J. Phys. Chem. A **2008,** *112,* 4308−4313

Nonequilibrium Thermodynamics Formalism for Marcus Theory of Heterogeneous and Self-Exchange Electron-Transfer Rate Constants

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Received: January 17, 2008; In Final Form: February 15, 2008

The cross-exchange electron-transfer rate constant expression of Marcus is derived from the Flux−force formalism of non-equilibrium thermodynamics. The relationship governing the Onsager's phenomenological coefficients for cross-exchange and self-exchange electron-transfer processes is deduced. Onsager's phenomenological coefficient pertaining to the Butler−Volmer equation is derived and estimated from the experimental exchange current densities. The correlation between the heterogeneous and the homogeneous electron-transfer rate constants derived by Marcus is analyzed in terms of the corresponding phenomenological coefficients.

1. Introduction

The estimation of cross-exchange electron-transfer rate constants using the constituent self-exchange rate constants occupies a pivotal role in the theory of reaction rates in view of its extensive validity.[1,2] The cross-exchange rate constant k_{12} for a redox reaction is related to the self-exchange rate constants k_{11} and k_{22} as

$$k_{12} = (k_{11}k_{12}K_{12}\, f_{12})^{1/2}\, W_{12} \tag{1}$$

where K_{12} denotes the equilibrium constant of the cross-exchange electron-transfer process while f_{12} and W_{12} consist of various work terms involving the reactants and products. If it is assumed that $f_{12} = 1$ and $W_{12} = 1$ as is customary, a simplified equation

$$k_{12} \approx (k_{11}k_{12}K_{12})^{1/2} \tag{2}$$

arises, thus enabling the estimation of the cross-exchange rate constants without any adjustable parameters. The validity of eq 2 has been extensively investigated for diverse types of reactions[3] and is particularly valuable when one of the two self-exchange rate constants is difficult to measure.[4]

In general, eq 2 is considered as a linear free energy relation on account of the linear dependence of the activation free energy upon the standard Gibbs free energy change. The original formalism of Marcus[1] leading to eq 1 is based upon statistical mechanical considerations in conjunction with classical electrostatics; however, several subsequent attempts have been made in order to analyze the functional dependence of the activation energy on the intrinsic barrier and reaction coordinate vis a vis progress variable. Notable among them are the investigations of Rehm and Weller,[5] Agmon and Levine,[6] Thornton,[7] and Murdoch.[8] It is of interest to note that the exponent to which the equilibrium constant in eq 2 is raised need not always be equal to[9,10] 0.5. A noteworthy feature of the Marcus formalism underlying eq 1 is that its basic premise holds good not only for electron transfer but also for methyl transfer,[11] hydride transfer,[12] proton transfer,[13] and so forth. Further, the correlation of the self-exchange rate constant with the electron-transfer rate constant at electrode surfaces has also been deduced by Marcus.[1]

The objectives of this manuscript are (i) to deduce the cross exchange electron-transfer rate constant of Marcus from Onsager's nonequilibrium thermodynamics formalism, (ii) to derive and estimate the Onsager's phenomenological coefficient for electron transfer at electrode surfaces, and (iii) to analyze the correlation between self-exchange and heterogeneous rate constants in terms of the phenomenological coefficients.

2. Nonequilibrium Thermodynamics Formalism for Cross-Exchange Electron-Transfer Reactions

The description of chemical kinetic schemes using nonequilibrium thermodynamics concepts has profound significance insofar as it provides a general framework in a unified manner. For example, the importance of fluctuations from equilibrium states and the concept of coupled and noncoupled biochemical reactions are elegantly brought about solely from the magnitude of Onsager's phenomenological coefficients.[14−16]

2.1. Chemical Kinetics Description of Cross-Exchange Electron-Transfer Reactions. Consider the cross-exchange electron-transfer reaction represented as

$$A_1^{\,r} + B_2^{\,r} \xrightarrow{k_{12}} A_1^{\,p} + B_2^{\,p} \tag{3}$$

where A_1 and B_2 represent the two redox couples while r and p denote the reactant and product states. Analogously, the constituent self-exchange reactions are as follows:

$$A_1^{\,r} + A_1^{\,p} \xrightarrow{k_{11}} A_1^{\,p} + A_1^{\,r} \tag{3a}$$

$$B_2^{\,r} + B_2^{\,p} \xrightarrow{k_{22}} B_2^{\,p} + B_2^{\,r} \tag{3b}$$

The equilibrium constant for the cross-exchange reaction is given by

$$K_{12} = \frac{C_{A_1^{\rm p}}^{\;eq} C_{B_2^{\rm p}}^{\;eq}}{C_{A_1^{\rm r}}^{\;eq} C_{B_2^{\rm r}}^{\;eq}} \tag{4}$$

