# ARTICLES

## Hydration Model for the Energy Barrier in Self-Exchange Electron Transfer Reactions in Solution

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This paper presents two new theoretical models for accurately determining activation energy and reorganization energy for an electron exchange reaction in solution. The hydration process of an ion is considered and two accurate potential functions (Morse function and anharmonic oscillator potential function) are defined in terms of experimental spectroscopic and hydration thermodynamic data. These functions are then used to depict the energy dependence of the reacting system on the separation between the central ion and the inner-sphere water molecules and the solvent reorganization. The activation energy and reorganization energy are obtained in terms of the proposed activation and reorganization models and the hydration potential functions. The experimental activation energy is corrected by taking into account the actual electronic transmission coefficient. The slopes of the potential energy surfaces are obtained from the proposed accurate hydration potential functions, and the coupling matrix element is determined by the two-state model and numerical integral method over the perturbed d-electron double-zeta Slater-type wave functions. The theoretical values of the activation energy are compared with the experimental values, and the relationship between the activation energy and the reorganization energy is tested. The applicability of these models are also discussed.

### 1. Introduction

The theory of electron transfer reactions is now highly developed, encompassing classical, semiclassical, and quantum-mechanical models.[1] In spite of several shortcomings, the classical model of the outer-sphere electron transfer reactions developed by Marcus,[2], Hush,[3] and Sutin,[4] among others, has been fundamental to the understanding of a wide range of homogeneous and heterogeneous processes in chemical and biochemical systems. The semiclassical and quantum-mechanical models developed on the basis of the classical model have been very successful in rationalizing several structure−reactivity relationships and in predicting novel features of reactivity.

From a classical viewpoint,[2,4,5] electron transfer reactions are generally explained within the activated complex formalism. These classical theories establish a formal relationship between the electron transfer rate and some parameters. These parameters nominally contain three elements: (i) electronic factor, (ii) nuclear tunneling factor, and (iii) the energy factors including the activation energy and the reorganization energy of the reactants and the medium in which the electron transfer occurs.

In terms of semiclassical electron transfer theory,[4,6] the rate constant for a nonadiabatic electron transfer reaction can be expressed as the product of a thermally averaged Franck−Condon factor and an electronic factor that is proportional to the square of the electronic coupling matrix element. The thermally averaged Franck−Condon factor depends on the driving force (the reaction free energy) and the nuclear reorganization energy accompanying the electron transfer.

An approach toward estimating the dependence of electron transfer rates on various factors is, first, to separate various contributing factors into exponential and preexponentials and, second, to disentangle different components of those factors and compare them with the corresponding predictions of contemporary theories. For the preexponential parts, the electronic factors, the effective frequency for the activating nuclear reorganization, and a nuclear tunneling factor are the main contribution factors. Likewise, the exponential part, viz. the Franck−Condon factor, is a composite of the structural activation or reorganization characteristics of the reactants and the surrounding medium.[7,8] These parameters and their effect on the electron transfer rate have been extensively studied by both experimental and theoretical methods.[8−14] These have shown that the electron transfer rate depends sensitively on the activation energy and the reorganization energy. It is well-known that the activation energy is the energy change of the reacting systems associated with the structural change of the reactants and the reorientation of the surrounding medium for the reacting system from the initial state to the transition state, while the reorganization energy is the vertical energy difference between the energy of the reactants in their equilibrium configurations (initial state) and their energy immediately after an electron has transferred (also at the reactants' equilibrium nuclear configurations). These two energy differences are generally divided into inner-sphere and outer-sphere contributions, as is also done in electron transfer theories for the corresponding chemical and the electrochemical quantities. The two contributions are treated microscopically and macroscopically, respectively. Their summation then gives the total energy contribution. In developing an accurate treatment of the activation and reorganization energies, great progress has been made,[15−29] and a considerable amount of theoretical work has been devoted to the development of models.

For the activation energy, after George−Griffith's model was

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presented on the basis of the harmonic oscillator potential in the 1950s,[15] Marcus rederived the activation free energy formula by considering of the vibrational energy increment caused by the collision interaction among the surrounding medium molecules,[2,16] Tunuli and Khan put forward the locked dipole orientation (LDO), improved average dipole orientation (IADO), and the semiclassical perturbed rotational state (PRS) models,[17,18] and Zhou and Khan proposed the intermediate neglect of differential overlap (INDO/II) MO method[19a] to improve the parametrization of the potential constant factors involved in the George−Griffith formula. Although these models generally work well, they sometimes give large errors in activation energy. Especially for systems with a large nuclear configuration change, the calculated values are very different from the experimental values extracted from the experimental rate constants. This phenomenon can be attributed to the following two causes. First, there is no accurate experimental method to directly obtain the activation energy from the experimental rate constant. At the present time, the experimental activation energy is generally extracted from the experimental rate constant data by assuming the electronic transmission coefficient to be unity instead of its actual value,[19b] because there is no direct experimental method to determine it. However, this assumption may not be true for many electron transfer reactions in solution. Obviously, the activation energy obtained in this manner must be larger than that obtained by using the actual transmission coefficient value. Second, sometimes the activation energy may also be theoretically obtained by summing the inner-sphere contribution and the outer-sphere contribution. In general, although the George−Griffith formalism based on the harmonic approximation cannot give the inner-sphere activation energy accurately, the improved self-exchange model can work well. However, the outer-sphere activation energy is generally calculated by using a Born-type electrostatic continuum medium model, which is based on slow, infinitesimal, and nonquantal charging of a conducting sphere over a very long time period. Obviously, such a slow process cannot completely be applicable to an electron transfer process, which involves quantal change of charge in a very short time domain of $1 \times 10^{-15}$ to $1 \times 10^{-16}$ s. Thus, this continuum model can only give an approximate result for the outer-sphere activation energy. In other words, this summation method for total activation energy can be inaccurate. In addition, the division of the solvated reacting system into the inner-sphere complex (generally a hexaligand complex) and the outer-sphere solvent medium is approximate, because this division neglects the interaction between the inner-sphere ligands and the outer-sphere solvent molecules.

