



On the evaluation of the rate constant of the heterogeneous non-adiabatic electron transfer reaction



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ABSTRACT

Some general characteristics of the rate constant of the non-adiabatic heterogeneous electron transfer are considered and the ways of the extensions of the Marcus approximation are studied. A number of the approximate formulas suggested earlier for the rate constant are examined critically with the emphasis on that obtained by Y. Zeng et al. [J. Electroanal. Chem. 735 (2014) 77–83]. We suggest the more accurate analytical formulas for the rate constant which can have applications in the practical calculations because they also permit avoiding the calculation of the improper integral over the Fermi distribution function. These approximate formulas are based on the integration by parts of the improper integral in the explicit expression for the rate constant without the use of any asymptotic matching and have $\leq 1\%$ error for all reaction free energies and realistic reorganization energies.

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1. Introduction

Recently, interest was renewed in the evaluation of the rate constant (RC) of the heterogeneous non-adiabatic electron transfer (ET) reaction [1–3]. In the pioneering work of Marcus [4] followed shortly by Hush [5] a theoretical evaluation of the RC of the homogeneous ET reaction was presented. This theory based on the transition state theory revealed the central role played by the fluctuations of solvent polarization and was extended later to the case of the heterogeneous ET reactions [6]. Only the adiabatic reactions were considered in Refs. [4–6]. The electron energy levels of an electrode also were not taken into account. Namely, all the calculations were performed in the model where the potential energy surfaces corresponding to the initial state of the ET from an electrode to an ion were replaced by one surface.

The first quantum-mechanical calculation of the RC of the homogeneous ET which permits to obtain the explicit expression for the pre-exponential factor was presented in [7] within the perturbation theory. The generalization of the method of Ref. [7] to the case of the non-adiabatic heterogeneous ET was given in Refs. [8–9] where the full ET was considered as a result of the independent ET from the one-particle electronic levels of an electrode to an ion or vice versa. A more consistent expression for the RC taking into account the electronic density of states of an electrode and the Fermi distribution function was reported by Levich and Dogonadze [10] and published later in [11] (Eqs. (9)–(10) of [11]). The results obtained in [8–10] were reviewed in detail by Marcus in Ref. [12]. If one assumes that the ET takes place mainly from the Fermi level of an electrode or vice versa, then the expression for the RC has the form first obtained in [8] and given by Eqs. (11)–(12) of Ref. [12]. We refer traditionally to this approximation

as the Marcus one due to the appearance in the expression for the RC the well-known Marcus exponential term (see Eqs. (2) and (9) of Ref. [6]).

Heterogeneous ET can be studied analytically in two opposite cases: the non-adiabatic and adiabatic ET reactions. In the case of the non-adiabatic ET the effective electronic matrix element Δ is very small ($\ll k_B T$, a weak coupling limit) so that the electron exchange between an electrode and an ion is very slow. Here $\Delta = \pi \sum_p |V_p|^2 \delta(\varepsilon - \varepsilon_p)$ is the effective electronic matrix element where V_p are the electronic matrix elements describing the coupling of the valence level of an ion with the electronic states $|p\rangle$ of the electrode having the energies ε_p . Therefore, a full relaxation of the solvent polarization to the final state where an electron is situated at the valence level of an ion is established. As a result, the total ET is the sum of the individual ET between two diabatic terms corresponding to the initial electronic state $|p\rangle$ of an electrode and the final state while the RC of each individual ET can be calculated using the second order perturbation theory in V_p . In the opposite case, the case of the adiabatic ET, the effective electronic matrix element is rather large so that the electron exchange between an electron and an ion is sufficiently fast in order to establish the electronic equilibrium in the system at all fixed values of the effective coordinates describing the fluctuations of the solvent polarization. As a result, in contrast to the case of the non-adiabatic ET, the activation free energy of the adiabatic ET reaction depends on the effective electronic matrix element.

