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Electron transfer reactions at metal electrodes: Influence of work function on free energy of activation and exchange current density

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The dependence of the free energy of activation on the work function of electrodes, solvation energies, and surface potentials of the reactant species pertaining to electron transfer reactions at metal/solution interfaces is derived using thermodynamic considerations. The standard exchange current density is calculated for $\text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+}$ at different metal electrodes and compared with experimental data as well as molecular dynamics simulations. © 2001 American Institute of Physics. [DOI: 10.1063/1.1398076]

I. INTRODUCTION

The theoretical analysis of charge transfer reactions at electrode/electrolyte interfaces has been a topic of numerous investigations during the past few decades and the mechanistic aspects of these reactions are essentially centered around the question of adiabaticity versus nonadiabaticity,¹ inner sphere versus outer sphere,² nature of solvent polarization modes,^{3–7} and the role of electronic density of states.⁸ The extraction of electrode kinetic parameters (exchange current density, transfer coefficients, overpotentials, double layer charging current, etc.) is usually accomplished with the help of different transient or steady state electrochemical techniques, on the basis of the classical Butler–Volmer equation.⁹ On the other hand, quantum mechanical studies in this context employ different molecular dynamics simulation versions, coupled with the Anderson–Newns Hamiltonian,¹⁰ incorporating electronic orbitals. The dependence of the current–potential relation on the nature of the supporting electrolyte, electronic structure of metals, and polarity of the solvent medium pertaining to simple redox couples constituted a central theme in early investigations on electrode kinetics. On the other hand, current experimental trend in heterogeneous electron transfer reactions emphasize the control of rate using the distance of separation between redox centers,^{11–17} characteristics of the intervening medium,¹⁸ adsorption behavior of molecules,¹⁹ and magnitude of driving force.^{20–22} A recent study concerning the influence of the electrode density of states on the rate of electron transfer when monolayers of osmium-containing redox couples are formed deserves mention in this context.¹⁹

The complete elucidation of microscopic details pertaining to the mechanism of interfacial electron transfer reactions is rendered especially difficult in view of a large number of “control variables” governing the system and in general, there is no one-to-one correspondence between the macroscopic observables and derived parameters. Consequently, it has become customary to analyze isolated issues such as (i) dependence of exchange current density on the nature of the metal surface,²³ (ii) role of solvent dielectrics,^{3–7} and (iii)

electronic effects which influence the coupling between the electrode surface and reactant species.²⁴

Among various parameters appearing in the classical Butler–Volmer equation of electrode kinetics, the standard exchange current density (i_0) has a central role insofar as it is a measure of the rate of the reaction at zero overpotential and has been extensively investigated using a variety of experimental techniques such as impedance spectroscopy, Tafel polarization, etc.²⁵ However, its explicit functional dependence on solvent medium, nature of single crystal surfaces, electron density of metals, work function, etc. has remained elusive. On the other hand, the hydrogen evolution reaction (HER) represented as $\text{H}^+ + e \leftrightarrow (1/2)\text{H}_2$ on a large number of electrode surfaces has been thoroughly studied during the past few decades²⁶ because of its importance in hydrogen embrittlement, fuel cells, and electrodeposition reactions. Recently the analysis of the reaction $\text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+}$ at the electrode/electrolyte interface has been a focus^{1,3,4} of investigation in view of its outer sphere nature as well as implication in electrocatalysis, and various simulation procedures are employed for calculating the activation energy barrier, solvent polarization effects, and quantum influences.

In this article we report an explicit expression for the exchange current density in terms of work function of the metal surface, surface potential of the reactants and products, and solvation energies. While the proposed methodology is applicable to any electron transfer reaction scheme, we demonstrate its usefulness for a ferric/ferrous reaction whose i_0 values have been reported for a variety of electrodes using experimental data and theoretical calculations. The essential feature in our analysis consists in partitioning the free energy of activation into different contributions and exploiting the availability of thermodynamic parameters.

