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Double Layer Effects on the Enthalpy of Activation of Heterogeneous Electron Transfer Reactions

by

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**Double Layer Effects on the Enthalpy of Activation of Heterogeneous Electron
Transfer Reactions**

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Summary

The contributions to the experimental enthalpy of activation due to temperature variation in the double layer effect and the pre-exponential factor of the rate constant are considered in detail for heterogeneous electron transfer reactions. It is shown that the magnitude of the double layer correction depends significantly on the electrical variable held constant when temperature is varied. Correction of real enthalpies of activation, the quantity most often reported, requires a knowledge of the temperature dependence of the standard potential, and of the electrode charge density and the differential capacity at the standard potential. Data in the literature for the enthalpies of activation for simple one electron redox reactions involving organic molecules and triply charged metal ions are reviewed and the double layer effects analyzed. It is emphasized that the simplest way to determine the enthalpy of activation corrected for double layer effects is by examining the temperature dependence of the double layer corrected rate constant.



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Introduction

Recent developments in the theory of electron transfer reactions [1-5] have resulted in increased interest in the activation parameters for these reactions. Although the significance of the various enthalpies of activation defined by Temkin [6] has been analyzed in some detail [7,8], the dependence of these quantities on double layer structure has seldom been considered. Randles and Somerton [9], who carried out the first systematic study of the effect of temperature on the kinetics of simple redox and metal amalgam formation reactions, pointed out that the magnitude of the enthalpy of activation should depend on double layer structure and composition. Convincing evidence for double layer effects was provided by Frumkin and Nikolaeva-Fedorovich [10] who showed that the apparent enthalpy of activation for the reduction of peroxydisulfate anion changes from a small positive value in the presence of NaCl to a large negative value in the presence of CsCl. Joshi, Mehl and Parsons [11] examined the temperature dependence of the potential drop across the diffuse layer in aqueous solutions and discussed its significance with respect to kinetic data for the V^{3+}/V^{2+} redox couple. The double layer data were presented on a rational potential scale and corrections to the real enthalpy of activation [6] analyzed by considering the role of the thermodynamic parameters for the specific reaction in determining the magnitude of the double layer correction term. Chauhan et al. [12] considered double layer effects on the enthalpies of activation for the reduction of hydrogen and periodate ions at mercury. In the case of the periodate system, not only was the enthalpy of activation dependent on the nature of the cation of the supporting electrolyte, but the apparent transfer coefficient was found to be temperature dependent. Weaver [13] has emphasized the importance of the ideal enthalpy of activation [6] in considering data for redox couples whose standard potential is not readily available, and has also considered double layer effects for this quantity. Most recently, Conway [14] discussed the temperature dependence of the transfer coefficient observed for some reactions. This subject is closely related to that being considered in this paper.

The chief reason for the failure to consider double layer effects quantitatively in most previous work was the lack of the necessary double layer data as a function of temperature. Calculations for the Hg/aqueous solution interface in the absence of ionic adsorption have been based on the data of Grahame for the NaF system [15]. More recently, the temperature dependence of the thermodynamic properties of the Hg/non-aqueous solution interface has been reported for a number of solvents [16]. Considering the availability of computerized digital data acquisition systems, double layer data can be obtained much more easily than in the past. For instance, these data can be collected together with electrode kinetic data when a.c. admittance techniques are used.

In view of the renewed interest in activation parameters for electron transfer reactions, it seemed worthwhile to reexamine double layer effects for these quantities. In this regard, it is very important to specify the parameters held constant when the temperature is changed. In his original paper [6], Temkin discussed two types of quantities, namely ideal activation parameters which are measured at constant electrode inner potential, and real activation parameters which are measured at constant overpotential. The quantities considered in detail here are the real activation parameters which are of fundamental theoretical interest and experimentally available. Estimation of the double layer correction in this case requires knowledge of the temperature variation of both the point of zero charge and the equilibrium potential of the reaction on a given experimental potential scale. Determination of activation parameters using kinetic data which have been corrected for double layer effects at each temperature where measurements were made is also considered. The main thrust of this paper is to assess the importance of double layer effects on activation parameters and to provide some general indications regarding when they should be considered, and when they are unimportant in determining the magnitude of the activation parameters. Finally, double layer effects on ideal activation parameters which are of interest under certain circumstances [13] are considered in the Appendix.

Theory

Consider a simple heterogeneous electron transfer reaction



involving transfer of one electron with no formation or breaking of chemical bonds.

According to transition state theory [8,17,18] the rate constant for the forward process, k_r , is given by the equation

$$\ln k_r = \ln k_0 + \ln (\gamma_A/\gamma_{\ddagger}) - z_A f \phi^r + \alpha f (\phi^r - \phi^m) \quad (2)$$

where k_0 is the value of the rate constant when $\phi^m = \phi^r = 0$, γ_A , the activity coefficient of A in the bulk of the solution, γ_{\ddagger} , that for the activated complex, ϕ^m , the inner potential of the metal, ϕ^r , the average potential on the reaction plane (r.p.), z_A , the charge on the reactant, α , the transfer coefficient, and $f = F/RT$. The activity coefficient γ_{\ddagger} takes into account any departure of the local potential at the reaction site from the average value on the r.p. [18]. Its variation with electrode potential and/or temperature becomes more important as the reaction site is located closer to the interface as will be discussed in more detail below. Since the position of the r.p. with respect to the electrode varies with the nature of the reactant and, in general, is not known, eq. (2) is usually written in terms of the average potential on the outer Helmholtz plane (o.H.p.), ϕ^d , as estimated by the Gouy-Chapman theory. Then, expressing ϕ^r in terms of ϕ^d and the potential drop in the inner layer,

$\phi^m - \phi^d$, one obtains

$$\phi^r = \phi^d + \lambda (\phi^m - \phi^d) \quad (3)$$

where λ is a dimensionless fraction which depends on the average potential profile in the inner and diffuse layers near the o.H.p. Detailed expressions for λ have been described elsewhere [19,20]; it suffices to say here that λ is positive for reaction sites in the inner layer and negative for those in the diffuse layer, and that λ may change somewhat with temperature. Substituting eq. (3) into eq. (2), and defining the apparent transfer coefficient α_a where

$$\alpha_a = \alpha - \lambda (\alpha - z_A) \quad (4)$$

one obtains the familiar result

$$\ln k_r = \ln k_0 + \ln (\gamma_A/\gamma_{\ddagger}) - z_A f\phi^d + \alpha_a f (\phi^d - \phi^m) \quad (5)$$

The potential independent rate constant k_0 may be written as

$$\ln k_0 = \ln Z - \Delta G_0^\ddagger/RT \quad (6)$$

where Z is a pre-exponential factor often discussed as a collision frequency [21], and ΔG_0^\ddagger , the standard free energy of activation, a quantity which is independent of potential.

