distance $r = r_A$, and β_m is known from experiment, then in the nonadiabatic limit, $k_m(E)$ can be determined from the following:

$$k_m(E) = k_{m,r_A}(E) \beta_m^{-1} e^{\{\beta_m r_A\}} \quad (28)$$

Then, substituting eq 28 into eq 25, one obtains

$$k_{sc,max} = k_{m,r_A}(E) \beta_m^{-1} e^{\{\beta_m r_A\}} D_m^{-1} \left[\frac{d_m}{d_{sc}} \right]^{2/3} \Gamma^{-1}(\lambda_m, E) \quad (29)$$

To incorporate adiabatic effects, the integral must be computed numerically using eqs 26 and 27.

D. Relation between Measurements through Insulating Layers at Metal Electrodes and Rate Constant Data for Randomly Dissolved Acceptors at Semiconductor Electrodes. The formalism presented above can also be used to relate $k_{sc,max}$ to a rate constant for charge transfer through a blocking layer on a metal electrode to a random distribution of acceptor species. If the thickness of the blocking layer is r_b , the attenuation coefficient through the blocking layer is $\beta_{m,b}$, and the potential-dependent rate constant observed for the metal electrode at this thickness is $k_{m,r_b}(E)$, then in the nonadiabatic limit, extrapolation to zero thickness of the blocking layer yields $k_m(E)$:

$$k_m(E) = k_{m,r_b}(E) e^{\{\beta_{m,b} r_b\}} \quad (30)$$

Again using eq 24, and assuming $\beta_{m,b}$ has been determined experimentally, one can determine $k_{sc,max}$:

$$k_{sc,max} = k_{m,r_b}(E) e^{\{\beta_{m,b} r_b\}} D_m^{-1} \left[\frac{d_m}{d_{sc}} \right]^{2/3} \Gamma^{-1}(\lambda_m, E) \quad (31)$$

V. Analysis of Experimental Data

The equations presented above can be used to compare the experimental results of various electrode systems in terms of the values of their electronic coupling. In addition, the equations can be used to relate the rate constant measured at a metallic electrode to the rate constant that would be measured for the same redox species at a semiconducting electrode, within the constraints of the assumptions described above. In this section, we perform such comparisons for various electrochemical systems of current interest.

Potential-step experiments using Au electrodes modified with ferrocene-terminated alkanethiols ($(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{CO}_2\text{-(CH}_2\text{)}_{16}\text{SH}$) have provided data that are especially suitable for such an analysis.¹ In this system, a heterogeneous rate constant, $k_{m,r_A}(E)$, of 6000 s^{-1} was observed at an overpotential of -0.68 V . A fit to the kinetic data at several values of the overpotential yielded a reorganization energy of 0.85 eV . Numerical integration at $\lambda_m = 0.85 \text{ eV}$ and $E - E^\circ = -0.68 \text{ V}$ results in a value of $I(\lambda_m, E) = 0.112 \text{ eV}$. Assuming a value of $\beta_m = 1.11$ per CH_2 unit,⁴ and 19 effective methylene units linking the redox

species to the metal surface, the value of $k_m(E)/I(\lambda_m, E)$ can be established from eq 28 as $7.3 \times 10^5 \text{ cm eV}^{-1} \text{ s}^{-1}$. Use of eq 29 yields a predicted value of $k_{sc,max} = 5.1 \times 10^{-17} \text{ cm}^4 \text{ s}^{-1}$ for this system.