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10.1021/jp800473k CCC: $40.75

The velocity of reaction 3 is

$$v_{12} = k_{12} C_{A_1^r} C_{B_2^r} \tag{5}$$

where k_{12} is the cross-exchange electron-transfer rate constant. In nonequilibrium thermodynamics formalism for chemical kinetics, it is customary to introduce the departure from equilibrium concentrations of the species involved in the reaction. Consequently, eq 5 becomes

$$v_{12} = k_{12}\,(C_{A_1^r}{}^{eq} + \alpha_{A_1^r})(C_{B_2^r}{}^{eq} + \alpha_{B2r}) = k_{12}\left[C_{A_1^r}{}^{eq}\left(1 + \frac{\alpha_{A_1^r}}{C_{A_1^r}{}^{eq}}\right) C_{B_2^r}{}^{eq}\left(1 + \frac{\alpha_{B_2^r}}{C_{B_2^r}{}^{eq}}\right)\right] = k_{12} C_{A_1^r}{}^{eq} C_{B_2^r}{}^{eq}\left(1 + \frac{\alpha_{A_1^r}}{C_{A_1^r}{}^{eq}} + \frac{\alpha_{B_2^r}}{C_{B_2^r}{}^{eq}} + \frac{\alpha_{A_1^r}\alpha B_2{}^r}{C_{A_1^r}{}^{eq} C_{B_2^r}{}^{eq}}\right]$$

Since $v_{12}{}^{eq} = k_{12} C_{A_1^r}{}^{eq}\, C_{B_2^r}{}^{eq}$, we may write

$$v_{12} - v_{12}{}^{eq} = k_{12} C_{A_1^r}{}^{eq} C_{B_2^r}{}^{eq}\left(\frac{\alpha_{A_1^r}}{C_{A_1^r}{}^{eq}} + \frac{\alpha_{B_2^r}}{C_{B_2^r}{}^{eq}} + \frac{\alpha_{A_1^r}\alpha_{B_2^r}}{C_{A_1^r}{}^{eq} C_{B_2^r}{}^{eq}}\right) \tag{5a}$$

For small departures from equilibrium, namely, $\alpha_{A_1^r}/C_{A_1^r}{}^{eq} \ll 1$ and $\alpha_{B_2^r}/C_{B_2^r}{}^{eq} \ll 1$, the above equation can be approximated as

$$v_{12} = k_{12} C_{A_1^r}{}^{eq}\, C_{B_2^r}{}^{eq}\left(\frac{\alpha_{A_1^r}}{C_{A_1^r}{}^{eq}} + \frac{\alpha_{B_2^r}}{C_{B_2^r}{}^{eq}}\right) \tag{6}$$

This equation is analogous to the velocity expression for a first-order reaction.[14]

2.2. Onsager's Flux−Force Formalism for Cross-Exchange Electron-Transfer Reactions. In order to obtain new insights provided by nonequilibrium thermodynamic concepts, it is customary to consider the same reaction using the flux−force formalism of Onsager as has been discussed for first-order reactions.[15]

2.2.1. Identification of Onsager's Phenomenological Coefficients. The affinity of reaction 3 is defined as[16]

$$A_{12} = (\mu_{A_1^r} + \mu_{B_2^r}) - (\mu_{A_1^p} + \mu_{B_2^p})$$

where $\mu_{A_1^r}$, $\mu_{B_2^r}$, and so forth denote the chemical potentials of the indicated species. Since the liquid-phase reactions are considered herein, we may employ the concentrations of the species. Consequently, we write the chemical potential for A_1^r as

$$\mu_{A_1^r} = \mu^0{}_{A_1^r} + RT \ln C_{A_1^r}$$

if we neglect the activity coefficient corrections. Analogous equations hold good for $\mu_{B_2^r}$, $\mu_{A_1^p}$, and $\mu_{B_2^p}$ Thus, the affinity of the reaction becomes

$$A_{12} = [\mu^o{}_{A_1^r} + RT \ln C_{A_1^r} + \mu^o{}_{B_2^r} + RT \ln C_{B_2^r}] - [\mu^o{}_{A_1^p} + RT \ln C_{A_1^p} + \mu^o{}_{B_2^p} + RT \ln C_{B_2^p}] \tag{7}$$