In order to obtain the real enthalpy of activation, eq. (5) is differentiated with respect to the reciprocal of the temperature holding the overpotential η constant, where the overpotential is defined as

$$\eta = \phi^m - \phi_e^m, \quad (7)$$

ϕ_e^m being the equilibrium potential on the inner potential scale. The result may be written as

follows:

$$\begin{aligned} \Delta H_r^\ddagger = -R \left[\frac{\partial \ln k_r}{\partial (1/T)} \right]_{\eta} &= \Delta H_0^\ddagger - R \left[\frac{\partial \ln (\gamma_A Z)}{\partial (1/T)} \right] + R \left[\frac{\partial \ln \gamma_{\ddagger}}{\partial (1/T)} \right]_{\eta} \\ &- (\alpha_a - z_A) F \left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\eta} - F (\phi^d - \phi^m) \left[\frac{\partial (\alpha_a/T)}{\partial (1/T)} \right]_{\eta} + \alpha_a F \left[\frac{\partial (\phi_e^m/T)}{\partial (1/T)} \right] + \alpha_a F \eta \end{aligned} \quad (8)$$

ΔH_0^\ddagger is called the true enthalpy of activation and is equal to the real enthalpy of activation at $\phi^m = 0$ when the contributions from the pre-exponential factor and the double layer have been considered. The second term which arises from the temperature dependence of the pre-exponential terms which are potential independent is called ΔH_Z^\ddagger in the following discussion. The following three terms arise from double layer effects. The one related to the temperature dependence of the ϕ^d , $(\Delta H_{GC}^\ddagger)_r$ is easily estimated from Gouy-Chapman theory and the appropriate double layer data. The other two are designated $(\Delta H_{dl}^\ddagger)_r$, it being noted that any estimate of the contributions from the temperature dependence of γ_{\ddagger} and α_a must be made at constant η . The temperature dependence of ϕ_e^m is obtained from the Nernst equation from which

$$\frac{\partial(\phi_e^m/T)}{\partial(1/T)} = \frac{\partial(\phi_o^m/T)}{\partial(1/T)} = -\frac{1}{F} \frac{\partial(\Delta G^o/T)}{\partial(1/T)} = -\frac{\Delta H^o}{T} \quad (9)$$

where ϕ_o^m is the standard potential for reaction (1), and ΔG^o and ΔH^o , the corresponding Gibbs energy and enthalpy changes, it being understood that the activity of A and B are held constant when the temperature is changed. It follows that the real enthalpy of activation may be written

$$\Delta H_r^\ddagger = \Delta H_o^\ddagger + \Delta H_z^\ddagger + (\Delta H_{GC}^\ddagger)_r + (\Delta H_{dl}^\ddagger)_r - \alpha_a \Delta H^o + \alpha_a F \eta \quad (10)$$

where

$$\Delta H_z^\ddagger = -R \left[\frac{\partial \ln(\gamma_A Z)}{\partial(1/T)} \right] \quad (11)$$

$$(\Delta H_{GC}^\ddagger)_r = (z_A - \alpha_a) F \left[\frac{\partial(\phi^d/T)}{\partial(1/T)} \right]_\eta \quad (12)$$

and

$$(\Delta H_{dl}^\ddagger)_r = R \left[\frac{\partial \ln \gamma_\ddagger}{\partial(1/T)} \right]_\eta - F(\phi^d - \phi^m) \left[\frac{\partial(\alpha_a/T)}{\partial(1/T)} \right]_\eta \quad (13)$$

The magnitude of correction terms in eq. (10) is discussed in detail below.

When double layer effects are important, the kinetic data at a given temperature are often presented in terms of a corrected Tafel plot using the Frumkin equation [18,22,23]. Then, eq. (5) is written

$$\ln k_{rc} = \ln k_r + z_A f \phi^d = \ln k_o + \ln(\gamma_A/\gamma_\ddagger) + \alpha_a f(\phi^d - \phi^m) \quad (14)$$

where k_{rc} is the double layer corrected rate constant. It seems appropriate to define an enthalpy of activation based on the change in $\ln k_{rc}$ measured at constant overpotential corrected by the diffuse layer potential drop, that is, at constant $\eta - \phi^d$. This quantity, which we call the Frumkin enthalpy of activation, is given by the equation

$$\Delta H_F^\ddagger = -R \left[\frac{\partial \ln k_{rc}}{\partial (1/T)} \right]_{\eta-\phi^d} = \Delta H_O^\ddagger + \Delta H_Z^\ddagger + (\Delta H_{dl}^\ddagger)_F - \alpha_a \Delta H^o + \alpha_a F (\eta - \phi^d) \quad (15)$$

The term $(\Delta H_{dl}^\ddagger)_F$ is given by eq. (12) but with the derivatives estimated at constant $\eta - \phi^d$.

In assessing the above equations, one should keep in mind that they have been written in the most general form possible. For many systems, the variation in $\ln \gamma_{\ddagger}$ and α_a with potential and temperature is negligible. Under these circumstances, the term ΔH_{dl}^\ddagger in the above expressions is zero, and the relationship between ΔH_T^\ddagger or ΔF_F^\ddagger and ΔH_O^\ddagger , much simpler. It follows that, if one can calculate ΔH_{GC}^\ddagger , all contributions to the real and Frumkin enthalpies of activation are specified except that coming from the pre-exponential factor, ΔH_Z^\ddagger .

Gouy-Chapman Contribution to the Enthalpy of Activation

Attention is now focussed on the derivative $\partial (\phi^d/T)/\partial (1/T)$ which makes up the major contribution to the double layer effect under most circumstances. The potential drop ϕ^d is assumed to be that given by the Gouy-Chapman theory, any defects in this model being ignored. Although problems with the Gouy-Chapman model are well known, the changes predicted in ϕ^d with potential and temperature are reasonably good in 1-1 electrolytes provided the electrode charge density is not too high [24]. In view of the fact that an alternative simple model is not available, it seems reasonable to use the Gouy-Chapman estimate of ϕ^d as the first means of estimating double layer effects in kinetic data, and to consider any deviations from the simple model as being associated with the activity coefficient of the activated complex, γ_{\ddagger} [18].

As pointed out by Joshi et al. [11], the most convenient way to estimate $(\Delta H_{GC}^{\ddagger})_r$ is by analyzing the double layer data on a rational potential scale. The required derivative is given by

$$\left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\eta} = \left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\phi^r} + \left[\frac{\partial (\phi^d/T)}{\partial \phi^r} \right]_T \left[\frac{\partial \phi^r}{\partial (1/T)} \right]_{\eta} \quad (16)$$

where ϕ^r , the potential on the rational scale is related to the overpotential by the equation,

$$\eta = \phi^r - \phi_e^r \quad (17)$$

ϕ_e^r , being the equilibrium potential on the rational scale. The derivative at constant temperature can be expressed as

$$\left[\frac{\partial (\phi^d/T)}{\partial \phi^r} \right]_T = \frac{C}{TC_d} \quad (18)$$

where C is the differential capacity of the double layer, and C_d , that of the diffuse layer. The latter quantity can be estimated from Gouy-Chapman theory. Making use of equation (17), and the relationship between the equilibrium potential and the standard potential assuming constant activities of reactant and product, the last term in equation (16) becomes

$$\left[\frac{\partial \phi^r}{\partial (1/T)} \right]_{\eta} = \left[\frac{\partial \phi_e^r}{\partial (1/T)} \right]_{\eta} = -T^2 \left[\frac{\partial \phi_o^r}{\partial T} \right] \quad (19)$$

where ϕ_o^r is the standard potential for reaction (1) on the rational scale. It follows that

$$\left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\eta} = \left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\phi^r} - \frac{TC}{C_d} \left[\frac{\partial \phi_o^r}{\partial T} \right] \quad (20)$$