Only the non-adiabatic ET is considered in the present paper so that the perturbation theory can be employed. Using the second order perturbation theory in V_p and the wide-band approximation for the electronic structure of the electrode, the expression for the RC for the non-

adiabatic single ET from an electrode to an ion with due account of the Fermi distribution function can be written in the form [13]

$$k = \frac{2\Delta}{\hbar} \left(\frac{k_B T}{\pi E_r} \right)^{1/2} \int \frac{d\varepsilon}{2k_B T} f(\varepsilon) \exp \left[- (E_r - \Delta F - \varepsilon)^2 / 4E_r k_B T \right]. \quad (1)$$

where energies ε and ε_p are counted from the Fermi level of an electrode and the parameter Δ is independent of the energy ε in the wide-band approximation. It was assumed that the harmonic approximation takes place both for the fluctuations of the solvent polarization and intramolecular vibrations. Only classical phonon modes were taken into account and E_r is the reorganization free energy of these modes. $f(\varepsilon)$ is the Fermi function and ΔF is the reaction free energy of the ET and is defined as the difference between the free energy F_0 of the system in the case when the valence level of an ion is empty and the free energy F_1 corresponding to the case when one electron is removed from the Fermi level of an electrode and is transferred to the valence level of an ion. It is important that, for the non-adiabatic ET, the factor in front of the integral in Eq. (1) comprises the product of the effective phonon frequency and the transmission coefficient so that the RC given by Eq. (1) depends only on the solvent reorganization energy. Since Eq. (1) can be also used in the theory of the electron tunneling in the electrochemical tunneling contacts [13–15], we introduce here just the reaction free energy ΔF which depends not only on the overvoltage but also on the bias voltage [14]. By the same reason we consider only the case when $E_r \geq 0.1$ eV $\approx 4k_B T$ where k_B is the Boltzmann constant and T is room temperature since the typical values of the reorganization free energies in the tunneling gap of the electrochemical bridged tunneling contacts are larger than 0.1 eV [16]. Just the RC given by Eq. (1) is used in Refs. [1–3,13–15]. We introduce the dimensionless value $\tilde{k} = k/[2\Delta/\hbar]$ where k is given by Eq. (1) and shall refer to it as the RC in what follows.

Due to the presence of the Fermi function the integral on the right hand side (rhs) of Eq. (1) cannot be expressed in terms of elementary functions. One may ignore this problem approximating the Fermi function by the step function (the Hale approximation (HA) [17]):

$$\tilde{k}_H = \frac{1}{2} \operatorname{erfc} \left[\frac{E_r - \Delta F}{2(E_r k_B T)^{1/2}} \right] = 1 - \frac{1}{2} \operatorname{erfc} \left[\frac{\Delta F - E_r}{2(E_r k_B T)^{1/2}} \right]. \quad (2)$$

However, this approximation is poor at small values of $|\Delta F|$ when the ET takes place mainly from the electronic states of an electrode which are close to the Fermi level (see Appendix A) and when the form of the Fermi function is of importance. In particular, at $E_r \gg |\Delta F|$, $k_B T$, the RC in the Marcus approximation (MA) has an additional factor $\pi/2$ as compared with that in the HA (see below) so that the HA underestimates a value of the rate constant in this case [18]. Recently, the integral on the rhs of Eq. (1) was expressed as a series in the complementary error functions [1–2,15]. However, in order to obtain a concrete numerical value of the RC, the expansions presented in [1–2,15] should be truncated at some member of the series which is different for different values of the physical parameters specifying the problem.