For electron transfer reactions in solution, there is no general method to experimentally determine the total reorganization energy, although one approach was developed in which the reorganization energy is obtained directly from relative experimental results on the energetic of photoelectron emission from aqueous solutions in the 6−11 eV range of photon energies.[20−22] This photoemission method allows the experimental determination of the reorganization energy provided that the thermodynamic data are available for the calculation of the free energy changes for the reactions. Another method for determining the total reorganization energy is to make use of the fact that the reorganization energy is related to the values of the activation energy extracted from the experimental kinetic data for electron transfer reactions.[8] Obviously, this method also may not give accurate reorganization energies due to the approximations involved in obtaining the activation energy. In addition, a summation method similar to the one used in the calculation of the activation energy may be used to calculate the reorganization energy. However, although many recent studies give some available schemes for the inner-sphere reorganization,[30−32] as mentioned above, the outer-sphere contribution may be easily overestimated by applying the Born-type continuum medium theory. Therefore, complementary and more reliable methods are needed.

It should be noted that although the activation energy and the reorganization energy are two different energy quantities and affect the electron transfer rate at different levels, there must be a relationship between them. In simple electron transfer theory, an approximation is often used to which the total reorganization energy is equal to 4 times the activation energy for the self-exchange reactions. Actually, as was pointed out by Newton,[33] this relationship is not strict for application in the electron transfer reaction because it does not include the anharmonicity feature of the reation potential energy surface. Sometimes this approximate relationship yields large errors in the evaluation of these energies. Further, these energies refer to the energy changes associated with the structural change of the reacting system and the surrounding medium in an electron transfer process in solution. This molecular structural change and solvent reorganization process are similar to the hydration process of an ion. In the hydration of a metal ion, there must be intermolecular reorganization, the hydration heat varying with the orientation of the solvent molecules and the distance between the central metal ion and the solvent molecules. After the hydration process reaches equilibrium, the total hydration heat may be experimentally obtained. When an electron is added to or removed from a hydration ion, the hydration heat must change along with the charge change of the reactant ion. Actually, the hydration process of a metal ion includes the metal ion−solvent molecule interaction process and the reorganization process that occur in the electron transfer process. Therefore, there must be a relationship between electron transfer kinetics parameters in solution and the hydration process and the corresponding hydration heat effect.

In order to establish accurate schemes for determining the activation energy and the reorganization energy values and testing the relationship between the two quantities, we present several new theoretical models. Two accurate potential functions (Morse function and anharmonic oscillator potential function) are expressed in terms of the experimental spectroscopic and the hydration thermodynamic data and are then used to depict the energy dependence of the reacting system on the separation between the central ion and the inner-sphere water molecules and the solvent reorganization. The activation energy and reorganization energy are obtained in terms of the proposed activation and reorganization models and the hydration potential functions. The experimental activation energy is corrected by taking into account the actual electronic transmission coefficient. The slopes of the potential energy surfaces are obtained from the proposed accurate hydration potential functions, and the coupling matrix element is determined by using the two-state model and numerical integral method over the perturbed d-electron double-zeta Slater-type wave functions, and also is calibrated with that from the energy difference between the theoretical activation energy and the energy of the reacting system at the crossing point. The theoretical values of the activation energy are compared with the experimental values, and the relationship between the activation energy and the reorganization energy is tested. The applicability of these models is also discussed.

## 2. Theoretical Models

**(i) Reorganization Model.** According to the definition that the reorganization energy is equal to the energy change of the

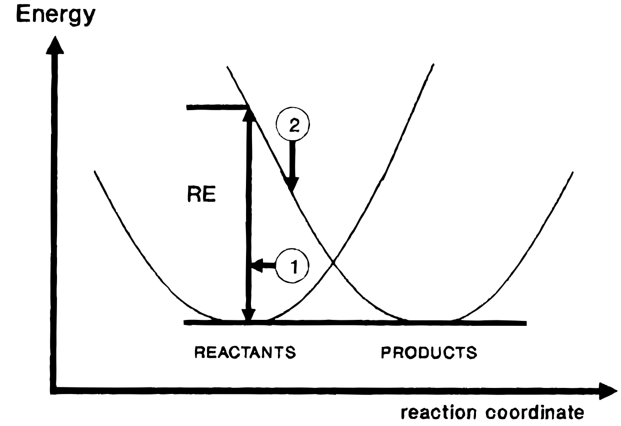

**Figure 1.** The reorganization model.

reacting system associated with the structural changes of the reactants and the reorientation of the solvent molecules required to proceed from the initial state geometrical configuration to the final state geometrical configuration after electron transfer, and the assumption that vertical electron transfer takes place from species $M^z$ (aq) to $M^{z+1}$ (aq) prior to the molecular structural reorganization, the electron transfer process between species $M^z$ (aq) and $M^{z+1}$ (aq) can be represented by the following four equations.