The first term gives the contribution to $(\Delta H_{GC}^\ddagger)_r$ which depends only on the properties of double layer, and the second, the contribution which is specific to the reaction in question through the quantity $[\partial \phi_o^r / \partial T]$. The double layer contribution is conveniently calculated on the basis of the following equation:

$$\begin{aligned} \left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\phi^r} &= \left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\sigma_m} - \left[\frac{\partial (\phi^d/T)}{\partial \phi^r} \right]_T \left[\frac{\partial \phi^r}{\partial (1/T)} \right]_{\sigma_m} \\ &= \left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\sigma_m} - \frac{C}{TC_d} \left[\frac{\partial \phi^r}{\partial (1/T)} \right]_{\sigma_m} \end{aligned} \quad (21)$$

where σ_m is the charge density on the electrode. The first term may be estimated from the Gouy-Chapman theory which gives the following result for 1-1 electrolytes:

$$\left[\frac{\partial (\phi^d/T)}{\partial (1/T)} \right]_{\sigma_m} = \frac{2RT}{F} \frac{\sigma_m / 2A}{(1 + \sigma_m^2 / 4A^2)^{1/2}} \cdot \frac{\partial \ln A}{\partial \ln T} \quad (22)$$

A is the Gouy-Chapman constant given by

$$A = (2RT \epsilon_s \epsilon_0 c_s)^{1/2} \quad (23)$$

ϵ_s , being the dielectric constant of the solvent, ϵ_0 , the permittivity of free space, and c_s , the electrolyte concentration. The parameter A changes with temperature due to explicit dependence on $T^{1/2}$ and the corresponding change in $\epsilon_s^{1/2}$, the net effect being a decrease with increase in temperature. As a result, $\partial \ln A / \partial \ln T$ is negative, and the sign of the derivative $[\partial (\phi^d/T) / \partial (1/T)]_{\sigma_m}$ opposite to the sign of the electrode charge density σ_m . In the case of

water at 25 °C for which $\partial \ln A / \partial \ln T$ is -0.183, this quantity varies from 0 to -9.4 mV for a change in σ_m from 0 to 20 $\mu\text{C cm}^{-2}$. The second contribution to the right hand side of equation (21) depends on the variation in rational potential with temperature and the corresponding capacities of the double layer for a given electrode charge density. In the case of the experimental systems discussed below, it was always several times larger than the first term.

Values of $[\partial(\phi^d/T) / \partial(1/T)]_{\phi^r}$ were estimated for the Hg/ aqueous solution interface on the basis of data obtained by Grahame with NaF as electrolyte in the temperature range 0 to 85 °C [15]. Plots of this quantity against the electrode potential ϕ^r are shown for various electrolyte concentrations in Figure 1. It is apparent that the derivative is positive at potentials positive of the p.z.c., and negative in the negative region, and that the maximum values occur at values of ϕ^r approximately 100 mV on either side of the p.z.c. As one would expect, this contribution to the double layer effect decreases as the ionic strength increases.

Results similar to those presented in Figure 1 were obtained earlier by Joshi et al. [11]. These authors also considered the effect of the standard entropy change for the electrode reaction on the value of $(\Delta H_{GC}^\ddagger)_r$. For electrode reactions involving the reduction of cations, $[\partial\phi^d/\partial T]$ is positive due to decrease in charge of the product with respect to the reactant in reaction (1). As a result, the corresponding value of $[\partial(\phi^d/T) / \partial(1/T)]_{\eta}$ is more negative to an extent which depends on the shape of the capacity curve (see equation (20)). In the case of reactions with negative values of $[\partial\phi^d/\partial T]$, the effect is the opposite, $[\partial(\phi^d/T) / \partial(1/T)]_{\eta}$ being more positive than the value of $[\partial(\phi^d/T) / \partial(1/T)]_{\phi^r}$. These effects have been considered in more detail by Joshi et al. [11] for representative values of $[\partial\phi^d/\partial T]$. Since the value of double layer contribution to the real enthalpy of activation depends on the thermodynamic parameters of the reaction as well as double layer properties, it needs to be assessed for each individual reaction. However, one can state that, in general, double layer effects are more important near the p.z.c., and increase in importance with the charge on the reacting species.

Estimates of $F[\partial(\phi^d/T) / \partial(1/T)]_{\phi^d}$ for the Hg/dimethylformamide interface are shown in Figure 2. The double layer capacity data used to estimate the Gouy-Chapman correction were those obtained earlier with tetraethylammonium perchlorate as electrolyte [25]. The features of the plots of $F[\partial(\phi^d/T) / \partial(1/T)]_{\phi^d}$ against electrode potential are somewhat different from those obtained in the aqueous system and the magnitude of the change near the p.z.c. is significantly smaller. Nevertheless, the double layer correction to observed enthalpies of activation is important especially for reactions occurring near the p.z.c.

If the Frumkin enthalpy of activation is estimated from kinetic data in the form of corrected Tafel plots then the Gouy-Chapman correction is clearly incorporated in the corrected data. However, it is important to emphasize that the temperature dependence of $\ln k_{rc}$ must be considered at constant $\eta - \phi^d$. Only under these circumstances can the derived activation parameters be compared with those obtained in the traditional manner.

Temperature Dependence of the Pre-exponential Factor

As formulated above, the pre-exponential factor contains the collision frequency Z and activity coefficient of reactant A in the bulk of the solution, γ_A , the contribution to the enthalpy of activation being given by eq. (11). The activity coefficient of the reactant in the pre-exponential factor and its temperature dependence are normally not considered explicitly, but it is clear that they should be considered on the basis of transition state theory.

In the traditional treatment of heterogeneous electron transfer [21], the parameter Z is assumed to equal the one dimensional gaseous collision frequency given by

$$Z = (2 RT / \pi M_A)^{1/2} \quad (24)$$

where M_A is the molecular weight of reactant A. It follows that the temperature dependence of $\ln Z$ is given by

$$\frac{\partial \ln Z}{\partial (1/T)} = -T/2 \quad (25)$$

More recently, the parameter Z has been discussed in terms of the encounter pre-equilibrium model [26,27] according to which Z is given by

$$Z = \kappa K_p \nu_n \quad (26)$$

where κ is the electronic transmission coefficient, K_p , the effective equilibrium constant for formation of the precursor state, and ν_n , a nuclear frequency factor which corresponds to the effective frequency with which the configuration of the various nuclear coordinates appropriate for electron transfer is reached from the precursor state. The expression given here for Z neglects the nuclear tunnelling factor which is definitely temperature dependent at low temperatures [26]. It is assumed that this factor is a constant close to unity for the temperature range and systems under consideration. In the case of heterogeneous electron transfer, the equilibrium constant K_p is written as an effective reaction zone thickness δr for the case that the rate constant has been corrected for double layer effects [27], that is,

$$K_p = \delta r \quad (27)$$

This formulation shows no explicit temperature dependence and implies that K_p is determined by entropic effects only. In the case of adiabatic reactions, the electronic transmission coefficient is unity, and is expected to remain constant with temperature over reasonable temperature ranges. The nuclear frequency factor depends on the relative importance of inner and outer sphere contributions to the free energy of activation and has been expressed as [26]

$$v_n = \left(\frac{v_{os}^2 \Delta G_{os}^* + v_{is}^2 \Delta G_{is}^*}{\Delta G_{os}^* + \Delta G_{is}^*} \right)^{1/2} \quad (28)$$