Although the numerical calculation of the RC is not a difficult problem and was performed long ago [18], it is of interest to obtain simple analytical approximations for the RC that can be of importance for the practical applications [3]. The simple analytical formula for the RC was obtained in [3] (Eq. (17) of [3]) which is based on some mathematical procedure. However, in contrast to the statement presented in [3], this formula (the ZSBB approximation) which in our notations has the form

$$\tilde{k}_{ZSBB} = \frac{1}{2[1 + \exp(-\Delta F/k_B T)]} \operatorname{erfc} \left\{ \frac{E_r - k_B T \left[1 + (E_r/k_B T)^{1/2} + (\Delta F/k_B T)^2 \right]^{1/2}}{2(E_r k_B T)^{1/2}} \right\} \quad (3)$$

is not the interpolation between the small and large $|\Delta F|/E_r$ limits because of the error slipped on Appendix B of [3] (see below). It seems also that the interpolation method of [3] has no clear physical grounds in the specific regions of the parameter space.

At the same time, the consideration of the approximate expressions for the RC can gain a new insight into the physics of the ET in the case of the different values of the reaction free energy. In the present paper we suggest a number of approximate expressions for the RC which are applicable in different regions of the parameter space and some of them have $\leq 1\%$ error for all reaction free energies and realistic reorganization energies. The basic properties of the RC are considered in Section 2. The comparison of the expressions for the RC in the HA and the ZSBB approximation with that in the MA (the large E_r limit) is carried out in Section 3. We also compare the exact RC and those obtained in [3,16]. Section 4 is devoted to the study of the possible extensions of the MA. In Section 5 we suggest our approximate expressions for the RC. Concluding remarks are presented in Section 6.

2. The basic characteristics of the exact RC

The exact RC (Eq. (1)) can be rewritten in the form [13,19]

$$\tilde{k} = (k_B T / \pi E_r)^{1/2} \exp \left[- (E_r - \Delta F)^2 / 4E_r k_B T \right] I(\lambda, \mu) \quad (4)$$

where $\lambda = E_r/k_B T$, $\mu = \Delta F/E_r$,

$$I(\lambda, \mu) = \int_{-\infty}^{\infty} \frac{dx}{1 + \exp(2x)} \exp[x(1-\mu)] \exp(-x^2/\lambda) \quad (5)$$

and $x = \varepsilon/2k_B T$. It can be readily shown that $I(\lambda, \lambda) = 0.5(\pi\lambda)^{1/2}$ and [19]

$$I(\lambda, \mu) = \int_0^{\infty} \frac{dx \cosh(\mu x)}{\cosh(x)} \exp(-x^2/\lambda) \quad (6)$$

so that the function $I(\lambda, \mu)$ is an even function of μ . The function analogous to $I(\lambda, \mu)$ was also considered in [1–2,15] where the exact expansions of this function in series in the complimentary error functions were presented. Since (see Eq. (11) of [1])

$$\tilde{k}(E_r, -\Delta F) = \tilde{k}(E_r, \Delta F) \exp(-\Delta F/k_B T), \quad (7)$$

it is sufficient to study only the positive ΔF . It can be easily shown analytically that the curve of the exact RC has the sigmoidal property (see Ref. [17]) which also takes place in the HA and which we write in the form:

$$\tilde{k}(E_r, \Delta F) = 1 - \tilde{k}(E_r, 2E_r - \Delta F). \quad (8)$$

It follows obviously from this property that $\tilde{k}(E_r, E_r) = 1/2$ (see also Eq. (29) of [1]). Eq. (8) also shows that the RC for $\Delta F < E_r$ when the ET from an electrode to an ion has mainly activation character is smaller than 1 by the RC for $\Delta F^{\text{th}} = 2E_r - \Delta F > E_r$. It is obvious that the exact RC in the activation region ($\Delta F < E_r$) increases with the increase of T . However, as follows from Eq. (8), the exact RC decreases with the increase of T in the region $\Delta F > E_r$. A physical meaning of this effect is connected with the increase of the activation free energies of the main individual ETs with the increase of T (see Appendix A).

On the other hand, in the region $\Delta F > E_r$ the activation free energies of the individual ETs which give the main contribution to the total RC tend fast to zero with the increase of ΔF (see Appendix A) so that the heterogeneous ET has mainly the activation-less character. At large values of $\Delta F \gg E_r$ (or, approximately, when ΔF is larger than some

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