$$M^z(\text{aq } r_0^{\text{r}}) + M^{z+1}(\text{aq } r_0^{\text{o}}) \rightarrow M^z(\text{aq } r_e^{\text{r}}) \ldots M^{z+1}(\text{aq } r_e^{\text{o}}) \quad (1')$$

$$M^z(\text{aq } r_e^{\text{r}}) \ldots M^{z+1}(\text{aq } r_e^{\text{o}}) \rightarrow M^{z+1}(\text{aq } r_e^{\text{r}}) \ldots M^z(\text{aq } r_e^{\text{o}}) \quad (1)$$

$$M^{z+1}(\text{aq } r_e^{\text{r}}) \ldots M^z(\text{aq } r_e^{\text{o}}) \rightarrow M^{z+1}(\text{aq } r_e^{\text{o}}) \ldots M^z(\text{aq } r_e^{\text{r}}) \quad (2)$$

$$M^{z+1}(\text{aq } r_e^{\text{o}}) \ldots M^z(\text{aq } r_e^{\text{r}}) \rightarrow M^{z+1}(\text{aq } r_0^{\text{o}}) + M^z(\text{aq } r_0^{\text{r}}) \quad (2')$$

The symbols ($r_e^{\text{r}}$) and ($r_e^{\text{o}}$) denote the nuclear equilibrium configurations of the corresponding species in their reduced and oxidized states in the reaction complexes, ($r_0^{\text{o}}$) and ($r_0^{\text{r}}$) denote the same quantities in the separated states, respectively, and aq denotes that the reduced or the oxidized ions are the hydrated ions in aqueous solution. Equations 1′ and 2′ are the processes of forming or dissociating the complexes. The energy change in process 1′ corresponds to the sum of the reaction free energy change forming the precursor complex and the electrostatic work required to bring the two reactants together, while that in process 2′ corresponds to the sum of the reaction free energy change dissociating the successor complex and the electrostatic work required to separate the two products from each other. Obviously, the energy changes in steps 1′ and 2′ are equal and opposite. Thus the total energy contributions from steps 1′ and 2′ to electron transfer process may be neglected. The main electron transfer steps are the processes 1 and 2. Step 1 is the electron transfer process by which the produced species reorganizes according to process 2. The energy change in process 2 corresponds to the total (vertical) reorganization energy. These two processes are shown in Figure 1. Obviously, for the self-exchange reaction, the energy changes in steps 1 and 2 are equal and opposite and correspond to the total reorganization energy. In detail, eqs 1 and 2 may be subdivided into four different subprocesses according to the features of donor−acceptor process. The electron transfer process can then be expressed as

$$M^z(\text{aq } r_e^{\text{r}}) \ldots M^{z+1}(\text{aq } r_e^{\text{o}}) \rightarrow M^{z+1}(\text{aq } r_e^{\text{r}}) \ldots M^{z+1}(\text{aq } \text{r}_e^{\text{o}}) + \text{e } (\text{IP}_{\text{v}}^{\text{D}}) \quad (3)$$

$$M^{z+1}(\text{aq } \text{r}_e^{\text{r}}) \ldots M^{z+1}(\text{aq } r_e^{\text{o}}) + \text{e} \rightarrow M^{z+1}(\text{aq } r_e^{\text{r}}) \ldots M^z(\text{aq } r_e^{\text{o}}) \ (\text{EA}_{\text{v}}^{\text{A}}) \quad (4)$$

and the reorganization processes can be represented by eq 5 for the donor species ($M^z$(aq)), and by eq 6 for the acceptor species ($M^{z+1}$(aq)) in the reacting complex.

$$M^{z+1}(\text{aq } r_e^{\text{r}}) \ldots M^z(\text{aq } r_e^{\text{o}}) \rightarrow M^{z+1}(\text{aq } r_e^{\text{o}}) \ldots M^z(\text{aq } r_e^{\text{o}}) \ (\text{RE}^{\text{D}}) \quad (5)$$

$$M^{z+1}(\text{aq } r_e^{\text{o}}) \ldots M^z(\text{aq } r_e^{\text{o}}) \rightarrow M^{z+1}(\text{aq } r_e^{\text{o}}) \ldots M^z(\text{aq } r_e^{\text{r}}) \ (\text{RE}^{\text{A}}) \quad (6)$$

The energy changes in the four processes correspond to those mentioned above (in parentheses), where $\text{IP}_{\text{v}}^{\text{D}}$ denotes the vertical ionization potential of the donor species, $\text{EA}_{\text{v}}^{\text{A}}$ denotes the vertical electron affinity of the acceptor species, and $\text{RE}^{\text{D}}$ and $\text{RE}^{\text{A}}$ denote reorganization energy of the donor and the acceptor species, respectively. These four subprocesses are shown in Figure 2. Obviously, the total reorganization energy (RE) is equal to the sum of $\text{RE}^{\text{D}}$ and $\text{RE}^{\text{A}}$ and also the sum of $\text{IP}_{\text{v}}^{\text{D}}$ and $\text{EA}_{\text{v}}^{\text{A}}$, viz.

$$\text{RE} = \text{RE}^{\text{D}} + \text{RE}^{\text{A}} \quad (7)$$

$$\text{RE} = \text{IP}_{\text{v}}^{\text{D}} + \text{EA}_{\text{v}}^{\text{A}} \quad (8)$$

According to Figure 2, the dependence of $\text{RE}^{\text{D}}$ and $\text{RE}^{\text{A}}$ on the ionization potentials and electron affinities are given by

$$\text{RE}^{\text{D}} = \text{IP}_{\text{v}}^{\text{D}} - \text{IP}_{\text{ad}}^{\text{D}} \quad (9)$$

$$\text{RE}^{\text{A}} = \text{EA}_{\text{v}}^{\text{A}} - \text{EA}_{\text{ad}}^{\text{A}} \quad (10)$$

where $\text{IP}_{\text{ad}}^{\text{D}}$ and $\text{EA}_{\text{ad}}^{\text{A}}$ are two adiabatic quantities corresponding to $\text{IP}_{\text{v}}^{\text{D}}$ and $\text{EA}_{\text{v}}^{\text{A}}$, and should be equal and opposite for the self-exchange reaction.

