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Temperature dependence of the electronic factor in the nonadiabatic electron transfer at metal and semiconductor electrodes

Shachi Gosavi, Yi Qin Gao, R.A. Marcus *

Arthur Amos Noyes Laboratory of Chemical Physics, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

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Dedicated to Professor R. Parsons on the occasion of his retirement from the postion of the Editor in Chief of the Journal of Electroanalytical Chemistry and in recognition of many contributions to electrochemistry

Abstract

The temperature dependence of the electronic contribution to the nonadiabatic electron transfer rate constant (k_{ET}) at metal electrodes is discussed. It is found in these calculations that this contribution is proportional to the absolute temperature T. A simple interpretation is given. We also consider the nonadiabatic rate constant for electron transfer at a semiconductor electrode. Under conditions for the maximum rate constant, the electronic contribution is also estimated to be proportional to T, but for different reasons than in the case of metals (Boltzmann statistics and transfer at the conduction band edge for the semiconductor versus Fermi–Dirac statistics and transfer at the Fermi level, which is far from the band edge, of the metal). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous electron transfer rate constant; Metal electrode; Semiconductor electrode; Temperature dependence of electronic coupling matrix element

1. Introduction

In this article, the temperature dependence of the electronic factor in the expression for the nonadabatic rate constant (k_{ET}) is discussed, both for metals and for semiconductors. In the case of the electrochemical exchange current at metal electrodes the temperature dependence of k_{ET} is due to two parts: one part arises from the well known variation with temperature of the Franck–Condon factor. It has an exponential term and a pre-exponential term which, classically, is proportional to $T^{-1/2}$. The second part of the temperature variation arises from the increasing range of energies of electronic states in the metal near the Fermi level that can contribute significantly to the rate constant with increasing temperature. An experimental system of an alkanethiol monolayer adsorbed on two different metals, Au and Pt, is considered to investigate how this temperature dependence of the Fermi–Dirac distribution affects the rate. The metal electronic state dependence of the metal–reagent electronic coupling matrix element is included in the calculation. To a good approximation, the averaged electronic factor for the exchange current rate constant is calculated below to be proportional to T, the known proportionality when the electronic coupling element is energy-independent.

The temperature dependence of the electronic factor for nonadiabatic electron transfer at semiconductor electrodes is also discussed. For the present purpose, in lieu of detailed calculations, this factor is estimated using the free electron model. It is found to be proportional to the temperature T under conditions for the maximum of the rate constant, but the origin of the proportionality is quite different from that in the case of the electrochemical exchange current at metal electrodes.

* Corresponding author. Tel.: +1-626-3956566; fax: +1-626-7928485.

E-mail address: ram@caltech.edu (R.A. Marcus).

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In the following sections the theoretical model used and the predictions that can be made from this model are described.

2. Theory

2.1. Metals

The rate constant for nonadiabatic electron transfer from a metal to a reactant at the interface (k_{ET}) is given by [1]

$$k_{ET} = \frac{2\pi}{\hbar}\int d\varepsilon FC|V(\varepsilon)|^2 f(\varepsilon) \quad (1)$$

where $f(\varepsilon)$ is the Fermi–Dirac distribution with ε measured relative to μ, the chemical potential of the electrons in the electrode,

$$f(\varepsilon) = \frac{1}{1+e^{\varepsilon/k_BT}} \quad (2)$$

FC is the Franck–Condon factor, which in its classical form is

$$FC = \frac{e^{-(\lambda - e\eta - \epsilon)^2/4\lambda k_BT}}{(4\pi\lambda k_BT)^{1/2}} \quad (3)$$

Here, λ is the reorganization energy, e the electronic charge, η the overpotential, and $|V(\varepsilon)|^2$ the square of the electronic coupling matrix element, integrated over the distribution of the electronic states at the given ε:

$$|V(\varepsilon)|^2 = \int d^3k |H_{kA}|^2 \delta(\varepsilon(k) - \varepsilon) \quad (4)$$

where $|H_{kA}|$ denotes $\langle \Psi_k | H | \Psi_A \rangle$ and describes the electronic coupling between the redox agent (A) and each electronic state of wave vector k of the electrode.