II. FREE ENERGY OF ACTIVATION AND STANDARD EXCHANGE CURRENT DENSITY

The electron transfer rate constant k_{et} is related to standard exchange current density i_0 as^{9,27}

$$i_0 = (nFC_R k_{\text{et}}/A) \exp\{-\beta nFE_e/RT\}, \quad (1)$$

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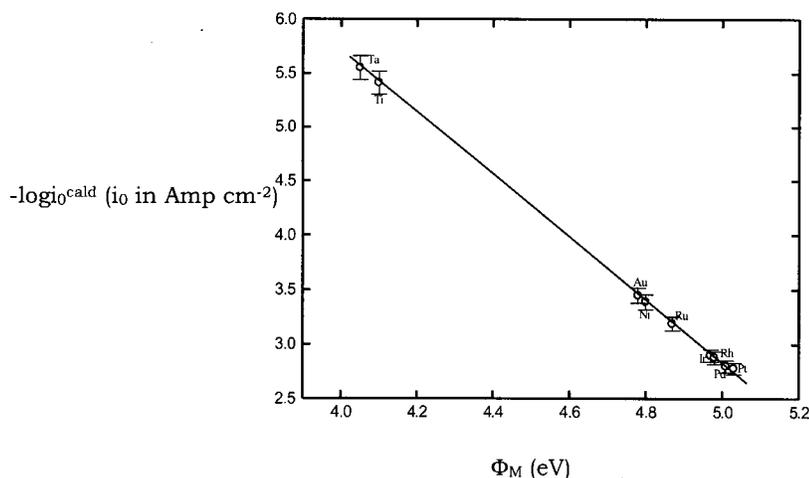


FIG. 1. Dependence of $\log i_0$ on work function of metals, calculated from Eq. (16). The effect of introducing $\pm 2\%$ errors in the calculated $\log i_0$ which may arise from the assumed set of system parameters is shown as error bars.

where β denotes the symmetry factor; n and A denote, respectively, the number of electrons and area of the electrode; C_R is the bulk concentration of the reactant (in moles) while E_e is the equilibrium potential of the redox reaction, and F denoting Faraday ($96\,500 \text{ C mol}^{-1}$). Further, one may express k_{et} in terms of free energy of activation^{9,27} (ΔG^\ddagger) as

$$k_{\text{et}} = (k_b T/h) \exp\{-\Delta G^\ddagger/RT\}, \quad (2)$$

where k_b and h represent the Boltzmann and Planck constant, respectively. Equations (1) and (2) enable the calculation of k_{et} and i_0 using ΔG^\ddagger estimates. Equation (2) implies that the transmission coefficient κ is unity²⁷ indicating that the frequency of formation of transition state equals k_{et} . However, the calculation of ΔG^\ddagger is a nontrivial exercise in view of its dependence on the nature of the electrode surface, reactant under consideration, and interfacial solvent behavior. Since we are presently investigating the metal dependence of ΔG^\ddagger vis-à-vis i_0 , we incorporate the work function characteristics explicitly in the formalism, as shown below.

III. SOLVATION ENERGIES AND SURFACE POTENTIALS

It is well known that the free energy of activation ΔG^\ddagger is influenced by work terms involving reactants and products viz.,

$$\Delta G^\ddagger = (w_r + w_p)/2. \quad (3)$$

The above equation is reminiscent of the customary interpretation of the free energy of activation arising from the classical Marcus theory^{28,29} which consists of contributions involving work terms and solvent influences. However, since our methodology of evaluating w_r and w_p of Eq. (3) is somewhat different from the procedure advocated by Marcus, terms involving the reorganization energy of solvent molecules do not occur explicitly at this stage. In order to investigate the metal dependence, Eq. (2) is modified as

$$\Delta G^\ddagger = (w_r + w_p)/2 + \Delta G_{\text{et}}, \quad (4)$$

where ΔG_{et} representing the free energy involved in the electron transfer process is influenced by the work function of the metal in the solvent environment. In general, ΔG_{et} is

composed of the electrochemical potential μ_M^S and surface potential χ_M^S of the metal³⁰ in solvent S . Thus