It becomes apparent that if the ionization potentials and the electron affinities can be obtained by various experimental spectroscopic methods (e.g., electron impact, photoelectron spectroscopy, photoionization, and optical spectroscopy, etc.), the reorganization energies for the raectants in the self-exchange electron transfer reaction can be experimentally determined via eqs 7−10.

In the absence of the $\text{IP}_{\text{v}}$, $\text{IP}_{\text{ad}}$, $\text{EA}_{\text{v}}$, and $\text{EA}_{\text{ad}}$ experimental data, these vertical and adiabatic energies can be obtained from the vibrational spectroscopic data by means of an accurate potential energy function. According to Figure 2, for the potential function

$$E = E(q) \quad (11)$$

the relevant ionization potentials and affinities are given by

$$\text{IP}_{\text{v}}^{\text{D}} = E_{\text{o}}(q^{\text{r}}) - E_{\text{r}}(q^{\text{r}}) \quad (12)$$

$$\text{IP}_{\text{ad}}^{\text{D}} = E_{\text{o}}(q^{\text{o}}) - E_{\text{r}}(q^{\text{r}}) \quad (13)$$

$$\text{EA}_{\text{v}}^{\text{A}} = E_{\text{r}}(q^{\text{o}}) - E_{\text{o}}(q^{\text{o}}) \quad (14)$$

$$\text{EA}_{\text{ad}}^{\text{A}} = E_{\text{r}}(q^{\text{r}}) - E_{\text{o}}(q^{\text{o}}) \quad (15)$$

where the symbols o and r denote the oxidized species or the reduced species, respectively (the same is true in the following), and $q^l$ ($l$ = r, o) denotes the molecular geometrical parameters

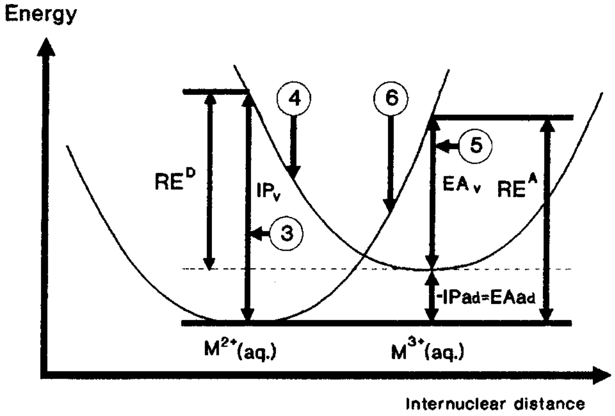

**Figure 2.** Energy plot and various energy indexes and four processes mentioned in the text.

of the $l$th species in the reacting complex. By using these equations (eqs 12−15), together with eqs 8−10, the corresponding reorganization energy can be obtained. It should be noted that calculation of these energies (IP, EA, and RE) strongly depends on the potential energy surfaces of the hydrated oxidized and the hydrated reduced species.

**(ii) Activation Model.** According to the modified self-exchange model[25] and the given function $E(q)$ mentioned above, the total energy of the reacting system at the crossing point before electron transfer (the initial state) is given by

$$E_i = E_r(q) + E_o(x-q) \tag{16}$$

After electron transfer (the final state), the energy becomes

$$E_f = E_o(x-q) + E_r(q) \tag{17}$$

where subscript i denotes the initial state and f denotes the final state and x is the change of the corresponding hydration radius of the reactant molecule from the reduced to the oxidized state. For a radiationless transition of an electron, the total energy must be conserved during the transition ($E_i = E_f$); the activation energy of the reacting system, $E_{ad}$, in solution is given by

$$E_{ad} = E_r(q_t) + E_o(x-q_t) \tag{18}$$

where $q_t$ is the activation parameter of the reactant molecule at the activated state and may be obtained via the minimization method of the potential energy surface.

$$\left|\left(\frac{dE_r(q)}{dq} + \frac{dE_o(x-q)}{dq}\right)\right|_{q=q_t} = 0 \tag{19}$$

It becomes apparent that calculation of these energies strongly depends on the potential energy surface of the reacting system.

**(iii) Hydration Function Model.** According to the structural characteristics of the hydrated ions, taking the solvent hydration sphere as a cavity from which the solvent has been excluded, and letting the metal ion occupy the center of the cavity, the interaction energy between the central metal ion and the hydration sphere is a function of the radius of the cavity and may be accurately expressed by the Morse-type function (Morse):

$$E = D(1 - \exp(-bq))^2 \tag{20}$$

or the anharmonic oscillator potential (AOP):

$$E = {}^1/_2 fq^2 - {}^1/_6 gq^3 \tag{21}$$

where $q$ is the hydration radius displacement from equilibrium configuration and $D$ is the interaction energy between the metal ion and the hydration sphere. This energy may be experimentally determined from the hydration heat by subtracting the vaporization heat of the metal ion. $f$ and $g$ are the quadratic and the cubic force constants, respectively. In general, the experimental $f$ value can be determined by utilizing the experimental vibrational spectroscopic frequency of reactants.

$$f = 4\pi^2 c^2 w^2 m_L/N \tag{22}$$

where $c$ is the velocity of light, $w$ is the experimentally obtained stretching−compression vibrational frequency of an ion hydration sphere, $m_L$ is the molecular weight of the inner hydration sphere. In addition, two other parameters ($b$ and $g$) may be obtained from the Dunham expansion of the Morse function.