Eqs. (1)–(4) are given for the reduction rate constant. The rate constant for the reverse reaction, which we will denote by k^r_{ET} is obtained by replacing ε by $-\varepsilon$ and η by $-\eta$. One can verify, for example, that the equilibrium constant k_{ET}/k^r_{ET} is then given by $\exp(e\eta/k_BT)$, as expected.

From Eqs. (1)–(3) we have

$$k_{ET} = \frac{2\pi}{\hbar}\frac{e^{-\lambda/4\kappa_BT}}{(4\pi\lambda k_BT)^{1/2}}\int_{-\infty}^{\infty} e^{\frac{-\varepsilon^2 + h(\varepsilon,\eta)}{4k_BT}} g(\varepsilon)|V(\varepsilon)|^2 d\varepsilon \quad (5)$$

where $g(\varepsilon)$ is given by

$$g(\varepsilon) = \frac{1}{2}\mathrm{sech}\left(\frac{\varepsilon}{2k_BT}\right) \quad (6)$$

and

$$h(\varepsilon,\eta) = 2(\lambda - \varepsilon)e\eta - (e\eta)^2 \quad (7)$$

In applications, the dependence of $|V(\varepsilon)|^2$ is normally neglected. The reorganization energy λ is then obtained in two different ways, one from a plot of $\ln k_{ET}$ versus η [2–13], and the other from a plot (noted below) involving $\ln(k^0/T^{1/2})$ versus $1/T$, or both [14–19]. While the effect of neglecting the dependence of $V(\varepsilon)$ on ε is expected to be small, it is estimated in the present paper. Results for finite η can also be estimated from the calculations, with appropriate additions, as discussed later.

When $\eta = 0$, Eq. (5) becomes k^0, the standard rate constant

$$k^0 = \frac{2\pi}{\hbar}\frac{e^{-\lambda/4k_BT}}{(4\pi\lambda k_BT)^{1/2}}\int_{-\infty}^{\infty} e^{-\varepsilon^2/4\lambda k_BT}(\varepsilon)|V(\varepsilon)|^2 d\varepsilon \quad (8)$$

We first consider, for comparison, the simplest case: both the dependence of $V(\varepsilon)$ on ε and the $\varepsilon^2/4\lambda k_BT$ term Eq. (8) are neglected. In that case the integral in Eq. (8) is a standard integral [20][1] yielding

$$k^0 \cong \frac{2\pi}{\hbar}\frac{e^{-\lambda/4k_BT}}{(4\pi\lambda k_BT)^{1/2}}\pi k_BT|V(0)|^2 \quad (9)$$

When the value of λ is obtained from Eq. (9) and a plot of the experimental rate constant k^0, $\ln(k^0/T^{1/2})$ versus $1/T$, we have

$$\lambda/k_B = -4\partial \ln(k^0 T^{-1/2})/\partial(1/T) \quad (10)$$

We next consider the case where the dependence of $|V(\varepsilon)|^2$ is neglected, as before, but where the $\varepsilon^2/4k_BT$ in Eq. (8) is included. In this case we have

$$k^0 \cong \frac{2\pi}{\hbar}\frac{e^{-\lambda/4k_BT}}{(4\pi\lambda k_BT)^{1/2}}\pi k_BT|V(0)|^2\langle e^{-\varepsilon^2/4\lambda k_BT}\rangle \quad (11)$$

where we have used [20] $\pi k_BT = \int_{-\infty}^{\infty} g(\varepsilon)d\varepsilon$ and where $\langle\rangle$ denotes an average over the distribution function, $g(\varepsilon)d\varepsilon/\int_{-\infty}^{\infty} g(\varepsilon)d\varepsilon$. The exponent is so small that the exponential in $\langle\rangle$ can be expanded, retaining only the first two terms. Use of standard integrals [20][1] then yields

$$k^0 = \frac{2\pi}{\hbar}\frac{e^{-\lambda/4k_BT}}{(4\pi\lambda k_BT)^{1/2}}\pi k_BT|V(0)|^2\left(1 - \frac{\pi^2 k_BT}{4\lambda}\right) \quad (12)$$

For a value [15] of $\lambda \cong 0.8$ eV and $k_BT \cong 0.025$ eV, the last factor in the parentheses, due to $\langle \exp(-\varepsilon^2/4\lambda k_BT)\rangle$ term, is 0.923, and so is close to unity. In the following the $\exp(-\varepsilon^2/4\lambda k_BT)$ in Eq. (8) will be replaced by unity.