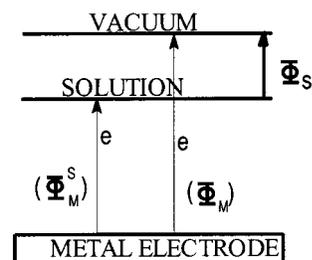
$$\Delta G_{\text{et}} = \mu_M^S + nF\chi_M^S, \quad (5)$$

where n is the number of electrons involved. μ_M^S is given as³⁰

$$\mu_M^S = -nF(\chi_M^S + \Phi_M^S), \quad (6)$$

Φ_M^S being the work function of the solvated electrode (Scheme 1). Further,

$$\Phi_M^S = \Phi_M - \Phi_S, \quad (7)$$



where Φ_S denotes the work function of the solvent defined as the energy required for the electrons in solvent to escape to vacuum,³¹ viz.,

$$\Phi_S = \mu_e^S - \chi_e^S, \quad (8)$$

where μ_e^S and χ_e^S denote, respectively, the electrochemical potential and surface potential of electrons in solution. Under electronic equilibrium μ_e^S and χ_e^S are identified as μ_e^M and χ_e^M , respectively. Rearrangement of Eq. (7) with the help of Eq. (8) leads to

$$\Phi_M^S = \xi \Phi_M, \quad (9)$$

where

$$\xi = 1 + [(\mu_e^M - \chi_e^S)/\Phi_M]. \quad (10)$$

This simplification enables the formulation of ΔG_{et} as

$$\Delta G_{\text{et}} = -nF\xi\Phi_M. \quad (11)$$

TABLE I. Estimation of $\log i_0$ at 298 K using Eq. (18). The area of the electrode is assumed to be 0.1 cm^2 . The symmetry factor β equals 0.5 and $C_{\text{Fe}^{3+}}=0.1 \text{ M}$.

Metal	Work function (eV)	$-\log i_0$ (i_0 in A cm^{-2}) [Eq. (18)]	k_{et} in 10^{-3} s^{-1} [Eqs. (2) and (15)]	ΔG^\ddagger (eV) [Eq. (15)]	$-\log i_0$ (i_0 in A cm^2), experimental data (Ref. 33)	μ_e^M (eV) (Ref. 31)
Ta	4.05	5.55	0.0951	0.9953	5.91	-3.762
Ti	4.10	5.41	0.132	0.9868	6.58	-3.803
Au	4.78	3.45	11.95	0.8712	3.60	-4.367
Ni	4.80	3.39	13.60	0.8678	3.44	-4.384
Ru	4.87	3.19	21.70	0.8559	3.04	-4.442
Ir	4.97	2.90	42.10	0.8389	2.82	-4.525
Rh	4.98	2.88	44.90	0.8372	2.77	-4.533
Pd	5.01	2.80	55.00	0.8320	2.22	-4.558
Pt	5.03	2.78	55.50	0.8290	2.60	-4.575

In the above equation ξ is a measure of the ease with which electrons leave the solvated electrode and reach the reactant species present in the reaction zone.

The physical significance of ξ is at first puzzling. However, numerical evaluation using Eq. (10) indicates that ξ equals 0.17 irrespective of the nature of the metal. This constancy is somewhat unanticipated since $\Phi_M - \Phi_M^S$ which denotes the solvation free energy of electrons is independent of the metal. In view of this, the metal independency of the ratio Φ_M^S/Φ_M , denoted as ξ here is *prima facie* unclear. However, the constancy of ξ may be rationalized via conceptual insights as well as numerical calculations in the following manner. Since the estimation of μ_e^S and μ_e^M themselves are not directly available, we invoke the occurrence of electronic equilibrium and hence rewrite $\mu_e^S - \chi_e^S$ as $\mu_e^M - \chi_e^M$. Further, when anisotropy of surface orientation is ignored at the first level of approximation³¹ χ_e^M has been reported to be -0.4 eV . In addition, $(\mu_e^M - \chi_e^M)$ is of the same order of magnitude as Φ_M thereby making $(\mu_e^M - \chi_e^M)/\Phi_M$ to be a constant (-0.83) leading to ξ as 0.17. Alternately ξ may be shown to be a constant from numerical considerations too. For this purpose we appeal to the definition of ξ as $\xi=1$