$$b = (f/2D)^{1/2} \tag{23}$$

$$g = 3f^{3/2}/(2D)^{1/2} \tag{24}$$

Obviously, these two functions not only include the relationship between the hydration heat effect and the hydration radius but also reflect the energy change accompanying the structural reorganization of the complex ion and the reorientation of the solvent molecules in the electron transfer process. For the self-exchange reaction, substituting these two hydration potential functions into the formulas mentioned in the activation model, the activation energy formula may be rewritten as

AOP:

$$E_{ad} = ({}^1/_2 f_r q_t^2 - {}^1/_6 g_r q_t^3 + {}^1/_2 f_o (x-q_t)^2 - {}^1/_6 g_o (x-q_t)^3 \tag{25}$$

where $f_j$ and $g_j$ ($j$ = r, the reduced, or o, the oxidized species) are the corresponding force constants of the $j$th species. The activation parameter (the minimum bond stretching) of the reduced species, $q_t$, satisfies eqs 26a and 26b.

$$(g_o - g_r)q_t^2 + 2(f_r + f_o - g_o x)q_t + g_o x^2 - 2f_o x = 0 \tag{26a}$$

Approximately, eq 26a may be further simplified to

$$q_t = \frac{2f_o x - g_o x^2}{2(f_r + f_o - g_o x)} \tag{26b}$$

Morse:

$$E_{ad} = D_r(1 - \exp(-b_r g_t))^2 + D_o(1 - \exp(-b_o(x - q_t)))^2 \tag{27}$$

in which the activation parameter, $q_t$, satisfies the equation

$$L(\exp(-b_r q_t) - \exp(-2b_r q_t)) - (\exp(-b_o(x-q_t)) - \exp(-2b_o(x-q_t))) = 0 \tag{28}$$

where $L = D_r b_r / D_o b_o$.

Similarly, substitution of these two hydration potential functions into the relevant formulas mentioned in the reorganization model may give the corresponding reorganization energy results.

## 3. Experimental Determination of the Activation Energy

In practice, the experimental activation energy is extracted from the experimental rate constant by assuming the electronic transmission coefficient to be unity. Obviously, this method is available for the more strongly coupled systems; however, for

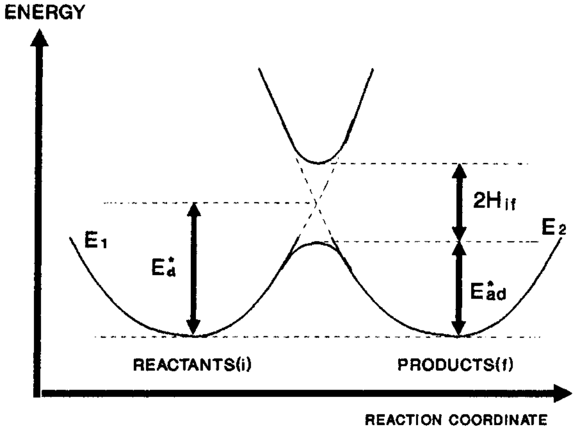

**Figure 3.** Parabolic energy profiles of two diabatic states along the reaction coordinate, displaying the crossing energy $E_d^*$ and the splitting of the adiabatic states ($2H_{if}$).

the weekly coupled systems, the same is not true because the electronic factor plays an important role in affecting the electron transfer rate. Thus the electronic factor should be accurately included in the determination of the experimental activation energy.

For the following type of outer-sphere electron exchange reaction involving hydrated transition metal complex ions

$$\mathrm{M}^{z+1}(\mathrm{aq}) + \mathrm{M}^{z}(\mathrm{aq}) = \mathrm{M}^{z}(\mathrm{aq}) + \mathrm{M}^{z+1}(\mathrm{aq}) \tag{29}$$

the dependence of the electron transfer rate on the electronic factor and some other parameters can be expressed as

$$k_r = \kappa_{el} Z_{eff} \exp(-E_{ad}/kT) \tag{30}$$

Thus the experimental value of the activation energy may be extracted from the experimental rate constant data by using

$$E_{ad} = kT \ln(\kappa_{el} Z_{eff}/k_r^{expt}) \tag{31}$$

where

$$\kappa_{el} = 2P_0/(1 + P_0) \tag{32a}$$

denotes the electronic transmission coefficient and summarizes all the electronic effects on electron transfer rate, and $Z_{eff}$ denotes the effective frequency associated with motion along the reaction coordinate, $k$ is the Boltzmann constant, and $T$ is the thermodynamic temperature. $P_0$ is the electron adiabatic transition probability for hopping from the initial (i) to the final (f) diabatic potential energy surfaces on a single passage of the system through the crossing region.

For the weak coupling electron transfer system in the outer-sphere mechanism, the Landau–Zener model[34,35] is available, the electron adiabatic transition probability $P_0$ may be expressed as

$$P_0 = 1 - \exp(-4\pi^2 H_{if}^2/(hv_s|S_2 - S_1|)) \tag{32b}$$

where $h$ is Planck's constant, $v_s$ is the relative velocity of the velocity (assumed constant) with which the reacting system, $\mathrm{M}^{z+}(\mathrm{aq}) + \mathrm{M}^{z+1}(\mathrm{aq})$ passes through the interaction region along the reaction coordinate. $|S_2 - S_1|$ is the net force exerted on the system tending to restore to its original state or take it to a final state. $S_1$ and $S_2$ are the negative slopes of the potential energy surfaces $E_1$ and $E_2$ (Figure 3), respectively.