In passing, we note that from Eq. (11) that the slope of $\ln(k^0(\lambda/k_BT)^{1/2})$ versus λ/k_BT equals $-(1/4)(1-\pi^2(k_BT/\lambda)^2)$, because of the smallness of k_BT/λ. The reciprocal of this quantity can, because of the smallness

[1] $\int_{-\infty}^{\infty} g(\varepsilon/2)^2 g(d\varepsilon) = (\pi k_BT)^3/4$, $\int_{-\infty}^{\infty} g(\varepsilon/2)^4 g(d\varepsilon) = (\pi k_BT)^5(5/16)$
$\int_{-\infty}^{\infty} g(\varepsilon/2)^6 g(d\varepsilon) = (\pi k_BT)^6(61/64)$

of the correction, be written, as -4.04. A numerical evaluation of the integral [15] gave -4.03, which is within the round off error. The difference of -4.03 from -4 is 1% and so can be neglected relative to other sources of error in λ.

The integral in Eq. (8) can now be written as

$$I(k_BT) = \int_{-\infty}^{\infty} g(\varepsilon)|V(\varepsilon)|^2 d\varepsilon \quad (13)$$

We have written the limits as $\pm\infty$, but of course the lower limit is finite. It equals the lower limit of the energy of the band, which is very negative. More than adequate for our purpose is changing the limits of integration to ± 1.1 eV.

The temperature dependence of $I(k_BT)$ arises from the weighting function, $g(\varepsilon)$, which becomes broader with increasing temperature. The $|V(\varepsilon)|^2$ depends only on ε and so is independent of temperature. However, because of the broadening of $g(\varepsilon)$ with increasing T, parts of $|V(\varepsilon)|^2$ at larger and smaller ε contribute more in the integral when the temperature is increased. For a $|V(\varepsilon)|^2$ replaced by $|V(0)|^2$, the integral in Eq. (12), is as already noted $|V(0)|^2\pi k_BT$.

For flat and broad bands, such as s and p bands, one expects $|V(\varepsilon)|^2$ to remain constant with ε. In that case, the temperature dependence arises mainly from the width of the weighting function, $g(\varepsilon)$, given in Eq. (6). For narrow bands such as d bands the density of states, ρ, changes fairly rapidly over a short energy range. If this feature leads to a large change in $|V(\varepsilon)|^2$ then widely varying values of $I(k_BT)$ become increasingly included in $I(k_BT)$ when the temperature is increased, and some deviation of the temperature dependence of $I(k_BT)$ from $|V(0)|^2\pi k_BT$ is expected. However, the d states do not couple as well into the donor/acceptor species in solution [21][2]; the large change in the density of d states with ε is diminished by the small coupling of these states, so leading again to an approximately constant $|V(\varepsilon)|^2$. In this case, the temperature dependence would remain about the same as in the case of the s and p bands, i.e., depending only on the width of the weighting function.

The accessible number of participating electronic states near the Fermi level ($\varepsilon = 0$) increases linearly with temperature, a result well known from the proportionality of the electronic specific heat of the metals to the temperature. However, this observation offers no information on the average strength of $|H_{kA}|^2$ as a function of ε. The question of the behavior of the matrix element, suitably averaged, is addressed in calculations in a later section.

Numerical results of the calculations based on Eqs. (4) and (8) (both with and without $\varepsilon^2/4\lambda k_BT$ neglected), are given in Section 3.1.

2.2. Semiconductors

In the case of electron transfer from a semiconductor to a reactant species in solution, the rate is first-order in the concentration of electrons in the semiconductor at the surface and first-order in the reactant. An expression for the second-order nonadiabatic rate constant k_{ET} was given earlier [22][3]

$$k_{ET} = \frac{2\pi}{\hbar}\frac{v}{\sqrt{4\pi k_BT}}\frac{1}{\beta_s} \frac{\int_0^{\infty} e^{-(\lambda+\Delta G^0-\varepsilon)^2/\lambda 4k_BT}\langle|\bar{V}(\varepsilon)|^2\rangle e^{-\varepsilon/k_BT}\rho(\varepsilon)d\varepsilon}{\int_0^{\infty} e^{-\varepsilon/k_BT}\rho(\varepsilon)d\varepsilon} \quad (14)$$

where $\langle|\bar{V}(\varepsilon)|^2\rangle$ is an electronic matrix element [22]

$$|\bar{V}(\varepsilon)|^2 = \frac{|V(\varepsilon)|^2}{\rho(\varepsilon)} \quad (15)$$

and

$$\rho(\varepsilon) = \int d^3\boldsymbol{k}\,\delta(\varepsilon(\boldsymbol{k}) - \varepsilon) \quad (16)$$

