



THE ROLE OF BOND ORDER AND ENTROPY OF TRANSITION STATES IN ELECTRON TRANSFER REACTIONS

Part 4. — Electrochemical Reactions and the Anodic-Cathodic Asymmetry of the Tafel Plots.

The free energy barriers of electrochemical electron transfer reactions are found to be dominated by the solvent reorganization in the primary shell of solvated metal ions. Work-corrected heterogeneous and homogeneous electron transfer processes can be treated within the same theoretical framework with the assumption $\Delta G_{hom} = 2 \Delta G_{het}$, both for the energy barrier and the reaction free energy. The origins of the anodic cathodic asymmetries of the Tafel plots for metal-aquo redox couples are amenable to interpretation within the intersecting-state model. Whereas the plots are virtually linear when the configuration entropy parameter, λ , has no effect on the displacement of the potential energy curves, i.e., when ΔS^\ddagger is high, negative curvatures are observed for low values of λ and ΔS^\ddagger . These findings seem to imply that for the very exothermic reactions the «transition state» does not coincide with the «saddle point» owing to configurational effects perpendicular to the reaction coordinate.

INTRODUCTION

The transfer of electrons between a metal or semiconductor and a dissolved or surface-bound reactant is not essentially different from the same process between two species in homogeneous solution, and the development of theories for these reactions has followed the progresses in the latter field [1-3]. Recently a great effort has been made by Weaver and coworkers [4-6] to assess the role of inner-shell reorganization and the outer-shell reorganization on the energy barrier of electrochemical reactions. Nevertheless, they were unable to explain quantitatively the large anodic-cathodic asymmetry of the Tafel plots for some metal-aquo redox couples in terms of the theory of Marcus [5]. For example, at an overpotential of 700 mV the cathodic reduction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is 200 times faster than the anodic oxidation of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ at the same overpotential. The possible effect of the difference on the force constants of the oxidized and reduced species in Marcus equation was also considered. Although some of the anodic-cathodic asymmetry is accounted for by this effect, its contribution (6 times) is much smaller than the experimental difference [5].

In previous papers [7, 8] we have shown that electron transfer reactions in solution can be treated as any other ordinary chemical reaction and an intersecting-state model (ISM) [9] has been employed for the study of electron transfer reactions in solution. The model has interpreted satisfactorily several areas where the theory of Marcus failed, such as discrepancies of the calculated and experimental rates of some electron exchange processes [7], the variety of the energy gap laws of electron transfer reactions [8] and «anomalous» cross-reaction relationships [10]. It, thus, seems useful to extend the applications of ISM to the study of electrochemical electron transfer reactions.

Although outer-sphere electron transfer reactions of solvated or coordinated metal ions at metal surfaces and in homogeneous solutions are closely related processes, for the

heterogeneous reactions double-layer effects can be significant. Fortunately most of the experimental data which we are going to analyze were obtained under experimental conditions selected to minimize such effects. These «work-corrected» rate constants [4, 5], in the absence of electrostatic work terms, have been employed in the calculations, except where stated otherwise.

THEORETICAL MODEL

According to the intersecting-state model [9] developed for reactions involving two molecular species, the activation free energy barrier of a chemical reaction can be found at the intersection of two potential energy curves. For harmonic oscillators

$$\frac{1}{2} f_r x^2 = \frac{1}{2} f_p (d-x)^2 + \Delta G_{\text{hcm}}^0 \quad (1)$$

where x is the bond distension from reactant to the transition state, d represents the horizontal displacement of the potential energy curves and, consequently, represents also the sum of the bond distensions from reactant and product to the transition state; f_i are the appropriate force constants of reactant and product, and ΔG_{hcm}^0 is the reaction free energy. The activation free energy of the reaction, here represented by $\Delta G_{\text{hcm}}^\ddagger$ in order to be distinguished from that of the heterogeneous electrochemical process ($\Delta G_{\text{het}}^\ddagger$), is