where v_{is} is the average frequency characterizing inner sphere bond vibrations, v_{os} , the frequency describing solvent molecule reorientation outside of the reactant, and ΔG_{is}^* and ΔG_{os}^* , the inner sphere and outer sphere contributions, respectively, to the free energy of activation for electron transfer. In the limit that the rate is controlled by inner sphere reorganization ($\Delta G_{is}^* \gg \Delta G_{os}^*$), eq. (28) reduces to

$$v_n = v_{is} \quad (29)$$

The average frequency, v_{is} , which is the order of 10^{13} s^{-1} , is temperature independent to a good approximation. In the limit that the rate is controlled by outer sphere reorganization ($\Delta G_{os}^* \gg \Delta G_{is}^*$) the nuclear frequency factor is given by [2,3]

$$v_n = v_{os} = \tau_L^{-1} \left(\frac{\Delta G_{os}^*}{4 \pi R T} \right)^{1/2} \quad (30)$$

where τ_L is the longitudinal solvent relaxation time. The frequency, v_{os} , is clearly temperature dependent, the main contribution coming from the temperature dependence of τ_L . The longitudinal relaxation time is related to the more familiar Debye relaxation time τ_D through the expression [28,29]

$$\tau_L = \frac{\epsilon_\infty}{\epsilon_s} \tau_D \quad (31)$$

where ϵ_{∞} is the high frequency dielectric constant [30]. The temperature dependence of τ_D can be written [28] as

$$\tau_D = A_{\tau} \exp (\Delta H_{\tau} / RT) \quad (32)$$

where A_{τ} is a pre-exponential factor assumed here to be independent of temperature and ΔH_{τ} , the activation barrier determining the relaxation time. Values of ΔH_{τ} are available in the literature and vary significantly with solvent nature from a low of 6.6 kJ mol⁻¹ for the small aprotic solvent, nitromethane [31] to a high of 19.3 kJ mol⁻¹ for the strongly hydrogen bonded solvent, N-methylformamide [32]. Neglecting the temperature variation of ϵ_{∞} , the temperature dependence of v_{os} may be expressed as

$$\frac{\partial \ln v_{os}}{\partial (1/T)} = \frac{\partial \ln \epsilon_s}{\partial (1/T)} - \frac{\Delta H_{\tau}}{R} + \frac{T}{2} \frac{\Delta H_{os}^*}{\Delta G_{os}^*} \quad (33)$$

Furthermore, the entropy of outer sphere reorganization is small [21], so that one may assume that ΔH_{os}^* is approximately equal to ΔG_{os}^* . As a result, the temperature dependence of Z for the case that $\Delta G_{os}^* \gg \Delta G_{is}^*$ is given by

$$\frac{\partial \ln Z}{\partial (1/T)} = \frac{\partial \ln (\kappa K_p v_{os})}{\partial (1/T)} = \frac{T}{2} - \frac{\Delta H_{\tau}}{R} + \frac{\partial \ln \epsilon_s}{\partial (1/T)} \quad (34)$$

The temperature dependence of the activity coefficient γ_A may be assessed on the basis of the Debye-Hückel theory. Accordingly,

$$\ln \gamma_A = -z_A^2 A I^{1/2} = \frac{-z_A \Theta I^{1/2}}{\epsilon_s^{3/2} T^{3/2}} \quad (35)$$

where A is the Debye-Hückel constant, I, the ionic strength, and Θ , the temperature independent part of the Debye-Hückel constant. Differentiating with respect to reciprocal temperature, one obtains the result

$$\frac{\partial \ln \gamma_A}{\partial (1/T)} = \frac{3}{2} T \ln \gamma_A \left(1 + \frac{\partial \ln \epsilon_s}{\partial \ln T} \right) \quad (36)$$

In the case of water, the coefficient $\partial \ln \epsilon_s / \partial \ln T$ is -1.365. Since $\ln \gamma_A$ is a small negative number at the ionic strength normally used in kinetic studies, the coefficient $\partial \ln \gamma_A / \partial (1/T)$ is a

small positive number much less than T . If one estimates the temperature dependence on the basis of the extended Debye-Hückel theory, the temperature dependence is even smaller. Thus, it is concluded that under most circumstances, the temperature dependence of γ_A can be neglected.

In summary, on the basis of the above analysis, the factor ΔH_Z^\ddagger is given by

$$\Delta H_Z^\ddagger = RT/2 \quad (37)$$

within the context of the collision frequency model, or it falls within the limits

$$0 \leq \Delta H_Z^\ddagger \leq \Delta H_\tau - RT/2 - R \frac{\partial \ln \epsilon_s}{\partial(1/T)} \quad (38)$$

on the basis of the encounter pre-equilibrium model. Thus, ΔH_Z^\ddagger is often a small positive quantity which should be considered in assessing the observed enthalpy of activation.

The Temperature Dependence of the Activity Coefficient of the Activated Complex and the Apparent Transfer Coefficient

In this section, we consider the term ΔH_{dl}^\ddagger which arises from the temperature dependence of the activity coefficient γ_{\ddagger} and the transfer coefficient α_a . Although the potential variable held constant in evaluating ΔH_{dl}^\ddagger must be specified as pointed out above, the following discussion is qualitative in nature so that this requirement is not considered further.

The importance of considering the activity coefficient γ_{\ddagger} has been elaborated several times in the literature [18,33-37], but the possible potential and temperature dependence of this term has often been ignored in the analysis of experimental data. When the interaction of the reactant with its environment in solution or with the electrode changes significantly with potential or with temperature, then the change in $\ln\gamma_{\ddagger}$ will also be significant and should be considered in assessing the transfer coefficient and activation parameters. In the case of redox reactions involving species which do not interact strongly with the electrode, one can distinguish three types of reaction environment as far as double layer effects are concerned [18]. A type I double layer effect is one in which the reaction occurs in an environment containing ions of the same sign as those involved in the reaction. A simple example is the reduction of $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ to $\text{Cr}(\text{H}_2\text{O})_6^{+2}$ at potentials negative of the p.z.c. where the ions in the double layer region, where the reaction occurs, are predominantly cations in the absence of ionic specific adsorption. A type II effect is one in which the ions of the environment are predominantly of a sign opposite to those involved in the reaction. An example of such a system is the reduction of anions such as peroxydisulfate at potentials negative of the p.z.c. for which the cation concentration at the o.H.p. is high and increases with negative charge density on the electrode. Under these circumstances the observed rate constant depends on the nature of the cation as well as on potential [38]. The type III effect is the most complex and is present for reactions occurring in ionic atmospheres with both cations and anions in close proximity. This situation obtains for any electron transfer reaction occurring in the presence of strong adsorption of an ion of one sign with ions of the opposite sign predominant on the

o.H.p. [18]. If one of the components of the redox system is chemisorbed on the electrode, the effects described above become more pronounced. An example is the electroreduction of H^+ ion at mercury, the product of the reaction being an adsorbed hydrogen atom. When this reaction occurs in the presence of specifically adsorbed halide ions, the activity coefficient of the activated complex is strongly influenced by the electrostatic effects of these ions [34,39].