The average $\langle\rangle$ was over all orientations of the reactant at the contact distance [2]. In Eq. (14), v is the volume of the unit cell in the semiconductor (the wave functions appearing in $V(\varepsilon)$ are normalized to that volume), and β_s is the exponent for the decay of the square of the matrix element with distance.

We note, in passing, that in the experiments [23] $\Delta G°$ is varied by varying the redox reagent in solution. The maximum k_{ET}, k_{ET}^{max} determined in this way, corresponds to $\lambda + \Delta G° = 0$.

The exponent of the first factor in the integral in the numerator of Eq. (14) can be written as

$$\frac{(\lambda+\Delta G^0-\varepsilon)^2}{4\lambda k_BT} = \frac{(\lambda+\Delta G^0)^2}{4\lambda k_BT} - \frac{(\lambda+\Delta G^0)^2\varepsilon}{4\lambda k_BT} + \frac{\varepsilon^2}{4\lambda k_BT} \quad (17)$$

The first term in the r.h.s. of the above equation is independent of ε and can be removed from the integral. The second term varies much more slowly with ε than the ε/k_BT in the exponent of the third term in the

[2] In this reference and the present paper the surface of the metal is a (111) face. For some simpler surfaces with more symmetry elements the Z-transform method that we use is not necessary and the wavefunctions can be described in these cases by a simple sine-like function. We use extended Hückel (EH) theory to calculate the bridge coupling matrix elements in both the above article and the present paper. The EH method gives more accurate results for relative matrix elements and rates than it does for absolute values.

[3] The V_k in this article is denoted in the present paper by H_{kA}. Since the form of the electronic matrix element is the same for both semiconductors and metals Eqs. (4), (15) and (16) remain valid for both types of electrodes.

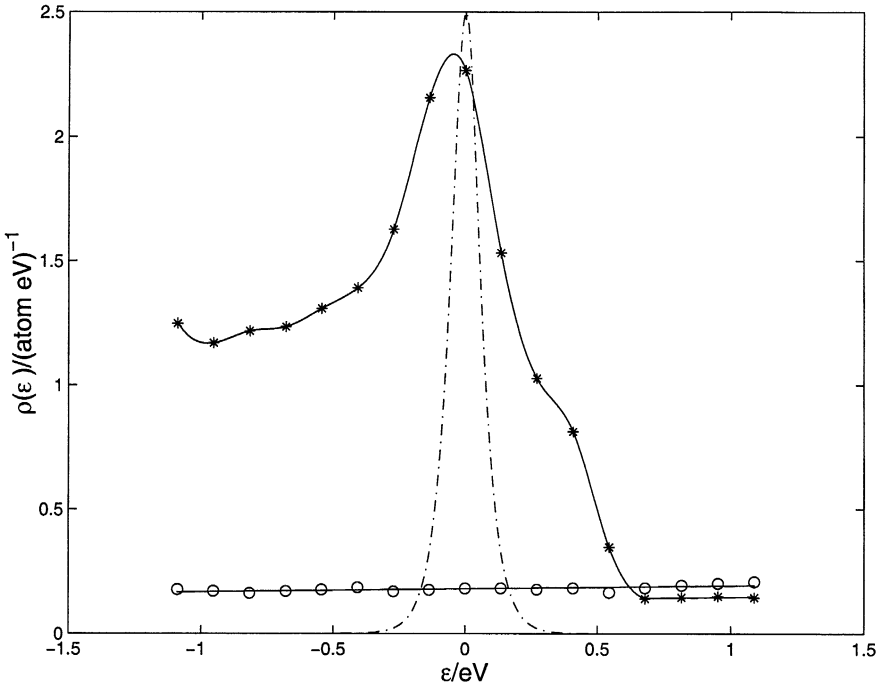

Fig. 1. Band structure of Au and Pt with the Fermi energies of each set to 0. ✱ is for Pt and ○ is for Au. $\rho(\varepsilon)$ is in units of number of states per atom per eV. The weighting function $g(\varepsilon)\times 5$ at $k_{\mathrm{B}}T = 0.025$ eV i.e. $T = 300$ K is also plotted (–·) to show the density of states which contribute to the integral in the rate constant k_{ET}. For simplicity a 'splined' fit is drawn through the points for $\rho(\varepsilon)$ for Pt.