$$\Delta G_{\text{hcm}}^\ddagger = \frac{1}{2} f_r x^2 \quad (2)$$

where x is estimated from eq (1), once d is known. This parameter is proportional to the sum of the equilibrium bond lengths [9]

$$d = \eta (l_r + l_p) \quad (3)$$

with the reduced bond distension, η , given by

$$\eta = \frac{a' \ln 2}{n^\ddagger} + \frac{a'}{2 \lambda^2} (\Delta G_{\text{hcm}}^0)^2 \quad (4)$$

n^\ddagger is the transition state bond order, λ is an energy parameter which can be viewed as an energy capacity of the activated complexes and a' is a constant ($a' = 0.156$).

Work-corrected electron transfer rates of electrochemical reactions can be studied in the same manner as the rates of homogeneous processes as long as the assumption $2\Delta G_{\text{het}} = \Delta G_{\text{hcm}}$ is made [11], because two species are undergoing rearrangement in the homogeneous reactions, whereas only one species is involved in the electrochemical process. Consequently eqs (1) (2) and (4) are now written as

$$\frac{1}{2} f_r x^2 = \frac{1}{2} f_p (d-x)^2 + 2 \Delta G_{\text{het}}^0 \quad (1')$$

$$2 \Delta G_{\text{het}}^\ddagger = \frac{1}{2} f_r x^2 \quad (2')$$

and

$$\eta = \frac{a' \ln 2}{n^\ddagger} + \frac{a'}{2 \lambda^2} (2 \Delta G_{\text{het}}^0)^2 \quad (4')$$

The rate constant of the heterogeneous electron transfer reaction is related with the activation free energy by

$$k_{\text{het}} = \kappa Z \exp (-\Delta G_{\text{het}}^\ddagger / RT) \quad (5)$$

where κ is an electronic transmission factor which is 1 for adiabatic processes and $\kappa < 1$ for the nonadiabatic reactions, and Z is the preexponential factor, taken as $Z = 10^4 \text{ cm s}^{-1}$ [11].

THERMONEUTRAL REACTIONS

We have shown that for electron transfer reactions in solution the overall activation free energy is dominated by the inner-shell reorganization process [7, 8] and the same procedure can be employed to study electrochemical reactions. As a preliminary test of the model for these reactions we will analyze some old data collected by Mar-

cus [11]. The inner-shell energy barrier for a thermoneutral situation can be calculated through the expression

$$2 \Delta G_{\text{het}}^{\ddagger} = \frac{1}{8} f d^2 \quad (6)$$

where f is the average force constant of the metal-ligand bonds, $f = \sqrt{6}(f_{\text{ox}} + f_{\text{red}})/2$ [7]. Table 1 presents the calculated bond distension parameters which reproduce $\Delta_{\text{het}}^{\ddagger}$, for some electrochemical reactions in aqueous solutions under reversible conditions [8, 12, 13]. The reduced bond distensions, η , are close to 0.108 (eq (4') at $\Delta G_{\text{het}}^{\circ} = 0$), which implies that we are dealing with outer-sphere processes with a bond order at the transition state close to 1. Such values compare well also with those in aqueous solutions [8]. This reveals that for these reactions there are no significant double-layer and nonadiabatic factors, otherwise η would be much higher than the theoretical value 0.108 for $n^{\ddagger} = 1$. The electron transfer reaction $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ is an outer-sphere process, but with $\eta = 0.07$ (Table 1), as is found also in solution, since $n^{\ddagger} = 1.54$ [7]. All these data reveal

that electrochemical electron transfer reactions are also largely dominated by the inner-shell reorganization, similarly to the electron transfer processes in solutions [7, 8].

TAFEL PLOTS

The driving force effect of electrode potential on the electrochemical rates is currently analyzed in terms of a Tafel plot. Hupp and Weaver [5] have analyzed the origins of the anodic-cathodic asymmetries of the Tafel plots for the work-corrected rate constants for the ions $\text{Cr}(\text{H}_2\text{O})_6^{2+/3+}$ and $\text{Eu}(\text{H}_2\text{O})_9^{2+/3+}$ at mercury-aqueous interfaces, which contrast with the symmetrical behaviour predicted by the conventional theoretical relationships [11, 14]. These authors have shown that such an asymmetry is not due entirely to differences in force constants between the oxidized and reduced species.