Introducing the departure from the equilibrium concentrations $\alpha_{A_1^r}/C^{eq}_{A_1^r}$, and so forth, we obtain

$$A_{12} = \left[\mu^{eq}_{A_1^r} + RT \ln\left(1 + \frac{\alpha_{A_1^r}}{C^{eq}_{A_1^r}}\right) + \mu^{eq}_{B_2^r} + RT \ln\left(1 + \frac{\alpha_{B_2^r}}{C_{B2^r}{}^{eq}}\right)\right] - \left[\mu^{eq}_{A_1^p} + RT \ln\left(1 + \frac{\alpha_{A_1^p}}{C^{eq}_{A_1^p}}\right) + \mu^{eq}_{B_2^p} + RT \ln\left(1 + \frac{\alpha_{B_2^p}}{C^{eq}_{B_2^p}}\right)\right] \tag{8}$$

However, at equilibrium,

$$\mu^{eq}_{A_1^r} + \mu^{eq}_{B_2^r} = \mu^{eq}_{A_1^p} + \mu^{eq}_{B_2^p} \tag{9}$$

For near-equilibrium conditions, we may expand the logarithmic terms and neglect terms other than linear as is customary in the nonequilibrium thermodynamics description of chemical kinetics.[15] Consequently, eq 9 becomes

$$A_{12} = RT\left(\frac{\alpha_{A_1^r}}{C_{A_1^r}{}^{eq}} + \frac{\alpha_{B_2^r}}{C_{B_2^r}{}^{eq}}\right) - RT\left(\frac{\alpha_{A_1^p}}{C_{A_1^p}{}^{eq}} + \frac{\alpha_{B_2^p}}{C_{B_2^p}{}^{eq}}\right) \tag{10}$$

Since reaction 3 is considered to be an irreversible process (cf. eq A29 of Marcus[1]), the above equation becomes

$$A_{12} = RT\left(\frac{\alpha_{A_1^r}}{C_{A_1^r}{}^{eq}} + \frac{\alpha_{B_2^r}}{C_{B_2^r}{}^{eq}}\right)$$

Since the velocity is linearly related to the affinity in the linear flux−force formalism, we may write

$$v_{12} = L_{12} A_{12}$$

However at equilibrium, $A_{12} = 0$; hence, $(v_{12} - v_{12}{}^{eq}) = L_{12}A_{12}$. Hence,

$$v_{12} - v_{12}{}^{eq} = L_{12} RT\left(\frac{\alpha_{A_1^r}}{C_{A_1^r}{}^{eq}} + \frac{\alpha_{B_2^r}}{C_{B_2^r}{}^{eq}}\right) \tag{11}$$

Comparing eqs 6 and 11, we obtain

$$L_{12} = \frac{k_{12} C_{A_1^r}{}^{eq} C_{B_2^r}{}^{eq}}{RT} \tag{12}$$

This equation is reminiscent of the Onsager's coefficient for reversible first-order reaction wherein[17] $L = k_1 C_x{}^{eq}/RT$ with k_1 denoting the forward rate constant. In an analogous manner, Onsager's coefficients for the two self-exchange reactions may be written as

$$L_{22} = \frac{k_{22} C_{B_2^r}{}^{eq} C_{B_2^p}{}^{eq}}{RT} \tag{13}$$

and

$$L_{11} = \frac{k_{11} C_{A_1^r}{}^{eq} C_{A_1^p}{}^{eq}}{RT} \tag{14}$$

2.2.2. Relation among Onsager's Phenomenological Coefficients for Cross-Exchange Electron-Transfer Reactions. Since the cross-exchange reaction is composed of the two self-exchange reactions and if the principle of microscopic reversibility is valid in this context,

$$v_{12}^{eq} = v_{11}^{eq} = v_{22}^{eq} \tag{15}$$

which implies that

$$\frac{k_{12}C_{A_1^r}^{eq}C_{B2^r}^{eq}}{RT} = \frac{k_{11}C_{A_1^r}^{eq}C_{A_1^p}^{eq}}{RT} = \frac{k_{22}C_{B2^r}^{eq}C_{B_2^p}^{eq}}{RT} \tag{16}$$