A similar system, employing thiols terminated with pentaamine(pyridine)ruthenium $[(\text{HS}(\text{CH}_2)_{15}\text{CONHCH}_2(\text{py}))\text{Ru}(\text{NH}_3)_5]^{2+}$,² has yielded values of $k_{m,r_A}(E) = 202 \text{ s}^{-1}$ at an overpotential of -0.37 V . Under these conditions, $I(\lambda_m, E) = 0.0439 \text{ eV}$ for the experimentally determined values of $\lambda = 0.6 \text{ eV}$ and $E - E^\circ = -0.37 \text{ V}$. Applying the measured value of $\beta_m = 0.98 \text{ \AA}^{-1}$ for this system, and assuming that the electroactive group is separated from the electrode by 19 effective methylene units (24 \AA) (ref 2), $k_m(E)/I(\lambda_m, E)$ and $k_{sc,max}$ are computed to be $7.7 \times 10^5 \text{ cm eV}^{-1} \text{ s}^{-1}$ and $5.4 \times 10^{-17} \text{ cm}^4 \text{ s}^{-1}$, respectively. Adiabatic effects were not considered in either of the two systems described above, since the computed values of $k_{m,r_A}(E)$ never exceeded $k_{m,ad}$, even at $r = r_o$.

Experimental rate constants for randomly dissolved species at metal electrodes coated with a blocking layer, $k_{m,r_b}(E)$, can also be related to $k_{sc,max}$ for semiconductor electrodes. In this situation, use of eq 31 is required. Terrettaz et al. have published voltammetric data for the reaction of freely diffusing $[\text{Fe}(2,2'\text{-bipyridine})_2(\text{CN})_2]^+$ on insulated Au electrodes. These data have yielded excellent agreement with the predicted dependence of $k_{m,r_b}(E)$ on E (eq 12). Specifically, a value of $k_{m,r_b}(E) = 7.8 \times 10^{-3} \text{ cm s}^{-1}$ has been reported at an applied bias of -0.73 V vs E° , and a fit of the entire data set yielded a value for $\lambda = 0.79 \text{ eV}$ for this redox couple at Au electrodes.³ With these values of $E - E^\circ$ and λ , the definite integral $I(\lambda_m, E)$ can be evaluated numerically to be 0.195 eV . Extrapolation of $k_{m,r_b}(E)$ to zero thickness of the blocking layer can be performed with the experimentally observed $\beta_{m,b}$ of 1.08 per methylene unit and assuming a 16-methylene-unit barrier length. This yields an expected value of $k_m(E)/I(\lambda_m, E) = 1.3 \times 10^6 \text{ cm eV}^{-1} \text{ s}^{-1}$ for the reaction of $[\text{Fe}(2,2'\text{-bipyridine})_2(\text{CN})_2]^+$ at an unmodified Au electrode. Use of eq 31 thus predicts $k_{sc,max} = 8.9 \times 10^{-17} \text{ cm}^4 \text{ s}^{-1}$ for this system.

VI. Discussion

The calculations presented above indicate that experimental data support previous estimates, based on various semiclassical and statistical mechanical models, that $k_{sc,max}$ for charge transfer from a semiconductor electrode to a randomly distributed, nonadsorbing, outer-sphere redox species should be approximately 10^{-17} – $10^{-16} \text{ cm}^4 \text{ s}^{-1}$.^{13,32} This value is in accord with recent experimental data obtained in our laboratories for InP/liquid and Si/liquid contacts.^{6,7} Moreover, this value for $k_{sc,max}$ is consistent with the upper bounds set on the charge-transfer rate constant from earlier kinetic studies of n-GaAs/ CH_3CN –ferrocene⁺⁰ interfaces.⁵

It is interesting to note that theory and experimental data comparing the behavior of semiconductor and metal electrodes appear to agree very closely even though a number of approximations have been made in the theoretical analysis of this work. The electronic coupling between redox acceptors and atoms in either the semiconductor or the metal electrode has been assumed to be constant in eq 23, even though this is most certainly only a rough approximation of the true physical situation. Similarly, the classical limit of the Marcus expression has been used in this work, as opposed to the full quantum-mechanical treatment of electron-transfer events.^{18,33} This limit seems to be an appropriate description of the experimental data available to date for charge transfer at metal/liquid interfaces,^{1,4} but more refined models would explicitly incorporate quantum modes of the electron-transfer events into treatments that