It becomes apparent that if the coupling matrix element and slopes of the potential energy surfaces are known, the experimental activation energy may be obtained from the experimental rate constant data in terms of eqs 31 and 32. It is also evident from eq 32 that the determination of the transition probability depends strongly on the coupling matrix element and the slopes of the potential energy surfaces. Therefore, in this paper, we present new methods for determining the coupling matrix element and the slopes of the potential energy surfaces.

**A. The Coupling Matrix Element $H_{if}$.** It should be noted from Figure 3 that $H_{if}$ represents the energy difference between the diabatic activation state (at the crossing point) and the adiabatic activation state (at actual transition state); thus $H_{if}$ can be also expressed as

$$H_{if} = E_d - E_{ad} \tag{33}$$

However, this approach involves equating the coupling element with the very small difference between two large energy quantities and can be subject to large errors.

Actually, the coupling matrix element $H_{if}$ in eq 32, strictly speaking, should be a many-electron quantity associated with the initial and the final state functions combined linearly from atomic orbitals. For weak interaction, the coupling matrix element may be reduced to a simple formalism.

$$H_{if} = \langle \psi_f | H_{int} | \psi_i \rangle \tag{34}$$

Some theoretical calculations of this many-electron quantity have been made[36,37] by Newton, German, and Kuznetsov.

In this work, a new method is presented. The Slater-type double-zeta orbital wave functions are used to depict the electronic state functions of the free metal ion in this method. On the basis of the perturbation theory, taking the potential field produced by the inner-sphere ligands and the outer-sphere medium as a perturbation potential, the perturbed d-electron wave functions of the hydrated metal ion in solution may be obtained by the perturbation method from the Slater-type double-zeta wave functions of the metal ion. Then substitution of these electronic state functions into eq 34 can give the results for $H_{if}$ by using numerical integral method.

**B. Slopes of Potential Energy Surfaces.** In many recent works,[3,4,6] the following expression for $v_s|S_2 - S_1|$ was used in determining $P_0$ via the Landau–Zener formalism.

$$|S_2 - S_1| = 8w_{eff}\sqrt{(\pi RTE_{ad})}/v_s \tag{35}$$

Obviously this formula is an approximate one and cannot give accurate slope differences of the potential energy surfaces. Thus, it is not appropriate to apply eq 35 in the accurate determination of the electronic transmission coefficient.

From the characteristics of the self-exchange electron transfer reaction between the hydrated transition metal redox pairs, the potential energy surfaces of the reactants and the products are symmetrical relative to the transition state so that the slope of the potential energy surface for the reactants is equal to that for the products with an opposite sign. Thus, $|S_2 - S_1|$ reduces to $2|S_1|$, viz.

$$v_s|S_2 - S_1| = 2v_s|S_1| = 2\partial E_1/\partial t \tag{36}$$

It should be noted that the potential energy surface of the reactants includes two contributions from the reduced and the oxidized species, respectively. Therefore, eq 36 may be rewritten as

$$|S_2 - S_1| = 2(|S_r| + |S_o|) \tag{37}$$

where $S_r$ and $S_o$ denote the slopes of the potential energy surfaces

**TABLE 1: Potential Constant Factors of Morse and Anharmonic Potential Functions Determined Experimentally**[a]

| | *f*/(mdyn/Å) | *g*/(mdyn/Å$^2$) | *b*/(1/Å) | *D*/(kcal/mol) |
|---|---|---|---|---|
| $V^{2+}$(aq) | 9.60 | 41.506 | 1.441 | 332.67 |
| $V^{3+}$(aq) | 14.64 | 46.627 | 1.062 | 934.94 |
| $Cr^{2+}$(aq) | 9.60 | 38.880 | 1.350 | 379.13 |
| $Cr^{3+}$(aq) | 15.24 | 47.331 | 1.035 | 1023.52 |
| $Mn^{2+}$(aq) | 9.90 | 40.870 | 1.376 | 376.29 |
| $Mn^{3+}$(aq) | 15.24 | 47.305 | 1.035 | 1024.67 |
| $Fe^{2+}$(aq) | 9.60 | 39.306 | 1.365 | 370.95 |
| $Fe^{3+}$(aq) | 15.24 | 48.509 | 1.061 | 974.40 |
| $Co^{2+}$(aq) | 9.60 | 39.165 | 1.360 | 373.64 |
| $Co^{3+}$(aq) | 15.24 | 49.920 | 1.092 | 920.12 |

[a] The potential constant *D* (in kcal/mol) is obtained by subtracting the vaporization heat from the hydration heat of an ion.

of the hydrated reduced and the hydrated oxidized species at the transition state and can be calculated in terms of the accurate hydration potential functions (eqs 20 and 21). The calculational formulas are expressed as

$$S_j = -2Db(1 - \exp(-bq_t))\exp(-bq_t) \qquad \text{(Morse)} \tag{38}$$

$$S_j = -fq_t + 1/2gq_t^2 \qquad \text{(AOP)} \tag{39}$$

where $j$ (=r and o) denotes the hydrated reduced and the hydrated oxidized species, respectively. Substituting eqs 32, 34, and 37−39 into eq 31, the experimental activation energy may be easily obtained.

In addition, for electron transfer reactions in solution, the electronic transmission coefficient $\kappa_{el}$ is generally about 0.01. Thus, the experimental activation energy may be also approximately extracted from the experimental rate constant for the electron transfer reaction by assuming the electronic transmission coefficient $\kappa_{el}$ as 0.01.