For a type I reaction in the absence of adsorption at the electrode, the activity coefficient γ_{\ddagger} is independent of potential and temperature to a good approximation. This follows from the fact that the free energy of the reacting system is influenced mainly by the field of the electrode and not by the nature of surrounding ions. Thus, ΔH_{dl}^{\ddagger} depends on the temperature dependence of the apparent transfer coefficient α_a . If this is negligible, then ΔH_{dl}^{\ddagger} can be neglected. As an example, the enthalpy of activation for H^+ reduction at Hg at far negative potentials is independent of the nature of the alkali metal cation in solution when the latter's concentration is much higher than that of the H^+ ion [12]. Moreover, the apparent transfer coefficient depends on the nature of the alkali metal cation in solution but is independent of temperature. Thus, the average potential on the reaction plane is influenced by its position relative to that of the o.H.p. Since attractive ion-ion interactions are absent, the electrostatic effects not included in the Gouy-Chapman term are temperature independent to a good approximation.

In the case of the type II effect, the activity coefficient γ_{\ddagger} depends on the nature and concentration of oppositely charged ions in the vicinity of the reaction site [18]. If σ_d is the charge density due to these ions in the vicinity of the o.H.p., the relationship between γ_{\ddagger} and σ_d may be expressed [18] as

$$\ln \gamma_{\ddagger} = a_{\ddagger} \sigma_d / RT \quad (39)$$

where a_{\ddagger} is an interaction parameter describing the attractive ion-ion interactions experienced by the activated complex. These interactions are expected to depend on electrode potential, the nature of the ions involved, and temperature. On the basis of eq. (14), the slope of a corrected Tafel plot (c.T.p.) is given by

$$\left[\frac{\partial \ln k_{rc}}{\partial(\phi^d - \phi^m)} \right]_T = \alpha_{af} - \left[\frac{\partial \ln \gamma_{\ddagger}}{\partial(\phi^d - \phi^m)} \right]_T = \alpha_{af} - \left[\frac{\partial(a_{\ddagger} \sigma_d / RT)}{\partial(\phi^d - \phi^m)} \right]_T \quad (40)$$

In the case of the electroreduction of peroxydisulfate anion [38,40], the slope of c.T.p.s. depends on the nature of the cation of the supporting electrolyte at potentials just negative of the p.z.c., increases as the electrode potential becomes more negative, and reaches a constant value at more negative potentials. These results can be attributed to local ion pair formation in the vicinity of the reaction site [18,36] which increases with the nature of the alkali metal cation in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. As the electrode potential becomes more negative, the charge density due to these cations near the reaction site increases and eventually reaches a constant value. As a result, the activity coefficient of the activated complex, which is a negative quantity, decreases and then becomes constant. The fact that the logarithm of the corrected rate constant increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ is due to a corresponding change in the interaction parameter a_{\ddagger} with decrease in the extent of solvation of the cation. Under these circumstances, one expects $\ln \gamma_{\ddagger}$ to vary also with temperature so that the term ΔH_{dl}^{\ddagger} is definitely non-zero. Frumkin and Nikolaeva-Fedorovich [10] found that the apparent enthalpy of activation for the reduction of peroxydisulfate anion decreases from a small positive value in the presence of Na^+ cation to a large negative value in the presence of Cs^+ cation. Their results suggest that ΔH_{dl}^{\ddagger} is a negative quantity whose magnitude increases with the strength of the interaction between the reacting anion and the cation of the supporting electrolyte. They are entirely reasonable when one considers the fact that the major contribution to ΔH_{dl}^{\ddagger} comes from the variation in $\ln \gamma_{\ddagger}$ with temperature (the term $\partial \ln \gamma_{\ddagger} / \partial (1/T)$ in eq. (11)). As temperature increases, the strength of ion-ion interactions decreases and $\ln \gamma_{\ddagger}$ increases; it follows that $\partial \ln \gamma_{\ddagger} / \partial (1/T)$ decreases and a negative contribution to the enthalpy of activation is observed. Similar results were obtained by Chauhan et al. [12] for the reduction of periodate anion in the presence of NaOH and KOH. For this system, the apparent enthalpy of activation decreased noticeably in going from the NaOH solution to a KOH solution of the same concentration. It was also observed that the apparent transfer coefficient defined as

$-RT/F [\partial \ln k_{rc} / \partial (\phi^m - \phi^d)]_T$ (see eq. (40)) decreased somewhat with increase in temperature. This observation can also be ascribed to a corresponding decrease in $\ln \gamma_{\ddagger}$ with temperature. In previous discussion [12], the change was attributed to a change in the parameter λ which defines the average potential profile at the reaction plane with respect to the o.H.p. However, it is undoubtedly also due to changes in the interaction term describing local ion pairing.

The above discussion is further illustrated by considering the case of a type III double layer effect, namely, the electroreduction of hydrogen ion at mercury in the presence of specifically adsorbed anions [39]. Parsons [34] showed that the accelerating effect of the adsorbed halide ions expressed as a change in the logarithm of the observed rate constant at constant overpotential was proportional to the surface excess of these ions at low coverages. If the potential experienced by the reacting ion at its reaction site is related to the average potential on the o.H.p. and the charge density of adsorbed halide ions, it can be shown that these observations are expected on the basis of rather simple models of the inner layer which consider the discrete nature of the adsorbed charge [18]. It follows that $\ln \gamma_{\ddagger}$ is a function of the adsorbed charge density, and is given to a good approximation by the following expression [18,34]

$$\ln \gamma_{\ddagger} = a_{\ddagger} \sigma_a / RT \quad (41)$$

where a_{\ddagger} is an interaction parameter describing the attractive ion-ion interactions experienced by the positively charged activated complex in the presence of adsorbed anions. Since $\ln \gamma_{\ddagger}$ is a negative quantity when the interactions are attractive, it increases as the amount of adsorbed anion decreases, that is, as the electrode potential is made more negative. At the same time, one expects to find a decrease in the slope of the c.T.p. under such circumstances. Such an observation is made when hydrogen ion is reduced in the presence of adsorbed halide ions at mercury [34]. Since the positive charge on the reactant decreases as a result of electron transfer, the anionic environment stabilizes the reactant more than the product. The environmental effect decreases as temperature increases at constant potential or overpotential because of a corresponding decrease in anionic adsorption. Thus, it leads to a decrease in the

observed enthalpy of activation. It should be remembered that the effect discussed here is in addition to the Gouy-Chapman double layer effect which plays a role in every heterogeneous electron transfer reaction. A quantitative analysis of the potential or temperature dependence of kinetic data obtained in the presence of specifically adsorbed ions must be based on experimental data which give the corresponding variation in the specifically adsorbed charge density, and in the dielectric properties of the inner part of the double layer. For instance, the analysis by Parsons [34] showed that the accelerating effect of Cl^- anions on H^+ reduction was significantly greater than that of I^- anions for a given surface excess of adsorbed halide ion. This result suggests that the potential at the reaction site is more negative in the presence of Cl^- ions than in the presence of I^- ions, other conditions being the same. Since the extent of adsorption and the properties of the inner layer also vary with temperature, ΔH_{dl}^\ddagger will depend on the extent of specific adsorption and the nature of the adsorbed species. A detailed analysis of these effects is possible given the necessary double layer data.