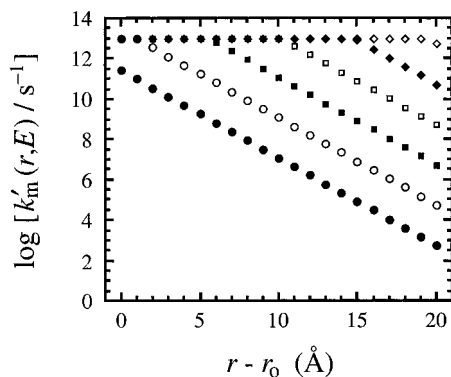


Figure 1. Plot of $k'_m(r,E)$ vs the relative distance of the redox species to the distance of closest approach to the electrode surface for various values of $H_{AB,m}^{o2}$ as indicated in Table 1. The value of β_m was taken to be 1.0 \AA^{-1} .

describe charge transfer at both semiconductor and metal electrode systems.^{18,33} Additionally, the Drude model has been used in the present work to provide an estimate of the density of states in the metal electrode, but more refined models would use band structure calculations and photoemission data to obtain more accurate values of ρ_m (and the energy dependence of ρ_m) for the specific metals used in the comparison with semiconductor electrodes. Similarly, the present level of analysis ignores the constraint of momentum conservation on the electron-transfer process. To date, such a level of detail has not been used to analyze the experimental data obtained on metal electrodes^{1,4} and thus has not been used in the present comparison, although it would be included in a more complete theoretical treatment of both systems. Finally, the comparisons between rate constants for charge transfer to random distributions of acceptors at metal and semiconductor electrodes implicitly assume similar dependencies of the solvent reorganization energy on the distance between the electrode and the acceptor in both types of solid/liquid contacts. Despite these approximations, the order-of-magnitude estimates of $k_{sc,max}$ obtained from the current level of theoretical treatment seem to be in excellent accord with the experimental data available at present on these electrode systems.

Nozik and co-workers have proposed that rate constants at semiconductor electrodes can possibly have values of 10^{-12} – $10^{-10} \text{ cm}^4 \text{ s}^{-1}$,^{34–38} although to our knowledge no robust experimental data to support such large rate-constant values are currently available in the literature.³⁹ The expressions presented above allow an evaluation of the electronic coupling that would be required in order to produce such a value of $k_{sc,max}$.

Figure 1 plots the value of $k'_m(r,E)$ calculated from eqs 9 and 27 as a function of $r - r_0$ for various values of the electronic coupling at contact, $H_{AB,m}^{o2}$, and $l_{sc} = 3 \times 10^{-8} \text{ cm}$. The corresponding values of $k_{sc,max}$, calculated using eq 26, are given in Table 1. Figure 2 plots the value of $k'_m(r,E)$ as a function of $r - r_0$ for various values of β_m , and Table 2 lists the corresponding values of $k_{sc,max}$.

In the nonadiabatic limit, the rate constant at each distance, and therefore the value of $k_{sc,max}$, increases linearly with the square of the electronic coupling per unit energy to the electrode. According to eq 26 with $l_{sc} = 3 \times 10^{-8} \text{ cm}$, this behavior occurs up to $k_{sc,max} = 10^{-16} \text{ cm}^4 \text{ s}^{-1}$. At this point, the electronic coupling matrix element at contact, i.e., at $r = r_0$, is at, or is very close to, the adiabatic limit at room temperature. This is also the situation observed experimentally for coupling between Au surfaces and a variety of redox species,^{1–4} indicating that, to first order, the behavior of semiconducting electrodes can

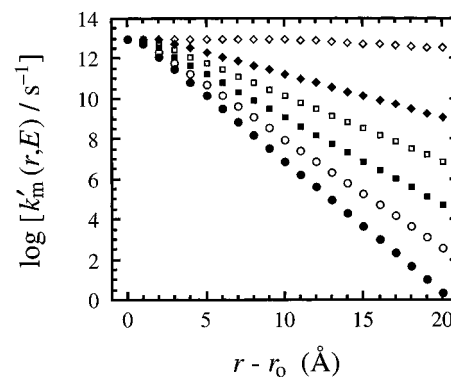


Figure 2. Plot of $k'_m(r,E)$ vs the relative distance of the redox species to the distance of closest approach to the electrode surface for various values of β_m as indicated in Table 2. The value of $H_{AB,m}^{o2}$ was taken to be $0.05 \text{ eV}^2 \text{ state}^{-1}$.