## 4. Results and Discussion

**(i) Results.** Utilizing relevant formulas mentioned above together with experimental spectroscopic and hydration thermodynamic data[10,14,17,38−41] of the hydrated transition metal ions $M^{2+}$(aq) and $M^{3+}$(aq) (M = V, Cr, Mn, Fe, and Co), the potential constant *D* may be obtained from the hydration heat of a metal ion by deducting its vaporization heat, the force constants (*f* and *g*) for the anharmonic oscillator potential function and the exponential factor (*b*) of the Morse potential function can be further obtained in terms of eqs 22−24. These results are given in Table 1. Subsequently, activation parameters and activation energy at the crossing point can be calculated in terms of eqs 25−28. The reorganization energies may be also obtained using eqs 7−15. In determining the experimental activation energies from the experimental rate constants, the accurate electronic factor is needed. The slopes of the potential energy surfaces are obtained by using the activation parameters of the reacting system at the crossing point in the slope formulas eqs 38 and 39. The coupling matrix elements are calculated by using numerical integral method and are also related to the energy difference of the reacting system between the crossing point and its actual activation state. Substitution of the coupling matrix element and the corresponding slope difference of the potential energy surfaces and other relevant quantities into eq 32 gives the values of the electronic transmission coefficient $\kappa_{el}$. The experimental values of the activation energy may be easily calculated from eq 31. These results for activation energies and the reorganization energies are given in Table 2.

In order to test the applicability of the approximate method for determining the activation energy from the experimental rate constant data, the experimental activation energies are also extracted by assuming the electronic transmission coefficient as unity and as 0.01, respectively, and are also given in Table 2.

**TABLE 2: Theoretical and Experimental Activation Energies and Reorganization Energies of the Self-Exchange Reactions of the Redox Pairs $M^{3+}$(aq) $M^{2+}$(aq) (M = V, Cr, Mn, Fe, and Co) in Solution**

| | methods | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| species | Morse | AOP[a] | AOP[b] | expt[c] | expt[d] | expt[e] | Born[f] | RE/$E_a$[g] |
| | Activation Energy/(kcal/mol) | | | | | | | |
| $V^{2+/3+}$ | 15.59 | 15.42 | 15.60 | 15.98 | 14.77 | 18.50 | 18.60 | 3.03 |
| $Cr^{2+/3+}$ | 17.11 | 16.91 | 17.31 | 16.54 | 18.69 | 22.20 | 19.30 | 3.04 |
| $Mn^{2+/3+}$ | 15.00 | 15.03 | 15.05 | 12.70 | 11.46 | 14.90 | 17.00 | 3.08 |
| $Fe^{2+/3+}$ | 13.47 | 13.34 | 13.60 | 12.54 | 11.42 | 14.30 | 14.80 | 3.15 |
| $Co^{2+/3+}$ | 13.45 | 13.32 | 13.62 | 12.69 | 11.57 | 14.80 | 16.00 | 3.15 |
| | Reorganization Energy/(kcal/mol) | | | | | | | |
| $V^{2+/3+}$ | 47.16 | 45.70 | 45.70 | 49.12 | | | | |
| $Cr^{2+/3+}$ | 52.04 | 50.36 | 50.36 | 47.27 | | | | |
| $Mn^{2+/3+}$ | 46.20 | 44.87 | 44.87 | 46.59 | | | | |
| $Fe^{2+/3+}$ | 42.45 | 41.32 | 41.32 | 48.66 | | | | |
| $Co^{2+/3+}$ | 42.32 | 41.17 | 41.17 | 52.12 | | | | |

[a] Obtained from the anharmonic oscillator potential function method (eqs 25 and 26a). [b] Obtained from the anharmonic oscillator potential function method (eqs 25 and 26b). [c] The corrected experimental activation energies by using the actual electronic transmission coefficient value, and the experimental reorganization energies are cited from the photoemission experimental results.[20−22] [d] The corrected experimental activation energies by using the approximate electronic transmission coefficient value (0.01). [e] The experimental activation energies derived early by assuming the electronic transmission coefficient as unity. [f] Obtained by summing the inner- and the outer-sphere contributions which are calculated by George−Griffith formalism and Born-type continuum medium model. [g] RE/$E_a$ values are calculated using the values in the Morse function model in column 2.

**(ii) Electronic Transmission Coefficient.** Before the detailed data presented here are discussed, it is useful to establish a reasonable comparison standard. From eq 31, it is known that the electronic transmission coefficient is an important parameter affecting electron transfer rate. Many recent studies have focused on this electronic factor. Newton and others introduced some reduced formalism to depict the electronic factor;[1] Khan also extended the original Landau−Zener formula by using semiempirical INDO/II molecular orbital method and some approximate activation parameters.[19b] Studies indicated that the electronic transmission coefficient of the electron exchange reaction in solution is generally about 0.01.[42,43] To determine the electronic transmission coefficient, the original Landau−Zener formalism is used in this work (eq 32). The involved parameters (the coupling element and the slopes of the potential energy surfaces) are determined using the numerical integral method over the perturbed d-electron Slater-type double-zeta wave functions and the hydration function model proposed in this paper (eqs 33, 37−39), respectively. The calculated values of this preexponential factor for the self-exchange reactions studied in this work are 0.0779 ($V^{2+/3+}$(aq)), 0.192 ($Cr^{2+/3+}$(aq)), 0.0889 ($Mn^{2+/3+}$(aq)), 0.0679 ($Fe^{2+/3+}$(aq)), 0.0686 ($Co^{2+/3+}$(aq); in the Morse hydration function model, respectively, they are very close to the quasiexperimental values (0.0626 ($V^{2+/3+}$(aq)), 0.182 ($Cr^{2+/3+}$(aq)), 0.0211 ($Mn^{2+/3+}$(aq)), 0.0137 ($Fe^{2+/3+}$(aq)), 0.0215 ($Co^{2+/3+}$(aq)). These results clearly imply that the experimental values of the activation energy derived earlier from the experimental rate constant data using the unit value of the electron transmission coefficient were overestimated. Therefore, the electronic factor should be actually taken into account in relevant analysis.