Thus

$$L_{12} = L_{11} = L_{22} \qquad \text{namely} \qquad L_{12}^2 = L_{11}L_{22} \tag{17}$$

Substituting the appropriate expressions for L's in terms of rate constants, we obtain

$$k_{12}^2 = k_{11}k_{22}K_{12} \tag{18}$$

which is identical with eq 2, arising from the Marcus theory.[1]

3. Nonequilibrium Thermodynamics Formalism for Electron Transfer at Electrode Surfaces

The current–potential response of electron-transfer processes at electrode surfaces is customarily represented by the Butler–Volmer equation[18] containing the standard exchange current density and transfer coefficient (or symmetry factor). The conventional formulation of the same relies upon the influence of the applied potential on the energy states of the reactant and product. It is of interest to investigate whether the Butler–Volmer equation has a nonequilibrium thermodynamic basis. This aspect will then enable the comprehension of the correlation proposed by Marcus[1] between the heterogeneous and the self-exchange rate constants.

3.1. Butler–Volmer Equation from the Concept of Affinity. In order to identify the Onsager's phenomenological coefficient for electron transfer at electrode surfaces, it is imperative to reformulate the Butler–Volmer equation from the perspective of nonequilibrium thermodynamics incorporating the concept of the affinity as shown below:

For a typical electron-transfer reaction[19] such as

$$\text{Oxidn} + ne^- \underset{k_b}{\xrightarrow{k_f}} \text{Redn} \tag{19}$$

the net current i is given in terms of the velocity v as

$$i = nFA_{el}\text{v} \tag{20}$$

and A_{el} denotes the area of the electrode. (A_{el} is denoted as the area of the electrode in order to avoid ambiguity with the symbol for affinity.) Further, the velocity of the forward (reduction) and backward (oxidation) reactions are

$$v = v_f - v_b \tag{21}$$

$$v_f = C_{\text{Ox}}k_f(E) \qquad \text{v}_b = C_{\text{Red}}k_b(E) \tag{22}$$

where C_{Ox} and C_{Red} are assumed to be the bulk concentrations of the respective species (ignoring mass transfer limitations).

The potential-dependent rate constants for forward and backward reactions may be represented as

$$k_f(E) = \frac{k_BT}{h}\exp\left(\frac{-\Delta G_f^{\neq}(E)}{RT}\right) \tag{23}$$

and

$$k_b(E) = \frac{k_BT}{h}\exp\left(\frac{-\Delta G_b^{\neq}(E)}{RT}\right) \tag{24}$$

where k_B and h denote the Boltzmann constant and Planck constant respectively. It is customary to introduce the symmetry factor α which incorporates the influence of the applied potential on the activation energy barrier. Consequently, the Gibbs free energies of activation are

$$\Delta G_f^{\neq}(E) = \Delta G_f^{\neq}(E_e) + \alpha nFE \tag{25}$$

and

$$\Delta G_b^{\neq}(E) = \Delta G_b^{\neq}(E_e) - (1-\alpha)nFE \tag{26}$$

for the reduction and oxidation respectively. The standard heterogeneous rate constant $k_{f,0}$ which refers to the rate constant at the equilibrium potential E_e is given by

$$k_{f,0} = \frac{k_BT}{h}\exp\left(\frac{-\Delta G_f^{\neq}(E_e)}{RT}\right) \tag{27}$$

$$k_{b,0} = \frac{k_BT}{h}\exp\left(\frac{-\Delta G_b^{\neq}(E_e)}{RT}\right) \tag{28}$$

Hence, we may write the rate constants as

$$k_f(E) = k_{f,0}\exp(-\alpha nFE/RT) \tag{29}$$

and

$$k_b(E) = k_{b,0}\exp[(1-\alpha)nFE/RT] \tag{30}$$

Substituting the values of $k_f(E)$ and $k_b(E)$ from eqs 29 and 30, the velocities become

$$v_f = C_{\text{Ox}}k_{f,0}\exp(-\alpha nFE/RT) \tag{31}$$

and

$$v_b = C_{\text{Red}}k_{b,0}\exp[(1-\alpha)nFE/RT] \tag{32}$$

In the above, $(E - E_e) > 0$. Since the experimental parameter conventionally measured is the standard exchange current density i_0/A_{el}, it follows that

$$i_0 = nFA_{el}C_{\text{Ox}}k_{f,0}\exp(-\alpha nFE_e/RT) = nFA_{el}C_{\text{Red}}k_{b,0}\exp[(1-\alpha)nFE_e/RT] \tag{33}$$