Such studies were based on the least-motion path approach [15] for the estimation of the reorganization energy barrier and on the use of the Marcus-equation [16] to assess the effect of ΔG° on the activation free energy barrier.

Table 1

Calculated bond distensions for electrochemical reactions

	$k_{\text{het}}/\text{cm s}^{-1}$ (a)	$2\Delta G_{\text{het}}^{\ddagger}/\text{kJ mol}^{-1}$	$f/\text{kJ mol}^{-1} \text{ \AA}^{-2}$ (e)	$d/\text{\AA}$	$1/\text{\AA}$ (f)	η
$\text{Fe}^{2+/3+}_{(\text{aq})}$	7×10^{-3}	69.9	3×10^3	0.428	4.14	0.104
$\text{V}^{2+/3+}_{(\text{aq})}$	4×10^{-3}	72.6	3×10^3	0.438	4.38	0.100
$\text{Eu}^{2+/3+}_{(\text{aq})}$	3×10^{-4}	85.4	2.7×10^3	0.50	4.8	0.104
$\text{Ru}^{2+/3+}_{(\text{aq})}$	5×10^{-2} (b)	60.2	2.8×10^3	0.41	4.15	0.100
$\text{Fe}(\text{CN})_6^{4-/3-}$	5.6×10^{-2} (c)	59.6	6.74×10^3	0.266	3.826	0.070 (g)
$\text{Fe}(\text{bipy})_3^{2+/3+}$	0.9 (d)	45.9	2.3×10^3	0.40	3.94	0.102

(a) Ref. 11 except where stated otherwise; (b) Ref. 6; (c) X. Zhang, J. Leddy and A.J. Bard, *J. Am. Chem. Soc.*, 1985, **107**, 3719; (d) T. Iwasita, W. Schmickler and J.W. Schultze, *Ber. Bunsenges. Phys. Chem.*, 1985, **89**, 138; (e) Ref. 13; (f) Ref. 12; (g) $n^{\ddagger} = 1.54$, Ref. 7.

The least motion approach has been shown to be inadequate for the study of electron transfer reactions between coordinated metal ions [7, 8], and Marcus equation is only obeyed when one can neglect any variation of η and d with the reaction free energy, i.e., when in eqs (4) and (4') $\lambda \gg |\Delta G^\circ|$, a condition which is not valid for all electron transfer reactions [8, 10].

The slope of a Tafel plot ($\alpha = \pm (RT/F)/(d \ln k_{\text{het}}/dE)$) can be estimated from eqs (1') and (4') together with the equation

$$\Delta G_{\text{het}}^\circ = \pm n_e F (E - E_f) \quad (7)$$

where n_e is the number of electrons transferred ($n_e = 1$), E is the electrode potential, E_f the standard potential and F the Faraday constant (the $-$ sign is for the anodic region and $+$ for the cathodic region). When $f_r = f_p = f$ the slope of $\ln k_{\text{het}}$ versus the standard potential is

$$\alpha = \frac{(2\Delta G_{\text{het}}^\circ + \frac{1}{2} f d^2)}{f d^2} \left[\left(1 + \frac{2f d a' l}{\lambda^2} \right) \Delta G_{\text{het}}^\circ d - 2\left(\Delta G_{\text{het}}^\circ + \frac{1}{2} f d^2\right) \frac{a' l}{\lambda^2} \Delta G_{\text{het}}^\circ \right] \quad (8)$$

where $l = l_p + l_r$. This equation reveals that $\alpha = 1/2$ when $\Delta G_{\text{het}}^\circ \rightarrow 0$. Far from this region and when we can neglect the effect of the configuration entropy parameter ($|\Delta G_{\text{het}}^\circ| \ll \lambda$)

$$\alpha \cong \left(\frac{1}{2} + \frac{2 \Delta G_{\text{het}}^\circ}{f d^2} \right) \quad (9)$$