integral in Eq. (14), when $\lambda + \Delta G^{\circ} \approx 0$ (the important region for $k_{\mathrm{ET}}^{\max}$, as noted above). The ratio of the third term in Eq. (17) to $\varepsilon/k_{\mathrm{B}}T$ is $\varepsilon/4\lambda$, which is very small since $\varepsilon \approx k_{\mathrm{B}}T$, i.e., 0.025 eV, and λ is typically 1 eV. The dependence of $(\lambda + \Delta G^{\circ} - \varepsilon)^2$ on ε in Eq. (17) can then be ignored, yielding

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}\frac{v}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}}\frac{1}{\beta_s} \mathrm{e}^{-(\lambda+\Delta G^{0}-\varepsilon)^2/4\lambda k_{\mathrm{B}}T}\frac{\int_0^{\infty}\langle|\overline{V}(\varepsilon)|^2\rangle \mathrm{e}^{-\varepsilon/k_{\mathrm{B}}T}\rho(\varepsilon)\mathrm{d}\varepsilon}{\int_0^{\infty}\mathrm{e}^{-\varepsilon/k_{\mathrm{B}}T}\rho(\varepsilon)\mathrm{d}\varepsilon} \quad (18)$$

as in eq. (A5) of Ref. [22]. Of particular interest is $k_{\mathrm{ET}}^{\max}$, which, obtained from Eq. (18) is

$$k_{\mathrm{ET}}^{\max} = \frac{2\pi}{\hbar}\frac{v}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}}\frac{1}{\beta_s}\frac{\int_0^{\infty}\langle|\overline{V}(\varepsilon)|^2\rangle \mathrm{e}^{-\varepsilon/k_{\mathrm{B}}T}\rho(\varepsilon)\mathrm{d}\varepsilon}{\int_0^{\infty}\mathrm{e}^{-\varepsilon/k_{\mathrm{B}}T}\rho(\varepsilon)\mathrm{d}\varepsilon} \quad (19)$$

When $|\lambda + \Delta G^{\circ}|/\lambda$ becomes different from zero, say, $\approx 1/2$, then the ratio of the second term in Eq. (17) to $\varepsilon/k_{\mathrm{B}}T$ becomes 1/4, which on integration, including a slowly varying $\overline{V}(\varepsilon)$ will affect the pre-exponential factor a little. The ratio of the last term in Eq. (17) to $\varepsilon/k_{\mathrm{B}}T$ becomes $\varepsilon/4\lambda$, which for an averaged value of $\varepsilon \approx \lambda/4$ in the sampling of εs for the exothermic direction, is still a relatively small though not negligible quantity. Accordingly, Eq. (18) is expected to suffice for typical conditions. When it does not suffice Eq. (14) could be used instead. However, our main interest here is in $k_{\mathrm{ET}}^{\max}$ and so in Eq. (19).

3. Applications

3.1. Metals

A particular system, an alkanethiol monolayer with 15 CH_2 units and with the redox agent $Ru(NH_3)_5Py^{2+}$ tethered to it is considered here. Only one alkanethiol molecule adsorbed on a metal electrode is used in our calculation, since it has been found that this approximation is reasonable, and adding more molecules does not have a large effect on the rate [24]. Two metals, gold (Au) and platinum (Pt) are considered, the method of Z-transforms and a tight binding Hamiltonian are used to obtain the wavefunctions of the metal. The details of the calculation are given elsewhere [21]. For the purpose of the calculations we use Eqs. (4), (15) and (16).

The metal Au has no d states near the Fermi level while the d band of Pt lies close to its Fermi level. The $\rho(\varepsilon)$ given by Eq. (16) is plotted in Fig. 1 for both these metals, as well as the $g(\varepsilon)$ at $T = 300$ K. The Fermi levels of both metals are used as the zeros for their respective εs.