While the foregoing equations are well-known,[19] in order to identify L, we introduce the concept of the affinity for electron transfer at electrode surfaces. The velocities are related to the affinity as[20]

$$\frac{v_f}{v_b} = \exp\left(\frac{A}{RT}\right) \tag{34}$$

and by substituting the expressions for v_f and v_b, the above equation becomes

$$\exp\left(\frac{A}{RT}\right) = \frac{C_{\text{Ox}}}{C_{\text{Red}}}\frac{k_{f,0}}{k_{b,0}}\frac{\exp(-\alpha nFE/RT)}{\exp[(1-\alpha)nFE/RT]} \tag{35}$$

Interestingly, the above functional form of $\exp(A/RT)$ arises only in the case of electron transfer at electrode surfaces, which is a consequence of the exponential dependence of the rate constant on applied potential.

Furthermore, by using eq 34, the net velocity v may be rewritten as

$$v = v_f\left[1 - \exp\left(\frac{-A}{RT}\right)\right] \tag{36}$$

Thus,

$$v = C_{\mathrm{Ox}} k_{f,0} \exp(-\alpha nFE/RT) \times \left[1 - \frac{C_{\mathrm{Red}}}{C_{\mathrm{Ox}}}\frac{k_{b,0}}{k_{f,0}}\frac{\exp[(1-\alpha)nFE/RT]}{\exp(-\alpha nFE/RT)}\right] \tag{37}$$

We recall that the above equation is essentially the Butler−Volmer equation rephrased in a different manner. Obviously,

$$i = nFA_{el}v = nFA_{el}v_f\left(1 - \frac{v_b}{v_f}\right) \tag{38}$$

Substituting the values of v_f and v_b from eqs 31 and 32,

$$i = i_0\left[1 - \frac{C_{\mathrm{Red}}}{C_{\mathrm{Ox}}}\frac{k_{b,0}}{k_{f,0}}\frac{\exp[(1-\alpha)nFE/RT]}{\exp(-\alpha nFE/RT)}\right] \tag{39}$$

Although the above equation could have been written directly, the detailed steps indicate the manner in which the velocity is related to the affinity for electrochemical reactions and the composition of the affinity in terms of the potential-dependent rate constants. It is of interest to point out that the affinity can also be written in terms of the electrochemical potentials of the oxidized and reduced species, resulting in the Butler−Volmer equation (cf. Appendix A). A similar strategy has been adopted elsewhere to derive diffusion migration equations arising in redox polymer electrodes[21,22]

3.2. Identification of the Onsager's Phenomenological Coefficient for Electron Transfer at Electrode Surfaces.

In order to identify the Onsager's phenomenological coefficient L pertaining to electron transfer at electrodes, we employ the linear dependence[23] of the net velocity on L, namely,

$$v = LRT\left[1 - \exp\left(\frac{-A}{RT}\right)\right] \tag{40}$$

Hence,

$$i = nFA_{el}LRT\left[1 - \exp\left(\frac{-A}{RT}\right)\right] \tag{41}$$

using eq 20. Substituting the expression for the affinity from eq 35, we obtain

$$i = nFA_{el}LRT\left[1 - \frac{C_{\mathrm{Red}}}{C_{\mathrm{Ox}}}\frac{k_{b,0}}{k_{f,0}}\frac{\exp[(1-\alpha)nFE/RT]}{\exp(-\alpha nFE/RT)}\right] \tag{42}$$

On comparing the above equation with eq 39, it follows that

$$L = \frac{i_0}{RTnFA_{el}} \tag{43}$$

where i_0 is given by eq 33. As anticipated, L is independent of the driving force and is a constant for a given reaction under chosen experimental conditions (constant temperature and constant n).