TABLE 1: Values of $k_{sc,max}$ as a Function of the Electronic Coupling at Contact for the Data Plotted in Figure 1

symbol in Figure 1	$H_{AB,m}^{o2} [\text{eV}^2 \text{ state}^{-1}]$	$k_{sc,max} [\text{cm}^4 \text{ s}^{-1}]^a$
●	5×10^{-4}	1.6×10^{-18}
○	5×10^{-2}	1.2×10^{-16}
■	5×10^0	4.1×10^{-16}
□	5×10^2	6.9×10^{-16}
◆	5×10^4	9.8×10^{-16}
◇	5×10^6	1.3×10^{-15}

^a A value of $\beta_m = 1.0 \text{ \AA}^{-1}$ was used for these calculations.

TABLE 2: Values of $k_{sc,max}$ as a Function of β_m for the Data Plotted in Figure 2

symbol in Figure 2	$\beta_m [\text{\AA}^{-1}]$	$k_{sc,max} [\text{cm}^4 \text{ s}^{-1}]^a$
◇	0.1	1.2×10^{-15}
◆	0.5	2.4×10^{-16}
□	0.75	1.6×10^{-16}
■	1.0	1.2×10^{-16}
○	1.25	9.7×10^{-17}
●	1.5	8.1×10^{-17}

^a A value of $H_{AB,m}^{o2} = 5 \times 10^{-2} \text{ eV}^2/\text{state}$ was used for these calculations.

be understood quantitatively using the same framework that has been developed to describe charge transfer in metallic electrode systems. The value for $k_{sc,max} = 10^{-16}$ – $10^{-17} \text{ cm}^4 \text{ s}^{-1}$ thus not only agrees with the theoretical expectations for a semiconducting electrode system that has a nearly adiabatic coupling at contact and a coupling attenuation factor similar in magnitude to that measured at metallic electrodes (eqs 26 and 27) but also agrees with the experimental behavior of such systems ($k_{sc,max}$ for Si/CH₃OH = $6 \times 10^{-17} \text{ cm}^4 \text{ s}^{-1}$; $k_{sc,max}$ for n-InP/CH₃OH = $3 \times 10^{-16} \text{ cm}^4 \text{ s}^{-1}$)^{6,7} in satisfying detail.

Inspection of Tables 1 and 2 also reveals that the value of $k_{sc,max}$ is close to 10^{-16} – $10^{-17} \text{ cm}^4 \text{ s}^{-1}$ for a wide range of parameters that are chemically reasonable for an outer-sphere charge-transfer process. For $H_{AB,m}^{o2} = 5 \times 10^{-2} \text{ eV}^2 \text{ state}^{-1}$ and $l_{sc} = 3 \times 10^{-8} \text{ cm}$, a variation over all chemically reasonable values of the coupling attenuation factor for electron tunneling through solvent,^{40–42} from $0.1 < \beta_m < 1.5 \text{ \AA}^{-1}$, yields $k_{sc,max} = 10^{-17}$ – $10^{-16} \text{ cm}^4 \text{ s}^{-1}$. Above this limit, $k_{sc,max}$ is rather insensitive to changes in $H_{AB,m}^{o2}$, l_{sc} , and β_m . Even a very large electronic coupling of $5 \text{ eV}^2 \text{ state}^{-1}$, which would certainly produce adsorption and other profound, readily observable chemical interactions between the redox species and the electrode (and thus probably would not produce a system

that obeyed the rate law of eq 4), only produces $k_{\text{sc,max}} = 4.1 \times 10^{-16} \text{ cm}^4 \text{ s}^{-1}$ if $\beta_{\text{m}} = 1.0 \text{ \AA}^{-1}$.⁴³ The Fermi golden rule-based treatment, at the level of analysis adopted in this work, thus appears to agree well with experimental data and with prior theoretical models predicting $k_{\text{sc,max}} = 10^{-17} - 10^{-16} \text{ cm}^4 \text{ s}^{-1}$ for outer-sphere charge-transfer processes at experimentally accessible semiconductor/liquid contacts.