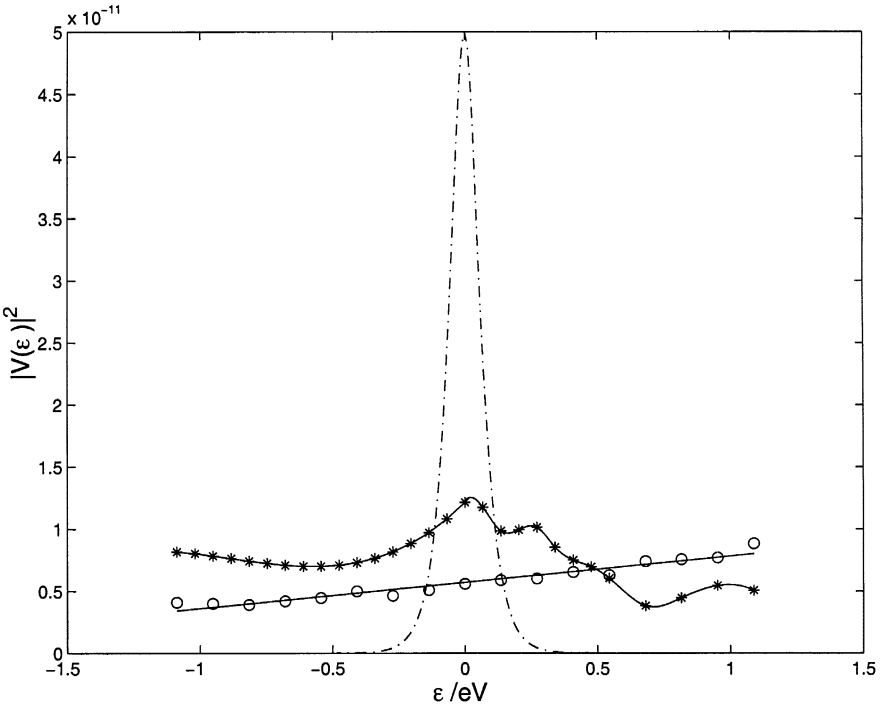

Fig. 2. A plot of $|V(\varepsilon)|^2$ vs. ε. ○ gives the plot for Au and ✱ gives the plot for Pt. A plot of $g(\varepsilon) \times 10^{-10}$ (–·) is also given. The Au curve is a best fit to the points, the Pt curve is a 'splined' fit.

The $|V(\varepsilon)|^2$ is plotted in Fig. 2 for the two metals as a function of ε. It is seen that even though the $|V(\varepsilon)|^2$ for Pt does change somewhat with the energy ε, the effect is considerably less than the change in $\rho(\varepsilon)$. Although the extent of ε is nonzero is $\sim \pm 0.3$ eV (Fig. 2) the validity of the $\lambda \ll \varepsilon$ approximation and the neglect of the ε^2 term should be checked against the full width at half maximum of the $g(\varepsilon)$ curve. The half-width is $\varepsilon \sim 0.066$ eV. Thus, with the usual values of $\lambda = 0.6$ to 1.2 eV the approximation is still valid.

Although only a narrow range of ε is needed for our purpose of calculating the standard reduction rate constant k^0, we have given in Fig. 2 a substantially larger range of ε. When large overpotentials $\pm e\eta$ are considered, electronic energy levels with a correspondingly large range of ε are needed for the evaluation of the integral. Accordingly, this larger range of εs is given in Fig. 2, should k_{ET} (or the reverse rate constant k_{ET}^{r} at larger $|\eta|$s, rather than just at $\eta = 0$, be needed. However, when large overpotentials are considered, the effect of the energy denominators should be included, e.g., Ref. [25].

The $\ln(I(k_BT))$ is plotted in Fig. 3 versus $\ln(k_BT)$ from $T \cong 120$–325 K with and without $\varepsilon^2/4\lambda k_BT$. A value of 0.8 eV is used for λ. The slope is close to unity without the $\varepsilon^2/4\lambda k_BT$ correction (1.00 for Au and 0.97 for Pt) and deviates a little from it with the correction (0.96 for Au and 0.93 for Pt). Thus, in both cases $I(k_BT) \propto k_BT$ is valid for the nonadiabatic electron transfer to Au and Pt. Accordingly, the temperature dependence of the electronic factor in Eq. (13) is proportional to T and so the k_{ET} in Eqs. (1)–(3) (apart from the exponential part of the Franck–Condon factor) is proportional to $T/T^{1/2}$, i.e. $T^{1/2}$. With the classical formulation for the Franck–Condon factor for the electrochemical exchange current $k_{ET} \propto T^{1/2} e^{-\lambda/4k_BT}$ for both metals and thus we expect it to apply for other metals at these temperatures.