We emphasize that, bypassing the above detailed analysis, the composition of L could have been written directly from the well-known expression for L pertaining to reversible first-order homogeneous reactions. From eq 3.1 of ref 15 for a reversible first-order reaction such as $X \xrightarrow[k_{-1}]{k_1} Y$, the Onsager's coefficient L_{homo} is given as

$$L_{\mathrm{homo}} = \frac{k_1 C_{\mathrm{X}}^{eq}}{RT} \tag{44}$$

where C_{X}^{eq} denotes the equilibrium concentration of X. In the case of the present formulation for the heterogeneous reactions at electrode surfaces, we need to incorporate the heterogeneous rate constant k_f as given by

$$k_f = k_{f,0} \exp(-\alpha nFE_e/RT) \tag{45}$$

Replacing k_1 of eq 44 by k_f of eq 45, we obtain

$$L = \frac{k_{f,0} \exp(-\alpha nFE_e/RT) C_{\mathrm{X}}^{eq}}{RT} \tag{46}$$

Employing the exchange current density i_0/A_{el}, the above equation becomes

$$L = \frac{i_0}{RTnFA_{el}}$$

which is identical with eq 43 derived earlier from the first principles.

3.3. Estimation of Onsager's Coefficient from Electrode Kinetic Data.

It is of interest to verify the validity of eq 43 for electron-transfer reactions at electrodes. For this purpose, the experimental data pertaining to the dependence of i_0 on temperature is required. Such measurements are conventionally obtained from Tafel polarization studies[24] and a few typical reactions are considered for illustrative purposes in Table 1. From the constancy of L as demonstrated in Table 1, it follows that, whenever the temperature-dependence of electrochemical reactions is studied, L is a more suitable parameter in view of its constancy. In cases where L is not a constant, it may indicate a change in the mechanism of the reaction.

Figure 1 depicts the constancy of the Onsager's coefficients calculated from eq 43 for the electrochemical reactions listed in Table 1.

4. Correlation between Homogeneous Self-Exchange and Heterogeneous Electron-Transfer Rate Constants

As deduced by Marcus,[1] the self-exchange rate constant is related to the heterogeneous electron-transfer rate constant at electrode surfaces by

$$\frac{k_f}{(k_{11})^{1/2}} = \frac{Z_f}{(Z_{11})^{1/2}} \tag{47}$$

where Z_f and Z_{11} denote the collision frequency factors for heterogeneous and self-exchange reactions, respectively. In order to obtain insight into the above correlation from the perspective of nonequilibrium thermodynamics, we employ the appropriate expressions for the Onsager's coefficients in terms of the corresponding rate constants. We recall that the Onsager's coefficient for self-exchange and heterogeneous rate constants are given respectively by eqs 14 and 46. From these equations,

$$\frac{k_f}{(k_{11})^{1/2}} = \frac{L(RT)^{1/2}}{(L_{11})^{1/2}} \tag{48}$$

TABLE 1: Estimation of the Onsager's Phenomenological Coefficient from Eq 43 for a Few Electron-Transfer Reactions

S no.	reaction	temperature range/K	current−density range/A cm^{-2}	L/J^{-1} mol^2 s^{-1} cm^{-2}
1	reduction of Ce^{4+} to Ce^{3+} ions at conductive diamond electrode[25]	3000−4000	$(1.44-7.94) \times 10^{-6}$	$(1.63 \pm 0.38) \times 10^{-15}$
2	oxygen reduction in alkaline medium at Pt/Nafion 117 interface[26]	303−343	$(0.84-11.5) \times 10^{-11}$	$(1.62 \pm 0.50) \times 10^{-19}$
3	oxygen reduction in alkaline medium at Pt/BAM 407 interface[26]	303−343	$(0.48-1.43) \times 10^{-11}$	$(3.47 \pm 0.44) \times 10^{-20}$
4	reduction of Zn^{2+} to Zn in ammoniacal NH_4Cl[27]	285.7−303	$(3.84-5.49) \times 10^{-2}$	$(9.86 \pm 0.40) \times 10^{-11}$
5	reduction of Cu^{2+} to Cu in NH_4Cl-NH_3[28]	303−322.5	$(0.86-1.06) \times 10^{-3}$	$(19.11 \pm 0.38) \times 10^{-13}$

The left-hand sides of eqs 47 and 48 are identical, and for the right-hand sides to be equivalent, we need to identify the right-hand side of eq 48 as $Z_f/(Z_{11})^{1/2}$, namely,

$$\frac{L(RT)^{1/2}}{(L_{11})^{1/2}} = \frac{Z_f}{(Z_{11})^{1/2}} \tag{49}$$

Thus, the correlation between heterogeneous and homogeneous electron-transfer rate constants arising from the Marcus theory[1] implies inter alia, eq 49 relating the Onsager coefficients to the appropriate frequency factors. In contrast to the eq 2 which arises from an equality among the Onsager's coefficients as given by eq 17, a firm theoretical basis underlying eq 49 is not obvious and requires further investigation. Presumably, rationalizing the above equation may require formulating the Onsager's coefficients in terms of parameters arising from the collision theory of reaction rates from the first principles.