Values of $k_{\text{sc,max}} \gg 10^{-16} \text{ cm}^4 \text{ s}^{-1}$ thus appear to require adiabatic charge transfer to occur over a significant distance into the electrolyte. In lieu of explicitly evaluating a full Landau–Zener expression for the transition between adiabatic and nonadiabatic limits,^{17,19} a value of $k_{\text{sc,max}}$ incorporating adiabaticity can be computed by assuming, for simplicity, a limiting value of $k_{\text{m,ad}} = 10^{13} \text{ s}^{-1}$.¹⁶ Using this approximation and eq 26, a value of $k_{\text{sc,max}} = 10^{-15} \text{ cm}^4 \text{ s}^{-1}$ requires adiabatic charge transfer over $\approx 16 \text{ \AA}$ into the electrolyte. Similarly, a value of $k_{\text{sc}} = 10^{-12} \text{ cm}^4 \text{ s}^{-1}$ would require adiabatic charge transfer over $\approx 1.6 \times 10^4 \text{ \AA}$ into the electrolyte, while $k_{\text{sc}} = 10^{-10} \text{ cm}^4 \text{ s}^{-1}$ would require adiabatic charge transfer over $\approx 0.2 \text{ mm}$ into the solution phase. Note that these values are not limited by any diffusional processes of redox species in the electrolyte solution, because if the charge-transfer rate constant to a redox species at a fixed distance falls below the value of $k_{\text{m,ad}}$ at a shorter distance from the electrode surface, then the result of an integration of the rate constant over distance into the electrolyte (eq 26) must produce a lower value of $k_{\text{sc,max}}$. The extremely rapid charge-transfer processes at extraordinarily long distances implied by $k_{\text{sc}} \geq 10^{-14} \text{ cm}^4 \text{ s}^{-1}$ appear to have no precedent, to our knowledge, in electrochemical^{1–4} or donor/acceptor systems.^{40–42,44–47} In view of the analysis presented above, it seems far more likely that such anomalously large interfacial rate constant values result from adsorption of redox species, charge transfer through surface states, or other types of interfacial kinetic processes that can produce large majority carrier currents at semiconductor/liquid contacts without reflecting the outer-sphere interfacial kinetic processes that are the focus of this theoretical analysis.

VII. Conclusion

We have shown it is possible to understand, in a unified framework, charge-transfer processes at metal/liquid and semiconductor/liquid contacts. Rate constants for these systems can be described in terms of the electronic coupling matrix elements that relate the two processes, and the two types of electrochemical rate constants can also be related to quantities commonly used in the literature to evaluate, both experimentally and theoretically, intermolecular and intramolecular donor/acceptor electron-transfer events. The quantum-mechanical, Fermi golden rule-based description of charge-transfer kinetics at semiconductor/liquid contacts agrees with prior statistical mechanical treatments and with prior electronic coupling estimates for such charge-transfer processes. It is also in excellent accord with robust experimental data available for the rate constants of such processes. The treatment also makes certain predictions regarding the experimental behavior of charge-transfer processes involving redox species immobilized on semiconducting electrode surfaces and forms the basis for further experimental investigations of such systems.