There has been considerable discussion in the recent literature [14,41-44] regarding the anomalous temperature dependence of the Tafel slope observed for a variety of electrode reactions, but especially for the hydrogen evolution reaction at mercury and other metals. In this regard, it should be noted that the Tafel slope is conventionally defined for one electron processes to be

$$b = - \left[\frac{\partial \phi^m}{\partial \log k_r} \right]_T = \frac{2.3 RT}{\alpha_{ex} F} \quad (42)$$

In some cases, the quantity b is found to vary with temperature in a manner which suggests that α_{ex} is a function of temperature. Conway [14,44,45] has attributed the anomalous temperature dependence of b to variation in the entropy of activation with potential. This follows a suggestion originally due to Agar [46], but is contrary to the usual understanding of the variation in the electrochemical free energy of activation with electrode potential [7]. According to the traditional treatment of the electrochemical potentials which are used to estimate the standard electrochemical free energy of activation, the potential dependence is

associated with the enthalpic part of the free energy change, the entropic part being potential independent [7]. These apparently opposing points of view are reconciled if one includes consideration of the activity coefficient γ_{\ddagger} in both the temperature and potential dependence of the free energy of activation. It is not surprising that this is necessary, in general, since one is dealing with reactions in condensed media. The activity coefficient contains both enthalpic and entropic contributions so that formally the approach taken here to describe the temperature dependence of double layer effects is not inconsistent with Conway's approach in which the entropy of activation is assumed to be potential dependent. Unfortunately, many of the data discussed with respect to this question were not corrected for double layer effects [14,44,45]. Tsionskii et al. [43] have emphasized that when kinetic data for the cathodic evolution of hydrogen from acidic aqueous solutions at mercury were carefully examined, no temperature dependence of the true transfer coefficient α was found after double layer corrections had been made. In some of the experiments discussed, the electroreduction of H^+ was studied in the presence of adsorbed anions. Thus, the experimental transfer coefficient α_{ex} and the Tafel slope b contain a factor which depends on the potential dependence of $\ln \gamma_{\ddagger}$. Therefore, it is not surprising that α_{ex} is temperature dependent under these circumstances because the amount of specific adsorption and thus $\ln \gamma_{\ddagger}$ change with temperature. On the other hand, experimental results demonstrating anomalous values of b have been obtained in the absence of specifically adsorbed ions [14]. Obviously, careful assessment of double layer effects is necessary to understand these systems more fully.

Discussion

Sufficient data exist in the literature for the enthalpy of activation of electron transfer reactions so that some comparison and general conclusions can be made with respect to the role of double layer effects. One group of reactions for which these effects are a minimum at constant temperature are the electroreduction or electrooxidation of organic molecules to the corresponding anion or cation radical, respectively. A summary of some data from the literature obtained in dimethylformamide (DMF) is given in Table 1. The experimental enthalpy of activation reported is defined as

$$\Delta H_{\text{ex}}^{\ddagger} = -R \left[\frac{\partial \ln k_s}{\partial (1/T)} \right]_{\eta=0} \quad (43)$$

where k_s is the standard rate constant. The corrected standard real enthalpy of activation is obtained by correcting $\Delta H_{\text{ex}}^{\ddagger}$ for the Gouy-Chapman contribution to the double layer effect and the temperature dependence of the pre-exponential factor, so that

$$\Delta H_{\text{TC}}^{\ddagger} = \Delta H_{\text{ex}}^{\ddagger} - (\Delta H_{\text{GC}}^{\ddagger})_T - \Delta H_{\text{Z}}^{\ddagger} \quad (44)$$

From dielectric relaxation data [32], the value of ΔH_{r} for DMF is 10.0 kJ mol⁻¹. The same data give a value of $R \partial \ln \epsilon_s / \partial (1/T)$ equal to 3.6 kJ mol⁻¹ for DMF. It follows that the maximum value of $\Delta H_{\text{Z}}^{\ddagger}$ in this solvent is 5.2 kJ mol⁻¹ (eq. (38)). In cases where analysis of solvent effects has shown [30] that the nuclear frequency factor is given by equation (30), $\Delta H_{\text{Z}}^{\ddagger}$ was set equal to 5.2 kJ mol⁻¹. Otherwise it was assumed to fall in the range 0 to 5.2 kJ mol⁻¹, and $\Delta H_{\text{TC}}^{\ddagger}$ reported with the appropriate error estimate.

On the basis of the data available, $\Delta H_{\text{ex}}^{\ddagger}$ falls in the range from 10 to 40 kJ mol⁻¹. The result for 1,4-diaminobenzene is probably influenced by a much larger double layer effect than the other systems because it was obtained at very positive potentials where anion specific adsorption is strong. The double layer effect is expected to be especially large for this system because of attractive interaction between the cation radical formed in the one-electron oxidation reaction and adsorbed perchlorate anions. In cases where double layer corrections can be

estimated, they are small, usually the order of a few kJ mol^{-1} . In this regard, the data for oxidation of 1,4-diaminobenzene and reduction of p-benzoquinone were not obtained at Hg so that the corrected standard enthalpy of activation should be regarded as approximate. The correction due to the temperature dependence of the pre-exponential factor is larger and results in values of $\Delta H_{\text{TC}}^{\ddagger}$ which are significantly less than $\Delta H_{\text{ex}}^{\ddagger}$ in the case of reactions which are adiabatic with minimum contributions of inner sphere reorganization energy to the overall Gibbs energy of reorganization [30]. Ignoring the result for 1,4-diaminobenzene, the value of $\Delta H_{\text{TC}}^{\ddagger}$ fall in the range from 10 to 20 kJ mol^{-1} . Thus, these reactions are characterized by rather small enthalpies of activation.

It is interesting to compare the values of $\Delta H_{\text{TC}}^{\ddagger}$ obtained here with independent estimates of ΔG^{\ddagger} . From an analysis of solvent effects on the heterogeneous rate constant [30], ΔG^{\ddagger} for the cobaltacene system is $\sim 11 \text{ kJ mol}^{-1}$. It follows that the real entropy of activation is $\sim 17 \text{ J K}^{-1} \text{ mol}^{-1}$, that is approximately 25% of the standard reaction entropy. This result is much larger than the value estimated by Gennett et al. [48] ($-2 \text{ J K}^{-1} \text{ mol}^{-1}$). Their estimate is based on a continuum model for the activation process and does not consider the discrete nature of the reaction environment, and supports the argument that $\Delta S_{\text{I}}^{\ddagger}$ should be close to zero [13]. On the other hand, there is clear experimental evidence that the kinetic parameters for some of the reactions considered depend on the nature of the ion in the inert electrolyte whose sign is opposite to that of the organic ion involved in the reaction [49,53]. Orientational effects are also important for molecules with large permanent or induced dipole moments [53]. These properties of reactions involving large organic molecules are undoubtedly the reason why the continuum model fails to give reliable estimates of the real entropy of activation.