Eq (9) reveals that $\alpha \cong 1/2$ and the Tafel plots are linear as long as $\Delta G_{\text{het}}^\circ \leq \Delta G(0)_{\text{het}}^\ddagger$ where $\Delta G(0)_{\text{het}}^\ddagger$ is the activation free energy at $\Delta G_{\text{het}}^\circ = 0$ ($\Delta G(0)_{\text{het}}^\ddagger = f d^2/16$). Obviously if $f_r \neq f_p$ α is different from $1/2$ at $\Delta G_{\text{het}}^\circ \rightarrow 0$. Table 2 presents the calculated α coefficients for several ratios of f_r/f_p ; when $\Delta G_{\text{het}}^\circ \rightarrow 0$ there is no effect of λ on the electron transfer rate constants. When the effect of λ is significant and $f_r \neq f_p$ eqs (1')-(4') and (7) should be used to estimate the transfer coefficient.

Table 2

Calculated transfer coefficients in electrochemical reactions near the standard potential (a)

f_r/f_p	α
10	0.80
6	0.74
3	0.66
1	0.5
0.5	0.47
0.33	0.37
0.17	0.30

(a) Calculations with $f_r = 3 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ and $d = 0.44 \text{ \AA}$.

This shows that the Tafel coefficient α is not a useful tool to analyse the molecular factors which contribute to electron transfer kinetics.

ANODIC-CATHODIC ASYMMETRY OF THE TAFEL PLOTS

Now we would like to discuss the origin of the asymmetry in the Tafel plots for some aquo-ions, reported by Weaver and coworkers [5]. Whereas the plot is virtually linear in the cathodic region it has a strong downward curvature in the anodic region. To explain this, we have to employ eqs (1') to (4') and eq (7) without any simplification. We have also to employ different force constants for reactant and product. For example, for the cathodic reduction $f_r = \sqrt{m} f_{\text{ox}}$ and $f_p = \sqrt{m} f_{\text{red}}$ where f_{ox} and f_{red} are the single metal-ligand bond stretches for the oxidized and reduced species, and m is the coordination number of the metal ions [7]. Figure 1 compares the observed Tafel plots with the calculated ones for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ (cathodic reduction) and $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ ions. The results show that although an asymmetry of the Tafel plots can be attributed to the differences in force constants of the oxidized

and reduced species, the strong negative curvature of the plot in the anodic region results from the significant dependence of η on $(\Delta G^\circ)^2$. As eq (4') reveals this can be interpreted in terms of a relatively low value of the configuration entropy parameter ($\lambda = 220 \text{ kJ mol}^{-1}$; non-Marcus situation). In contrast, in the cathodic region agreement with experiment was found with a constant η , i.e. the parameter λ is reasonably high ($\lambda > 350 \text{ kJ mol}^{-1}$; Marcus situation).