$+(\mu_e^M/\Phi_M) - (\chi_e^M/\Phi_M)$. Interestingly, (μ_e^M/Φ_M) varies from 0.910 to 0.928 as one passes from Pt ($\Phi_M=5.03 \text{ eV}$) to Ta ($\Phi_M=4.05 \text{ eV}$). On the other hand, χ_e^M , representing the surface potential of electrons in solution, is estimated to be -0.4 eV on the basis of simple jellium models.³¹ Since the work functions of metals considered here vary from 4.05 to 5.03 eV, $|\chi_e^M/\Phi_M|$ is in general less than 10% of $|\mu_e^M/\Phi_M|$ thereby making ξ to be effectively a constant, independent of the nature of the metal.

w_r can be written³² as the sum of the energy required in bringing the reactant from (a) bulk to OHP (which involves the solvation energy ΔG_{r-s}) and (b) OHP to reaction zone (dictated by the surface potential of reactants, χ_r). Analogous considerations apply for w_p . Although χ_r and χ_p denoting the surface potentials cannot be estimated in the general case, under zero overpotential limit vis-à-vis establishment of electronic equilibrium, it follows that $\chi_r = z_r \chi_e^S$; $\chi_p = -z_p \chi_e^S$. (The negative sign indicates that the movement of products is in the direction opposite to that of the reactant.) Thus it is possible to write

$$w_r = \Delta G_r^{\text{inter}} + z_r F \chi_e^S \quad (12)$$

and

$$w_p = -\Delta G_p^{\text{inter}} - z_p F \chi_e^S. \quad (13)$$

The interfacial Gibbs free energy of solvation is a crucial quantity which is dictated by the double layer thickness, electron density of the metal and extent of imaging. A first-principles calculation of the same is a tedious task; however, the fact that ΔG_{r-s} is considerably diminished from its bulk value in the presence of electrode surfaces is well known.^{10,24} We incorporate this feature by invoking the solvation number S_N and express $\Delta G_r^{\text{inter}}$ as $\Delta G_{r-s}/S_N$ and analogously $\Delta G_p^{\text{inter}} = \Delta G_{p-s}/S_N$. The justification behind the division by solvation number S_N arises from the fact that the free energy of solvation of ions in the adsorbed state will be smaller than the bulk value in view of the image energy corrections.¹⁰

Combining Eqs. (11), (12), and (13)

$$\Delta G^\ddagger = (\Delta G_{r-s}/S_N + z_r F \chi_e^S)/2 + (-\Delta G_{p-s}/S_N - z_p F \chi_e^S)/2 - nF \xi \Phi_M. \quad (14)$$

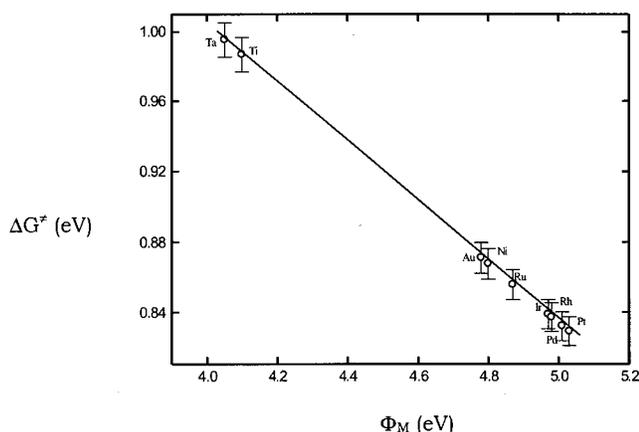


FIG. 2. Influence of work function on the free energy of activation (ΔG^\ddagger) estimated from Eq. (15). The effect of introducing $\pm 2\%$ errors in the calculated $\log i_0$ which may arise from the assumed set of system parameters is shown as error bars.