The slopes from Fig. 3 can be used to evaluate the value of the prefactor in Eq. (10). We proceed by writing the integral in Eq. (8) as $C(k_BT)^{1+\Delta n}$, where Δn is the deviation of the slope from unity and C is some constant. Eq. (8) can then be written as

$$k^0 = \frac{2\pi}{\hbar} \frac{e^{-\lambda/4k_BT}}{(4\pi\lambda k_BT)^{1/2}} C(k_BT)^{1+\Delta n} \tag{20}$$

The above equation can then be used to find the value of $\partial \ln(k^0 T^{-1/2})/\partial(1/T)$. It equals $-\lambda/k_B[1/4 + \Delta n k_BT/\lambda]$, which gives instead of the factor of 4 in Eq. (10) a factor of $4/(1 + 4\Delta n k_BT/\lambda)$. For the slopes from Fig. 3, with $\lambda = 0.8$ eV and $k_BT = 0.025$ eV we get values of 4.02 and 4.04 for Pt (with and without $\varepsilon^2/4\lambda k_BT$ correction) and 4.00 and 4.02 for Au (with and without correction).

The slopes of the $\ln(I(k_BT))$ versus $\ln(k_BT)$ given above $(1 + \Delta n)$ could also have been obtained from an

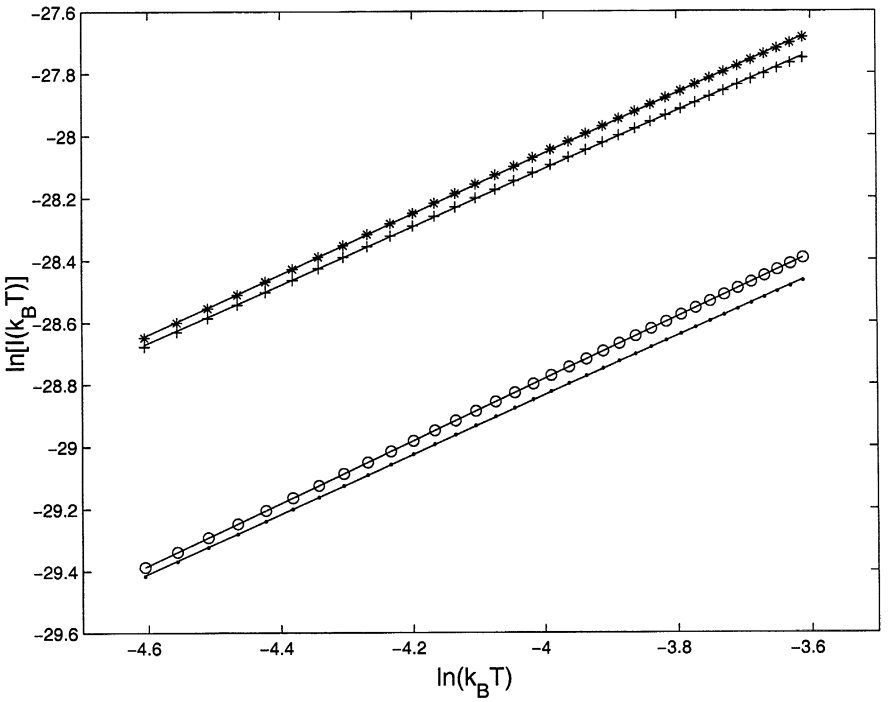

Fig. 3. A plot of ln $[I(k_BT)]$ vs. ln (k_BT). The slope gives the exponent of k_BT in $I(k_BT)$. The ✱ and + (with the $\varepsilon^2/4\lambda k_BT$ correction) points are for Pt and ○ and · (with correction) points are for Au. The slope for Au is 1.00 and 0.96 (with correction) and the slope for Pt is 0.97 and 0.93 (with correction).

expansion of $|V(\varepsilon)|^2$ in the vicinity of $\varepsilon = 0$, using the data in Fig. 2.

$$|V(\varepsilon)|^2 = |V(0)|^2(1 + a\varepsilon + b\varepsilon^2 + c\varepsilon^3 + d\varepsilon^4\ldots) \quad (21)$$