Kinetic data for the electroreduction of triply charged metal ions in water and DMF are shown in Table 2. For these systems, the double layer correction is large as one would expect. The correction due to the the temperature dependence of the pre-exponential factor is less certain and was assumed to be given by the collision model (eq. (37)). Values of $\Delta H_{\text{TC}}^{\ddagger}$ fall in the range from 30 to 50 kJ mol^{-1} and reflect large contributions from both inner and outer

sphere reorganization processes associated with the electron transfer step. The results for highly charged ions are considerably larger than those for the organic redox systems in which the reorganizational work is much smaller. For the systems available, the solvent is involved as a ligand, and thus, the properties of the metal-solvent bonds determine the inner sphere reorganization energy. It must be emphasized that the values of $\Delta H_{\text{ex}}^{\ddagger}$ quoted for the $\text{Cr}^{+3}/\text{Cr}^{+2}$ and $\text{Eu}^{+3}/\text{Eu}^{+2}$ systems in water are ideal enthalpies of activation measured at a potential negative of the standard potential [13]. In order to obtain $\Delta H_{\text{TC}}^{\ddagger}$, the experimental quantities were first corrected for the Gouy-Chapman contribution to the double layer effects by estimating $(\Delta H_{\text{GC}}^{\ddagger})_i$ from Grahame's capacity data [15] (see the Appendix). The values of the corrected ideal enthalpy of activation at the standard potential were estimated on the basis of the potential dependence of ΔH_1^{\ddagger} (eq. (A1)), and then converted to the corrected real enthalpy of activation at the same potential (eq. (A3)). Although Weaver [13] has reported ideal enthalpies of activation for many redox systems involving transition metal ions, the standard entropy change can only be measured for a few systems so that the value of $\Delta H_{\text{TC}}^{\ddagger}$ is not available. Finally, it is noted that the result for the $\text{V}^{3+}/\text{V}^{2+}$ is somewhat higher than those for the other systems. Since specifically adsorbed perchlorate ions were present in the potential region where the data were obtained [11], the attractive interaction between the adsorbed ions and the reactant undoubtedly contributes to the observed value of $\Delta H_{\text{ex}}^{\ddagger}$.

On the basis of the present results, it is concluded that double layer effects should be carefully considered in analyzing the activation parameters for electron transfer reactions. This is especially true when one wishes to assess model estimates of parameters such as the entropy of activation. Small errors in estimates of ΔG^{\ddagger} or ΔH^{\ddagger} can lead to a large error in the estimate of ΔS^{\ddagger} . Problems with the Gouy-Chapman model used to calculate the major fraction of the double layer correction are often cited as reasons for uncertainty in corrected kinetic parameters. However, these are undoubtedly less important for the enthalpy of activation since a temperature derivative of the o.H.p. potential is involved.

In examining the equations presented for the double layer effect on the enthalpy of activation, it is clear that they are rather cumbersome, requiring careful specification of the electrical variables held constant when the temperature is changed. However, the analysis of kinetic data is made considerably simpler if the temperature dependence of double layer corrected results are examined directly to obtain the Frumkin enthalpy of activation (eq. (22)). It is surprising that this procedure does not seem to have been used previously. Hopefully, the analysis presented here will prompt further consideration of temperature effects for electrode reactions in which environmental effects are important.

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Appendix

In this appendix, double layer effects on the ideal enthalpy of activation are considered. This quantity, which cannot be measured experimentally without making extrathermodynamic assumptions, is defined by the change in the logarithm of the rate constant with the reciprocal of the temperature when the inner potential ϕ^m is held constant. Thus, it follows from equation 5 above that

$$\Delta H_1^\ddagger = -R \left[\frac{\partial \ln k_r}{\partial (1/T)} \right]_{\phi^m} = \Delta H_0^\ddagger + \Delta H_Z^\ddagger + (\Delta H_{GC}^\ddagger)_i + (\Delta H_{dl}^\ddagger)_i + \alpha_a F \phi^m \quad (A1)$$

where ΔH_0^\ddagger and ΔH_Z^\ddagger are the true enthalpy of activation and the contribution from the temperature dependence of the pre-exponential factor as discussed above, and $(\Delta H_{GC}^\ddagger)_i$ and $(\Delta H_{dl}^\ddagger)_i$ are the double layer contributions defined by equations (12) and (13) above with the exception that the derivatives are measured at constant ϕ^m not constant η . The experimental method of estimating ΔH_1^\ddagger is to determine $\ln k_r$ in a non-isothermal cell in which the temperature of the reference electrode is held constant, and the temperature of the electrode at which the reaction of interest occurs is varied [7,13]. The assumption which is usually made is that the temperature dependence of the thermal junctions which result are negligible. It is not the object of this paper to consider this subject fully but we state with emphasis that the assumption must be considered carefully in each experimental situation.

It is interesting to calculate values of $(\Delta H_{GC}^\ddagger)_i$ from the available double layer data and compare them with the results presented above for $(\Delta H_{GC}^\ddagger)_r$. The required derivative is given by

$$\left[\frac{\partial(\phi^d/T)}{\partial(1/T)} \right]_{\phi^m} = \left[\frac{\partial(\phi^d/T)}{\partial(1/T)} \right]_{\sigma_m} - \frac{C}{TC_d} \left[\frac{\partial\phi^m}{\partial(1/T)} \right]_{\sigma_m} \quad (A2)$$

where the first term on the right hand side is estimated from Gouy-Chapman theory (eq. (22)), and the second from the appropriate double layer data. Values of $[\partial(\phi^d/T)/\partial(1/T)]_{\phi^m}$ were calculated for the Hg/aqueous solution interface also using the data obtained by Grahame with

NaF as electrolyte [15]. Grahame used a normal calomel electrode held at constant temperature as reference, and observed a small but significant positive change in the potential of zero charge with temperature. Thus, neglecting any contributions to the potential difference between the polarizable electrode and reference electrode from the temperature dependence of the liquid junction potential, the inner potential of the Hg electrode may be considered constant when the temperature of the reference electrode is held constant. Plots of $F [\partial(\phi^d/T)/\partial(1/T)]_{\phi^m}$ against electrode potential are shown as a function of electrolyte concentration in Figure A1. First of all, it is apparent that this quantity is positive at potentials positive of $-0.6V$ and negative at more negative potentials. Secondly, the magnitude of the derivative is much larger in the positive potential region, reaching a value of 19 kJ mol^{-1} at $-0.4V$ in $0.01M$ NaF. Finally, as one would expect, the double layer correction decreases with increase in ionic strength.

When one compares the present results with those given above for $[\partial(\phi^d/T)/\partial(1/T)]_{\phi^r}$, it is immediately apparent that the two quantities are quite different. Thus, the magnitude of $[\partial(\phi^d/T)/\partial(1/T)]_{\phi^m}$ is much larger for potentials positive of the p.z.c. (-0.472 V against the NCE at 25°C [15]) and the shape of the curves much more asymmetrical. These differences are due to the variation in the p.z.c. with temperature observed by Grahame [15], that is, from -0.480 V at 0°C to -0.440 V at 85°C .

Weaver [13] discussed the double layer correction to ideal heats of activation for a series of reactions involving Cr(III) and Co(III) complexes studied at a constant inner potential (-0.8 V against the S.C.E.), and estimated a double layer correction of 1.7 kJ mol^{-1} when the electrolyte was $1M$ NaClO_4 or $1M$ KF . According to the present calculation, the double layer correction for these conditions is -0.9 kJ mol^{-1} . The disagreement between our estimate and that reported by Weaver [13] is apparently due to the fact that the derivative in question was written as $(1/T) \partial\phi^d/\partial(1/T)$ instead of $\partial(\phi^d/T)/\partial(1/T)$ (see eq. (7) in [13]). As a result of this error, the corrected heats of activation reported by Weaver are low by $\sim 6.5 \text{ kJ mol}^{-1}$ for reactants with a charge of $+3$. This amounts to a 10% error in the reported double layer corrected values of

ΔH_1^\ddagger , the error in the reported values of the double layer corrected entropy of activation undoubtedly being somewhat larger.