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- (21) The conventional electrochemical sign convention where positive energies are further from the vacuum level is used throughout this paper; hence $\mathcal{F}(\mathbf{E}, E) = (1 + e^{(qE + \mathbf{E}(\text{A/A}^-) - E)/kT})^{-1}$, where $\mathbf{E}(\text{A/A}^-)$ is the electrochemical potential of the solution. Also, q is unsigned, and electrochemical potentials $\mathbf{E}(\text{A/A}^-)$ are related to their Nernst potentials, $E(\text{A/A}^-)$, by $\mathbf{E}(\text{A/A}^-) = qE(\text{A/A}^-)$, so that positive redox energies and potentials are both further from the vacuum level. All redox potentials in this work are written as reduction potentials, so that more negative conduction band energies indicate larger driving forces for charge transfer to an acceptor of formal potential $E^\circ(\text{A/A}^-)$. Thus, under such conditions the effective driving force for interfacial electron transfer, ΔG° , equals $-nF(E^\circ(\text{A/A}^-) - (\mathbf{E}_{\text{cb}}/q))$, and ΔG° is negative for a thermodynamically favorable reduction of the acceptor A by an electron in the conduction band of the semiconductor.
- (22) The Fermi level is strictly defined for equilibrium conditions; thus, the equations presented herein are only rigorously applicable for calculation of the rate of the equilibrium exchange process between the solid and the liquid. However, as long as the rates of electron equilibration and thermalization in the solid are sufficiently rapid, the equations presented herein are readily modified to describe the situation away from equilibrium through use of a quasi-Fermi level formalism which describes the occupancy statistics of carriers in the solid when a potential, E , is applied to the solid/liquid contact. The occupancy of states in the solid under such conditions can be computed according to the definition of $\mathcal{F}(\mathbf{E}, E)$ given in footnote 21 for any potential E , including the equilibrium case in which $E = E(\text{A/A}^-)$. This treatment allows recovery of the conventional Marcus-type or Butler–Volmer type current–potential relationships at a metal electrode and recovery of the standard exponential diode-like behavior of a semiconductor at various applied potentials from the equations presented herein; systems for which this Fermi level occupancy treatment do not apply are beyond the scope of this work and must be treated by a more sophisticated analysis than is available, to our knowledge, for any electrochemical system to date.
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(30) It is not necessary that the conditions $\overline{H_{AB,m}^2(r)} = \overline{H_{AB,sc}^2(r)}$ and $l_m = l_{sc}$ are satisfied separately to obtain eq 23. Only the product of the coupling per state and the coupling depth into the electrode affects the measured rate constant, so it is therefore sufficient that $\overline{H_{AB,m}^2(r)}l_m = \overline{H_{AB,sc}^2(r)}l_{sc}$ in order to obtain eq 23 and the relationships derived therefrom.

(31) A more rigorous approach to account for adiabaticity would be to incorporate a Landau–Zener-type treatment for the probability of crossing from the reactant to the product diabatic surfaces¹⁹ but the treatment used herein is reasonably accurate in most cases.¹⁹

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(39) Although values of $k_{sc} \approx 10^{-12} \text{ cm}^4 \text{ s}^{-1}$ have been reported for certain InP and GaAs electrodes,^{37,38} careful examination of these rate constants reveals that experimental artifacts resulting from electrode corrosion and/or passivation are likely responsible for the anomalously large rate constant values initially reported for these systems.⁵ Also see: Bansal, A.; Tan, M. X.; Tufts, B. J.; Lewis, N. S. *J. Phys. Chem.* **1993**, 97, 7309 and Nozik, A. J. Presented at the 211th National Meeting of the American Chemical Society; New Orleans, LA, March 1996, paper PHYS 11.

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(43) Note that our treatment has assumed that the coupling per state that is reached at the adiabatic limit is similar for a metal and for a semiconductor electrode, allowing eqs 26 and 27 to be derived. A treatment in which the adiabatic limit for the semiconductor electrode is defined as the coupling obtained when the prefactor in eq 18 has a value of 10^{13} s^{-1} produces limiting rate constants that are smaller by a factor of 10–20 than those calculated using eqs 26 and 27 as described in the text. A more detailed theoretical analysis would be required in order to obtain more improved estimates of $k_{sc,max}$ relative to those provided by these procedures and also to treat the transition region between the adiabatic and nonadiabatic situations in depth.

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(47) For example, assuming an attenuation coefficient of $\beta = 1.0 \text{ \AA}^{-1}$ for the electronic coupling matrix element through the solvent, the electronic coupling at contact that would be required to achieve a value of $k_{sc,max} = 10^{-12} \text{ cm}^4 \text{ s}^{-1}$ is $\approx 10^{70000} \text{ GeV}^2/\text{state}$, which is clearly nonphysical.