5. Perspectives and Summary

The foregoing analysis has demonstrated that it is possible to deduce (i) Marcus cross-exchange electron-transfer rate constants in terms of the self-exchange rate constants and (ii) the correlation between self-exchange and heterogeneous electron-transfer rate constants, from Onsager's flux−force formalism when certain approximations are introduced. Interestingly, experimental data do indicate satisfactory validity of eq 2 in genera,l[3] and hence, the assumptions invoked while deriving eq 2 seem reasonable. Thus, the dichotomy between the activated complex theory and nonequilibrium thermodynamic formalism may be exploited for mechanistic analysis of electron-transfer processes. Further, the availability of the phenomenological expressions for the affinity and Onsager's coefficient enables the estimation of the rate of entropy production for the process under consideration.

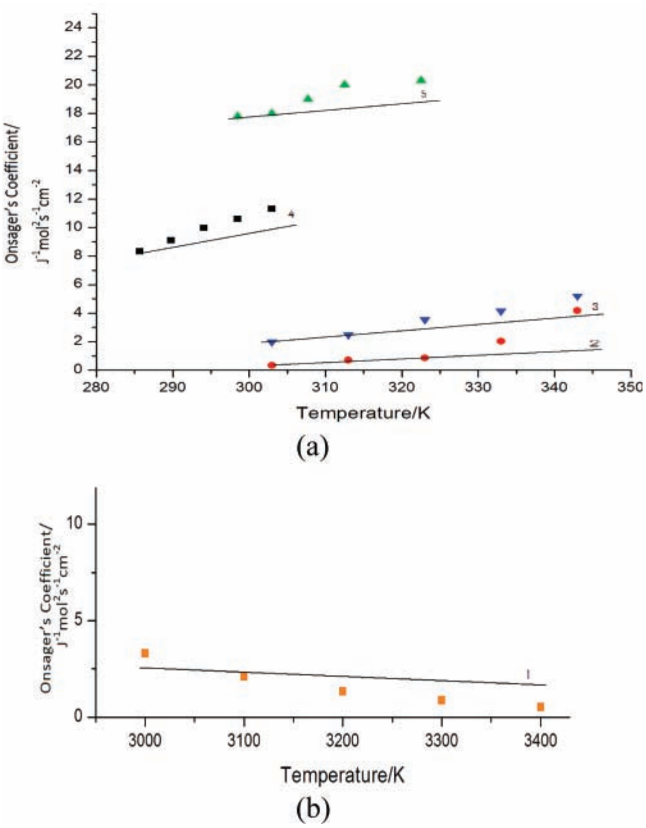
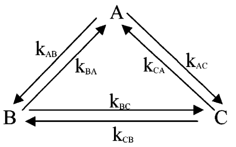


Figure 1. Points denote the estimates of L from eq 43 using experimental exchange current densities reported in Table 1. Lines are drawn as a guide to the eye. (a) reaction 1 to 4 and (b) reaction 5 as listed in Table 1. The orders of magnitude of L in the graph for reactions 1 to 5 are respectively 10^{-15}, 10^{-19}, 10^{-20}, 10^{-11}, and 10^{-13}.

In order to comprehend the validity of eq 47, it becomes essential to identify the phenomenological coefficient in terms of the standard heterogeneous rate constant at electrode surfaces. This has been accomplished by two different methods as shown in 3.2 and in Appendix A. Further, it is of interest to note that the Butler−Volmer equation for electron transfer at electrode surfaces has a nonequilibrium thermodynamic basis and that the Onsager's phenomenological coefficient can indeed be estimated from electrode kinetic parameters. In this context, it is worth noting that an alternate method of deriving the Butler−Volmer equation from Onsager's formalism has been propounded by Keizer elsewhere.[29]