Estimates of $F [\partial(\phi^d/T) / \partial(1/T)]_{\phi^m}$ for the Hg/dimethylformamide interface [25] are shown in Fig. A2. In this case, the reference electrode was the Ag/Ag⁺ system in DMF in which the reference electrode compartment contained 0.1M AgNO₃ and 0.1M tetraethylammonium perchlorate (TEAP). When the reference electrode was held at 25 °C, the p.z.c. varied from -0.722V at -5 °C to -0.700V at 45 °C. The features of these curves are qualitatively similar to those obtained in water, the double layer correction being more important at potentials positive of the p.z.c. However, the magnitude of the correction is considerably smaller than that estimated for the Hg/aqueous solution interface. It should be emphasized that even though available double layer may be obtained using a reference electrode of varying temperature, or reported on a rational potential scale, these data are easily converted to the required potential scale by measuring the potential of zero charge as a function of temperature using a reference electrode held at constant temperature. If the assumptions discussed above hold, then one can estimate the variation in inner potential with temperature at constant electrode charge density.

Finally, the large differences apparent between the values of $[\partial(\phi^d/T) / \partial(1/T)]_{\phi^m}$ and $[\partial(\phi^d/T) / \partial(1/T)]_{\phi^r}$ serve to emphasize the importance of defining carefully the electrical variable held constant in measuring temperature effects. If the assumptions made regarding the suitability of the non-isothermal cell for measurement of ideal activation parameters are not valid, then large errors are expected in the derived experimental quantities. In cases that one wishes to estimate the value of the real enthalpy of activation from the ideal value at the standard potential, neglecting double layer effects and making use of eq. (10) and eq. (A1) at $\eta = 0$ and $\phi^m = \phi_o^m$, respectively, one obtains

$$\Delta H_{i0}^\ddagger = \Delta H_{r0}^\ddagger + \alpha_a T \Delta S^\circ \quad (\text{A3})$$

This result is well known from the literature [6-8].

Table 1. Kinetic Parameters for Heterogeneous One Electron Redox Reactions of Organic Molecules in Dimethylformamide^a

Reactant	Electrolyte	Standard		Experimental		Standard		Corrected Standard Real Heat of Activation ΔH_{rc}^\ddagger, kJ mol⁻¹
		Potential^b ϕ_0^m, V	Rate Constant k_s, cm s⁻¹	Heat of Activation ΔH_{ex}^\ddagger, kJ mol⁻¹	Entropy Change ΔS°, J K⁻¹ mol⁻¹			
1,4-diaminobenzene (+0) [47]	0.1M NaClO ₄ (Pt)	0.411	0.092 (20 °C)	32.5	88	(33±3)		
decamethylferrocene (+0) [48]	0.1M TBAP	0.258	~2 (23 °C)	18.8	50	18±3		
p-benzoquinone (0/-) [49,50]	0.1M TEAP (Au)	-0.194	0.13	18.6	-116	(13±3)		
bis(benzene)chromium (+0) [48]	0.1M TBAP	-0.512	~1.2 (23 °C)	23.0	69	19		
cobaltacene (+0) [48]	0.1M TBAP	-0.632	~1.0 (23 °C)	20.9	67	16		
nitromesitylene (0/-) [51,52]	0.1M TEAP	-1.182	0.43	17.4	(-96)	15±3		
p-dicyanobenzene (0/-) [52,53]	0.1M TBAP	-1.320	0.57	14.3	-73	12±3		

^a Data obtained at Hg electrodes at 25 °C except as noted.

^b Potential measured with respect to the point of zero charge on Hg in 0.1M TEAP

Table 2. Kinetic Parameters for Heterogeneous One Electron Reduction of Trivalent Metal Cations

<u>Reactant</u>	<u>Medium</u>	<u>Standard</u>		<u>Experimental</u>		<u>Standard</u>		<u>Corrected Standard Real Heat of</u>
		<u>Potential^a</u>	<u>Rate Constant</u>	<u>Heat of Activation^b</u>	<u>Entropy Change</u>	<u>ΔS°, J K⁻¹ mol⁻¹</u>	<u>ΔH_{rc}[‡], kJ mol⁻¹</u>	
<u>Activation</u>		<u>E_s, V</u>	<u>k_s, cm s⁻¹</u>	<u>ΔH_{ex}[‡], kJ mol⁻¹</u>	<u>ΔS°, J K⁻¹ mol⁻¹</u>	<u>ΔH_{rc}[‡], kJ mol⁻¹</u>		
V (H ₂ O) ₆ ⁺³ [11]	1 M HClO ₄ in water	-0.470	3.2 x 10 ⁻³ (20 °C)	32.6	148	50.2		
Eu (H ₂ O) ₆ ⁺³ [13]	1 M NaClO ₄ in water	-0.624	2.3 x 10 ⁻⁴	60.2	190	36.7		
Cr (H ₂ O) ₆ ⁺³ [13]	1 M NaClO ₄ in water	-0.655	7.6 x 10 ⁻⁶	73.2	205	45.1		
Cr (DMF) ₆ ⁺³ [54]	0.1 M TEAP in DMF	-0.700	6.1 x 10 ⁻³	27.1	254	35.8		

^a Potential measured with respect to an aqueous SCE.

^b For V (H₂O)₆⁺³ and Cr (DMF)₆⁺³, this value is the apparent real heat of activation at the standard potential; in the case of Eu (H₂O)₆⁺³ and Cr (H₂O)₆⁺³, it is the apparent ideal heat of activation measured at -0.8 V against the SCE.

Legends for Figures

- Figure 1.** Plot of the Gouy-Chapman parameter, $F[\partial(\phi^d/T) / \partial(1/T)]_{\phi^r}$ against the rational electrode potential ϕ^r on the basis of double layer data for the Hg / aqueous NaF interface [15] at varying electrolyte concentrations: (a) 0.01 M; (b) 0.1 M; (c) 1 M.
- Figure 2.** Plot of the Gouy-Chapman parameter, $F[\partial(\phi^d/T) / \partial(1/T)]_{\phi^r}$ against the rational electrode potential ϕ^r on the basis of double layer data for the Hg / DMF interface [25] with varying concentrations of tetraethylammonium perchlorate as electrolyte: (a) 0.01 M; (b) 0.1 M; (c) 1 M.
- Figure A1** Plot of the Gouy-Chapman parameter, $F[\partial(\phi^d/T) / \partial(1/T)]_{\phi^m}$ against the electrode potential ϕ^m on the basis of the double layer data for the Hg / aqueous NaF interface [15] at varying electrolyte concentrations: (a) 0.01 M; (b) 0.1 M; (c) 1 M. The electrode potential ϕ^m is defined in a non-isothermal cell against a reference electrode held at constant temperature.
- Figure A2** Plot of the Gouy-Chapman parameter, $F[\partial(\phi^d/T) / \partial(1/T)]_{\phi^m}$ against the electrode potential ϕ^m on the basis of double layer data for the Hg/DMF interface [25] with varying concentrations of TEAP as electrolyte: (a) 0.01 M; (b) 0.1 M; (c) 1 M. The ordinate scale is correct for curve a; curves b and c have been shifted down by 1 and 2 units, respectively for clarity. The electrode potential ϕ^m is defined in the same way described for Fig. A1.