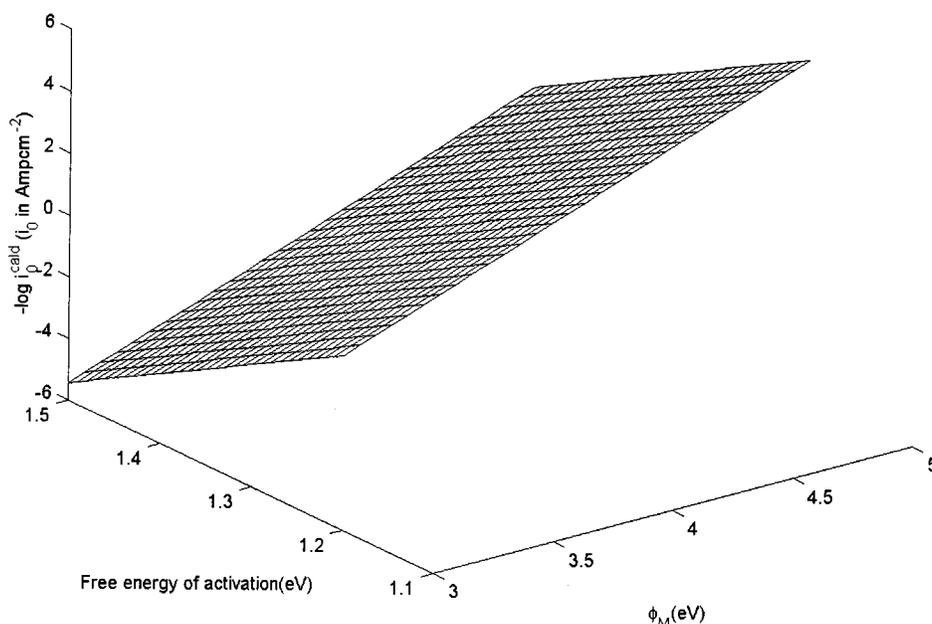


FIG. 3. Three-dimensional mesh plot depicting the simultaneous dependence of $\log i_0$ on work function (Φ_M) and free energy of activation (ΔG^\ddagger) obtained using Eq. (16). The range of values chosen for mesh plot are 3:0.067:5 and 1.2:0.01:1.5 for work function and free energy of activation, respectively.

For the ferric/ferrous couple, ΔG_{r-s} and ΔG_{p-s} become $\Delta G_{\text{Fe}^{3+}-s}$ and $\Delta G_{\text{Fe}^{2+}-s}$, respectively, while n equals unity; thus Eq. (14) becomes

$$\Delta G^\ddagger = (\Delta G_{\text{Fe}^{3+}-s}/S_N + z_r F \chi_e^S)/2 + (-\Delta G_{\text{Fe}^{2+}-s}/S_N - z_p F \chi_e^S)/2 - F \xi \Phi_M. \quad (15)$$

The above equation incorporates charges of reactants and products, surface potentials, solvation number, and Gibbs free energies.

IV. EXCHANGE CURRENT DENSITY

Equation (15) representing the free energy of activation ΔG^\ddagger can be substituted in Eq. (1) to obtain

$$\log i_0 = A + B \Phi_M, \quad (16)$$

where

$$A = \{\log(FC_{\text{Fe}^{3+}}k_b T/Ah)\} - (\Delta G_{\text{Fe}^{3+}-s}/4.606S_N RT) - (\Delta G_{\text{Fe}^{2+}-s}/4.606S_N RT) - (3F\chi_e^S/4.606RT) - (-2F\chi_e^S/4.606RT) - (\beta F E_e/2.303RT) \quad (17)$$