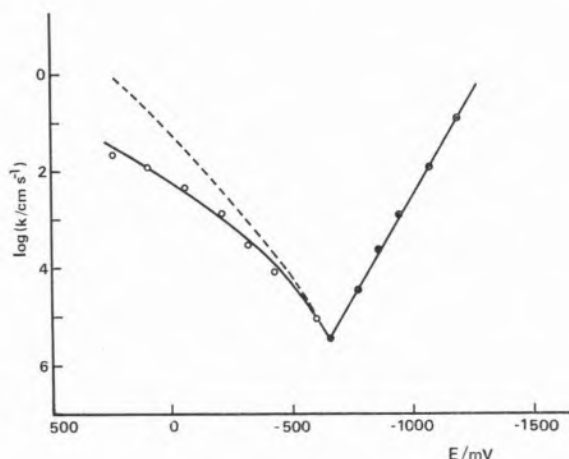


Fig. 1 — Tafel plots for the electron transfer reaction $\text{Cr}(\text{H}_2\text{O})_6^{2+}/3+$: Experimental plots: —. Calculated plots: ● cathodic reduction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$; $f_r = 3.67 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$; $f_p = 2.36 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$, $d = 0.545 \text{ \AA}$ independent of the electrode potential; ---- anodic oxidation of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$; $f_r = 2.36 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$; $f_p = 3.67 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ and $d = 0.545 \text{ \AA}$ independent of E ; O the same set of parameters for the anodic region with d variable with electrode potential, $d = 0.545 \text{ \AA}$ at the standard potential and $a'/2\lambda^2 = 1.6 \times 10^{-6} \text{ kJ}^2 \text{ mol}^{-2}$. With $l \cong 4.2 \text{ \AA}$ these reactions have $\eta(0) \cong 0.13$ which suggests that they are nonadiabatic processes at a mercury electrode with a common $\kappa \cong 10^{-3}$.

Differences in λ values for solvated and coordinated metal ions were found to be correlated with activation entropies [8], $\lambda/\text{kJ mol}^{-1} = 360 + 4 T\Delta S^\ddagger$ (standard state 1 mol dm^{-3}). For example, with typical standard entropy values for the hydrated ions [17], $T\Delta S^\circ(\text{Cr}^{3+}) \cong -87 \text{ kJ mol}^{-1}$ and

$T\Delta S^\circ(\text{Cr}^{2+}) = -25 \text{ kJ mol}^{-1}$ at 298 K, and a transition state entropy which is intermediate between reactant and product, we can reproduce the experimental data with $T\Delta S^\circ[(\text{Cr}^{2+}, \text{Cr}^{3+})^\ddagger] = -60 \text{ kJ mol}^{-1}$. Consequently, for the cathodic reduction the energy contribution of the activation entropy is positive, $T\Delta S^\ddagger_{\text{cat}} = 27 \text{ kJ mol}^{-1}$; λ is high and there is no dependence of η on ΔG° ; for the anodic oxidation the activation entropy is very low, $T\Delta S^\ddagger_{\text{an}} = -35 \text{ kJ mol}^{-1}$, and there is a strong increase of η with $|\Delta G^\circ|$.

The calculated curve assumes a constant λ (and (ΔS^\ddagger) through the whole electrode potential energy range (Figure 1). A ΔS^\ddagger variable with the electrode potential [5], ca. $T\Delta S^\ddagger = -35 \text{ kJ mol}^{-1}$ at $E = 300 \text{ mV}$ and $T\Delta S^\ddagger = 7 \text{ kJ mol}^{-1}$ (298 K) at $E = -400 \text{ mV}$ will further improve the agreement in the anodic region.

NONEQUILIBRIUM SITUATIONS

Several less empirical theories have been employed to study electrochemical electron transfer reactions, such as the theories of Levich, Dogonadze, Kuznetsov, Ulstrup and coworkers [18]. Nevertheless such treatments can be reduced [19] to the same quadratic form of the theory of Marcus,

$$\Delta G^\ddagger = c_0 + c_1 (\Delta G^\circ) + c_2 (\Delta G^\circ)^2$$

where c_i are coefficients independent of ΔG° . However, we have shown that such a quadratic free energy relation is unable to interpret the asymmetry of the Tafel plots. This requires a more general theoretical model, such as ISM which for harmonic oscillators of a common force constant leads to

$$\Delta G^\ddagger = c_0 + c_1 (\Delta G^\circ) + c_2 (\Delta G^\circ)^2 + c_4 (\Delta G^\circ)^4 + c_6 (\Delta G^\circ)^6 + \dots$$

owing to the quadratic dependence of η on $(\Delta G^\circ)^2$.