**(iii) Activation Energy.** The values of the activation energy are obtained from the experimental electron transfer rate constant by using the calculated electronic transmission coefficient. The corrected experimental results of the activation energy are much smaller than those derived earlier. This difference between before-and-after correction may be observed from Table 2 and are about 2.0 kcal/mol for the self-exchange reactions in solution studied here.

Comparison of the activation energy data in Table 2 shows that the values obtained from the Morse-type hydration potential function method are in good agreement with those obtained from the anharmonic hydration potential function method, and all of them agree very well with the corrected experimental values, except for the $Mn^{2+}(aq)/Mn^{3+}(aq)$ redox system whose theoretical values are slightly greater than the experimental value. These theoretical values are also in reasonable agreement with approximate ones extracted from the experimental rate constant by using the approximate value of the electronic transmission coefficient (0.01) and are obviously smaller than the experimental ones extracted by taking electronic transmission coefficient as unity (compare columns 2, 3, and 4 with column 7 in Table 2).

In addition, the activation energy may be evaluated by dividing the hydrated ion into the inner-sphere complex and the outer-sphere solvent medium, and summing the inner-sphere contribution and the outer-sphere contribution. These two energy contributions to the activation energy are obtained by using the microscopic and macroscopic methods, respectively.

In general, for the inner-sphere part, the improved activation model[25,26] works well. However, for the outer-sphere part, the classical Born-type electrostatic continuum medium model cannot give accurate results, because this classical model is based on the slow, infinitesimal, and nonquantal charging process of a conducting sphere over a very long time period. On the other hand, the summation method actually is approximate becuase it neglects the interaction between the inner-sphere complex and the outer-sphere solvent medium. The data in Table 2 (compare column 8 with others) supports the above analysis.

**(iv) Reorganization Energy.** For the reorganization energy, no method has been developed to directly obtain this energy from the experimental kinetic data of the electron transfer process. Only one indirect approach has been proposed in which the reorganization energy is extracted from relative photoemission experimental results. Table 2 gives a comparison between the indirect experimental results and the theoretical values obtained from the proposed reorganization models (Morse, AOPa, AOPb). Good agreement is obtained except for the $Co^{2+}(aq)/Co^{3+}(aq)$ redox couples. This error may be due to the following two aspects: the error of the thermodynamics data of reactants in the indirect photoemission experimental method and the different kinetic (or dynamic) properties of the thermal electron exchange process from that of the photoelectron emission process.

Another method which is used is to relate the reorganization energy to the activation energy. For the self-exchange reaction, it is usually assumed that the reorganization energy is 4 times the activation energy. Obviously, this relationship is approximate because the anharmonicity of the potential energy surfaces of the reacting system is not considered. From Table 2, it is noted that when the anharmonicity effect is taken into account the reorganization energy is only about 3 times the activation energy. The ratio of reorganization energy to the activation energy depends strongly on the property of the potential energy surfaces of the reactants and the products. This indicates that the accurate determination of the potential energy surfaces is the key to calculating various energy changes for the electron transfer reaction and other types of reactions. On the other hand, the overestimated activation energy obtained by summing the inner-sphere and the outer-sphere contributions may result in larger error for the reorganization energy. Therefore, it may be said that this evaluation method from the activation energy for the reorganization energy is not reliable.

**(v) Hydration Function Model.** The observed reasonable agreement between the theoretical and the experimental values fully indicates that the hydration potential function presented in this paper can be used for determining the activation and the reorganization energies of electron self-exchange reaction between the hydrated transition metal redox pairs in solution. The activation model gets around some shortcomings in the classical model and utilizes the accurate potential functions (Morse, AOP) including the anharmonicity feature to calculate the activation energy and the reorganization energy, and should be a reliable method. This arises because the accurate hydration potential function model takes into account the properties and the real behavior of the hydration process of the transition metal ion and accurately gives the potential energy surface. Thus, the energy change in the electron transfer process may be interpreted in terms of the thermodynamic data in the hydration process.

In conclusion, this paper presents some new models which are the reorganization model, the activation model, and the hydration function model from which the potential energy surfaces are accurately determined. The results of the energy barriers of the self-exchange electron transfer reactions in solution are obtained. The experimental standard values are also discussed. Good agreement between the theoretical and the experimental values indicates that two new models (activation model and reorganization model) yield accurate values of the two energy quantities. This result also confirms the utility of the hydration potential function model in determining the potential energy surfaces. This hydration potential function takes into account the common features of the activation process (or reorganization process) and the hydration process and gives an accurate description of the energy dependence on the central ion−hydration sphere separation in solution. Results also show that the ratio of the reorganization energy to the activation energy is about 3 instead of 4, and the traditional relationship between the two energy quantities is not valid for the electron transfer reactions especially for reacting systems with more anharmonic potential energy surfaces. In addition, the classical summation method from the outer- and the inner-sphere contributions overestimated the two energy quantities.

It should be pointed out that the electron transfer reactions of the hydrated ions in solution in the outer-sphere mechanism the electronic transmission coefficient is generally about 0.01, and the experimental activation energy should be obtained from the experimental rate constant data by using the actual electronic transmission coefficient value. This correction may lower the experimental value of the activation energy.

In addition, this hydration function model may be applied to other solvated ion systems in solution with couterions and different ion strength by utilizing the solution heat of the reactant species at the given ion strength.

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