and

$$B = F \xi / 2.303 RT. \quad (18)$$

While the symmetry factor is 0.5 for a variety of electron transfer reactions, E_e is dictated by the nature of the redox couple; further, $\Delta G_{\text{Fe}^{3+}-s} = 51.42 \text{ eV}^{32}$ and $\Delta G_{\text{Fe}^{2+}-s} = 20.55 \text{ eV}^{32}$ while the solvation number for Fe^{3+} and Fe^{2+} , respectively, is 11 and 12 as deduced from compressibility measurements and thermodynamic calculations.³³ Before we verify the validity of Eq. (15) for $\text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+}$, it is imperative to point out that the linear dependence of $\log i_0$ on Φ_M has been first reported in the experimental studies of HER on a large number of *sp* and *d* metals.³² However, the formal dependence of the type predicted by Eq. (16) has

been reported here for the first time. Further, the constant slope of 3.3 eV^{-1} obtained for the ferric/ferrous reaction when $-\log i_0$ versus Φ_M is plotted (cf. Fig. 4 of Trasatti *et al.*²³) can now be attributed to the factor $F \xi / RT$ which is independent of the metal being considered (in this analysis $F \xi / RT$ is ca. 2.9 eV^{-1} at 298 K deduced from Fig. 1).

V. DISCUSSION

Equations (14) and (16) are the central results of the present approach and depict the explicit role of the metal electrode in dictating the standard exchange current density whose evaluation requires no adjustable parameters. In Table I the computed $\log i_0$ values are compared with experimental data³⁴ and a satisfactory agreement may be noticed in all cases. Further, a linear correlation between $\log i_0$ and Φ_M in agreement with the experimental data of Bockris *et al.* is obtained.³⁴ Alternatively, by substituting appropriate parameters pertaining to the solvent in Eq. (15), ΔG^\ddagger for various metals can be obtained leading to Fig. 2 which enables the prediction of ΔG^\ddagger vis-à-vis $\log i_0$ for any unknown metal from the linear regression equation $\Delta G^\ddagger = \alpha_1 + \alpha_2 \Phi_M$, where $\alpha_1 = 1.69 \text{ eV}$ and $\alpha_2 = -0.17$ and Φ_M is in eV which is consistent with the algebraic calculation resulting from Eq. (15). In view of any uncertainties in the bulk Gibbs free energy of solvation for Fe^{3+} and Fe^{2+} , we introduce error bars by allowing $\pm 2\%$ deviations in the calculated $\log i_0$ and ΔG^\ddagger values (Figs. 1 and 2) so that these will grossly reflect the uncertainties involved in various energetic contributions appearing in Eq. (16). Since $\log i_0$ varies with ΔG^\ddagger which in turn is dependent upon Φ_M , a three-dimensional mesh plot is convenient in depicting the simultaneous influence of these two parameters on $\log i_0$ (Fig. 3). As can be seen from Table I, k_{et} depends upon the work function of the metals and provides a possible interpretation of the recently observed work function influence of k_{et} in the case of monolayers of osmium complexes formed on Au, Pt, and glassy carbon

electrodes.¹⁹ We note that while Φ_M pertaining to the metals in Table I spans a range of 4 to 5 eV, ΔG^\ddagger varies from 0.829 to 0.995 eV and will show a stronger dependence if metals with widely varying work functions are considered. k_{et} for Pt is ≈ 584 times larger than that for Ta and is attributed to the fact that the work function of Pt is ≈ 1 eV higher.