The intersecting-state model [9] was developed for equilibrium situations and, consequently, d and η are the same for the forward and backward reactions, i.e. λ is independent of the direction of the reaction. Can the present model go beyond its derivation and contemplate nonequilibrium situations? The answer appears to be yes, because the interpretation of the asymmetry of the Tafel plots requires different λ values for the oxidation and reduction processes. Under the view that λ is a measure of the «energy capacity» of the activated complexes, different λ s imply different generalized transition states for the anodic and cathodic electron transfers. Variational transition state theories [19-21] show that recrossing, tunnelling, internal state nonequilibrium, and solvent friction effects can introduce significant modifications on the conventional transition state theory. Since the anomalous features appears to be the slowness of the anodic process, the only effects which can contribute to the present findings appear to be recrossing and/or internal state nonequilibrium; frictional effects are only significant for high viscosity systems. The dependence of λ on ΔS^\ddagger suggests that the former effect is the more important one. A nonequilibrium situation for the internal states implies a relatively inefficient vibrational energy reorganization for the $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ species, compared with $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ [22]. Although there are some differences in the stretching frequencies of these aquo-metal ions, these are not very large (1.26 times [23]). Conventional transition state theories are based essentially on the assumption that the passage via the saddle point is rate determining and, consequently, the reaction rate can be computed as the rate of passage at the saddle point. This implies that every trajectory en route from reagents to products crosses the saddle point only once. Having scaled the mountain pass and started its descent into the product region, a trajectory does not turn back. However, under certain conditions, for example at high energies, the saddle point region can lose its strategic

importance and other dynamical features of the potential energy surface start to control the probability of reaction [20]. Here we would like to suggest a possible interpretation for the present findings.

Let us consider the model reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$. When the reaction is thermoneutral, the relative kinetic energy of A and BC and AB and C will provide the motion along the reaction coordinate. The trajectories which go over the saddle point do not turn back, and the transition state coincides with the saddle point. However, if the reaction is exothermic or endothermic, the reaction energy must be accommodated as internal energy of the activated complexes. Because there is an interconversion of translational and vibrational and rotational energies, the trajectories can suffer the influence of constraints perpendicular to the reaction coordinate, which will be reaction energy dependent. If after the saddle point the reaction valley is a narrow one, because of such constraints some trajectories which have passed the saddle point will be reflected back into the reactants valley. A critical configuration between the regions of «return» and of «no return» can possibly be established [20]. This configuration is crossed only once by the trajectories, but is displaced from the saddle point towards the narrow valley of the products. Consequently, the transition state does not coincide with the saddle point and is displaced towards the products. On the contrary if the valley of products is wide, no constraints will be forced upon the trajectories, after the saddle point. The saddle pass region is only crossed once by the trajectories, and the transition state coincides with the saddle point.

ACKNOWLEDGMENTS

We are grateful to Prof. D.G. Truhlar for a most stimulating and helpful discussion on the nonequilibrium effects. This work is supported by Instituto Nacional de Investigação Científica.

Received, 17th October, 1986

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RESUMO

O papel da ordem de ligação e da entropia dos estados de transição nas reacções de transferência de electrões.

Parte 4 — Reacções electroquímicas e a assimetria dos gráficos de Tafel entre as regiões anódica e catódica.

As barreiras de energia livre das reacções electroquímicas de transferência de electrões são dominadas pela reorganização da primeira camada de coordenação de iões metálicos. As reacções de transferência de electrão, homogéneo e heterogéneo (corrigidos do efeito da dupla camada eléctrica) podem ser estudadas dentro do mesmo formalismo com $\Delta G_{\text{hom}} = 2 \Delta G_{\text{het}}$, para a energia de reacção e a barreira de energia. A origem da assimetria dos gráficos de Tafel entre a região anódica e catódica é explicado pelo modelo de intersecção de estados nos seguintes termos: se λ (e ΔS^\ddagger) é elevado os gráficos de Tafel são lineares; mas se λ (e ΔS^\ddagger) é baixo os gráficos têm uma curvatura negativa. Estas interpretações parecem implicar que para reacções exotérmicas e S^\ddagger baixo o ponto de sela não corresponde ao estado de transição devido a restrições dinâmicas ao longo do vale de reacção após o ponto de sela.