It is of interest to enquire whether any new insights have emerged from the approach suggested here. First, with regard to eq 2, the departure from equilibrium concentrations of the reactants were explicitly introduced in the present analysis and these were assumed small enabling us to neglect higher order terms in the expansion of the affinity. A possibility that remains un-clear is whether incorporation of the fluctuations from equilibrium concentrations will yield the complete Marcus expression 1 consisting of the work terms too. In cases wherein eq 2 is not valid while comparing with the experimental data, it may imply that the assumption of small deviations from equilibrium may become invalid (cf. eq 6). Second, it is customary[17] to estimate the Onsager's phenomenological coefficient for reversible first-order reaction wherein the corresponding phenomenological coefficient is given by eq 44. The fact that an analogous exercise is feasible for cross-exchange reactions (composed of the constituent self-exchange processes) may indicate a much more general applicability of Onsager's formalism than hitherto envisaged. One of the methods of verifying Onsager's Reciprocity Relation (ORR) consists in analyzing a triangular cyclic reaction scheme of coupled chemical reactions given by



On the other hand, the phenomenological coefficients L_{11}, L_{22}, and L_{12} are related in the present context via eq 17.

Although the correlation between homogeneous and heterogeneous electron-transfer reaction rates as given by eq 47 leads to an equality among the corresponding phenomenological coefficients (eq 49), the basis underlying the latter is not obvious at present. This limitation is however in stark contrast to the rationale behind eq 2 pertaining to the homogeneous case and may partially be attributed to the problems arising in the definition of Z_{11} and Z_f for homogeneous and heterogeneous processes.[30] Nevertheless, the identification of the Onsager's coefficients (L) in terms of the exchange current density indicates that L may probably be a more convenient parameter for electrode kinetic analysis. This is not all. By merely incorporating different prescriptions for electrochemical potentials[21] of the reduced and oxidized species in lieu of eq A3, current−potential equations can be deduced that go beyond the Butler−Volmer formulation. A related flux−force formalism of Onsager using the electrochemical potentials of the species has led to a hierarchy of diffusion migration equations for electron hopping in redox polymer electrodes.[21,22] In view of the isomorphism between the kinetic Ising model descriptions[31] and the Onsager nonequilibrium thermodynamic formalism[21] for transport phenomena, one would anticipate that a generalized microscopic formulation for the Marcus theory of electron transfer may indeed exist. Furthermore, the extensive validity of the Marcus approach for different classes of reactions such as electron transfer, proton transfer, methyl transfer, hydride transfer, and so forth becomes transparent, when viewed from the perspective of Onsager's formalism.

In summary, the flux−force formalism of Onsager is shown to yield the cross-exchange electron-transfer rate constant expression of Marcus and to provide an insight into the correlation between the heterogeneous and the self-exchange electron-transfer rate constants. Onsager's phenomenological coefficients are identified for electron transfer at electrode surfaces as well as for homogeneous electron-transfer reactions. The phenomenological coefficients are estimated for a few typical electrochemical reactions from the experimental data.

Acknowledgment. The helpful comments of the reviewers are gratefully acknowledged. This work was supported by the DST, Government of India.

Appendix A

In this appendix, we demonstrate that the Butler−Volmer equation can be derived by employing the alternate definition of the affinity in terms of the electrochemical potentials of the species, namely,[15]

$$-A = \overline{\mu_{\mathrm{Red}}} - \overline{\mu_{\mathrm{Ox}}} \qquad \text{(A1)}$$

and the affinity at equilibrium A_{eq} is zero; that is,

$$A_{eq} = \overline{\mu_{\mathrm{Red},eq}} - \overline{\mu_{\mathrm{Ox},eq}} = 0 \qquad \text{(A2)}$$

Consequently,

$$A_{eq} - A = (RT \ln C_{\mathrm{Red}} + z_{\mathrm{Red}} FE) - (RT \ln C_{\mathrm{Ox}} + z_{\mathrm{Ox}} FE) \qquad \text{(A3)}$$

Hence, the affinity becomes

$$-A = RT \ln \frac{C_{\mathrm{Red}}}{C_{\mathrm{Ox}}} + nFE \qquad \text{(A4)}$$

n being the number of electrons transferred ($z_{\mathrm{Red}} - z_{\mathrm{Ox}}$) and E being the electrode potential. However, the velocity is related to the affinity via eq 40. Substitution of the expressions for A and L from eqs A4 and 43 respectively in eq 40 leads to the Butler−Volmer equation. This methodology of formulating the Butler−Volmer equation is especially useful since more involved prescriptions of the electrochemical potentials such as incorporation of the interparticle interactions, partial charge transfer, and so forth can be invoked.

References and Notes

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