The availability of an explicit expression for the free energy of activation in terms of work function of the metal nature of the reactant species, and solvent characteristics enables investigating a variety of issues arising in heterogeneous electron transfer reactions. The dependence of the exchange current density on the electronic structure of metals has been a central focus of investigation in density functional theory pertaining to electrode kinetics.^{1,2} The electron transfer rate of $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ on Pt and Au was shown to be independent of the nature of the metal and ascribed to the fact that metal electrodes essentially function as electron reservoirs.³⁵ On the other hand, a plot of experimental $\log i_0$ versus work function in the case of d metals such as Au, Pt, Pd, etc. for a ferric/ferrous reaction is linear (cf. Fig. 2 of Bockris *et al.*³⁴). The formalism propounded here also supports such a linear correlation. However, it is imperative to examine the extent to which the metal under consideration contributes to the free energy of activation. For this purpose we recall that the work function of metal electrodes employed usually vary from 4 to 5 eV. Since ξ of Eq. (11) is 0.170 for all metals, the contribution of $F\xi\Phi_M/RT$ varies from 0.68 to 0.85 eV. On the other hand, the rest of the terms of Eq. (15) in this reaction when water is employed as a solvent has a magnitude of 1.69 eV for the ferric–ferrous couple. In general, therefore, this indicates that solvent-dependent terms play a predominant role when compared with the influence of the metal. However, when other solvents such as dimethylsulphoxide, acetone, etc., whose free energy of solvation is lower and ions having smaller surface potentials are considered, the metal dependence may become crucial. Thus the occurrence or nonoccurrence of the influence of electrode surfaces in the free energy of activation for heterogeneous electron transfer reactions is largely an interplay between solvent contribution and work function magnitudes. Further, the extent of spillover of electronic density profile into the metal/solvent interface using jellium models and pseudopotentials is a central issue in analyzing equilibrium properties of the electrical double layer.^{36–38}

In recent years, detailed investigations on the reorganization energy of solvent molecules pertaining to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ reaction on Pt(111)^{1,3,4} have been carried out by computer simulation methods. The essential outcome of these simulations is that the solvent reorganization energy λ of Marcus analysis^{1,39} is 2.4 eV for $\text{Fe}^{3+}/\text{Fe}^{2+}$ at Pt electrodes. It is of interest to verify the prediction of Eq. (15) regarding the role of solvent energetics in electron transfer reactions. First, we note that no explicit term pertaining to solvent reorganization energy occurs in our analysis thereby precluding a direct comparison with values hitherto reported. Also, the calculations of w_r and w_p of Eq. (2) are carried out here in a different manner, employing solvation energy and surface potentials well known in thermodynamics of solution chemistry. In order to comprehend the role of solvent in our

formalism, the work function term of Eq. (15) is deleted and the remaining part of Eq. (15) then yields a value of 1.69 eV which corresponds to the contribution of solvent molecules in the free energy of activation in comparison with $\lambda \approx 2.4$ eV obtained using Umbrella sampling of molecular dynamics simulations.³

Since work function of any metal is linearly related to its potential of zero charge (pzc), Eq. (18) is able to describe the effect of pzc on the free energy of activation of electron transfer reactions. This feature is especially attractive in interpreting electron transfer reactions occurring at monolayer covered electrodes insofar as the functional dependence of the potential of zero charge on the surface coverage of ions or adsorbed molecules is customarily analyzed in electrosorption.¹⁰ Further, since i_0 can be interpreted using nonequilibrium statistical thermodynamic considerations,⁴⁰ the dependence of the free energy of activation pertaining to electrochemical reactions is amenable for analysis through Onsager's flux-force formalism. The possibility of incorporating metal dependence into the study of heterogeneous electron transfer reactions offers a framework by which electrochemical data can be analyzed using the concept of hardness,⁴¹ a current topic in the application of density functional theory to chemical reactions.

While the above phenomenological approach is useful in estimating the standard exchange current density on different metal surfaces (and single crystals) and employs no adjustable parameters, it has a limitation in not taking into account microscopic details concerning solvent polarization modes. Consequently, the above formalism is unable to depict the explicit role of solvent dielectric responses and/or nature of potential energy surfaces governing the coupling of the reactant with electrodes. A more unified treatment in this context would therefore require the incorporation of the metal dependence via density functional theory in conjunction with (non-linear) dielectric polarization of solvent molecules using appropriate energy coordinates. This, when accomplished, is likely to provide a global description pertaining to the current–potential relation for electron transfer reactions at metal electrodes.

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