The terms having odd powers of ε do not contribute, and so we have

$$I(k_BT) = |V(0)|^2\pi k_BT[1 + (\pi k_BT)^2 b + 5(\pi k_BT)^4 d + \ldots] \quad (22)$$

Since the $|V(\varepsilon)|^2$ for Au is linear in ε at $\varepsilon = 0$, Fig. 2, b vanishes and it is clear why a plot of ln $(I(k_BT))$ versus ln (k_BT) was 1.00 for Au. Expanding $|V(\varepsilon)|^2$ around $\varepsilon = 0$ for Pt by fitting the Pt curve in Fig. 2 with various polynomial functions it was found that the calculated slope varied from 0.9 to 1.0, thus yielding an almost linear plot[4].

3.2. Semiconductors

To treat the T dependence for semiconductor electrodes using Eq. (18) or Eq. (19), calculations such as those given in Ref. [22] would need to be repeated at various temperatures. In the absence of those particular results we use here the free electron model [26][5] in which the matrix element H_{kA} (i.e. $\langle \Psi_k | H | \Psi_A \rangle$) at small ε is found to be proportional to k_z [27][6] (because Ψ_k is proporational to k_z), and so $|H_{kA}|^2 \propto k_z^2 \propto k^2/3 \propto \varepsilon$, where ε is the energy. Since $\rho(\varepsilon)$ varies as some (known) power of ε, one finds that the electronic factor, $\langle|\bar{V}(\varepsilon)|^2\rangle$ in Eq. (4), is proportional to k_BT. A consequence is that k_{ET}^{max} varies as $T/T^{1/2}$, i.e., $T^{1/2}$.

4. Discussion

Two differences between metals and the present nondegenerate semiconductors may be noted: (1) In the former the Fermi–Dirac distribution is needed, while the Boltzmann distribution suffices for the semiconductor. (2) As a first approximation the H_{kA} in Eq. (4),

[4] For a particular fit function we find a value of $b = -10.84$ and $d = 203.47$ which gives an average correction of 0.96 for a k_BT range of ~ 0.01 to 0.027 eV, i.e., $120 \leq T \leq 325$ K. Because of the peak of the Pt curve in Fig. 2 at the Fermi energy, the slopes of the Pt plots in Fig. 3 are sensitive to the fitted polynomial used.

[5] If in other cases, H_{kA} were proportional to a linear combination of k_x k_y and k_z, then $|H_{kA}|^2$ averaged near the conduction band edge would still be proportional to ε. In general, Ψ_k and thus the matrix element is proportional to $\sin(k_z)$, which becomes k_z only at a band-edge (small k_z). Like k_z, the distribution of $\sin(k_z)$ is hardly changed when ε is changed in the case of a metal since $\Delta \gg \varepsilon$.

[6] In the case of indirect bandgap semiconductors the k_x, k_y and k_z are replaced by $k_x - k_0$, $k_y - k_0$ and $k_z - k_0$ throughout and the same conclusion applies.

appearing via Eq. (15) in Eq. (19) or k_{ET}^{max}, is approximately proportional to k_z in the free electron model for the semiconductor [26]. Since $\langle|\bar{V}(\varepsilon)|^2\rangle$ is, as seen from above, proportional to k_z^2 and since the transfer is from the edge of the conduction band, it is also proportional to ε. In the case of the metal, however, the distribution of the ks is hardly changed when the energy ε relative to the Fermi level is changed. Thus, now $\langle|\bar{V}(\varepsilon)|^2\rangle$ is essentially independent of ε. Specifically, at the high energies associated with ks near the Fermi level in free electron metals, k_z^2 would be proportional to $(\Delta + \varepsilon)$, where Δ is the energy of the Fermi level relative to that of the bottom of the band, namely about 2 or more eV. Thus, as ε is varied, the distribution of the k_zs is hardly changed, since $\Delta \gg \varepsilon$. This behavior is in marked contrast to that of the semiconductor at its band edge, where $k_z^2 \propto \varepsilon$.

These two effects, seen to be different for the semiconductor and the metal, never the less, for different reasons, gave rise to a proportionality of the electronic factor to $k_B T$ for k_{ET} for the exchange current in the case of the metal and for k_{ET}^{max} in the case of the maximum rate constant for the semiconductor.

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