The Transfer Coefficient in Electrode Reactions

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The usual, formal definition of α, the transfer coefficient of an electrode reaction, is satisfactory for the unambigous description of an experiment. More detailed knowledge of the mechanism of an electrode reaction requires distinction between the intrinsic (or *true*), α_I and the environmental, α_E, part of the overall coeficient α. The suggestion is made to use the symbol β for the cathodic transfer coefficient of an elementary step. Caution is suggested in giving more than arbitrary significance to these distinctions which have to be discussed in terms of the model adopted for a particular system.

INTRODUCTION

It has recently been pointed out[1] that there is some confusion in the electrochemical literature concerning the transfer coefficient α. This arises both from differences in the way that this quantity is defined and also from differences in its interpretation in terms of different models of the electrode reaction. Since the transfer coefficient is an expression of the unique nature of electrode reactions, it is clearly important for this quantity to be unambiguously defined and if possible to be clearly understood.

The unique nature of electrode reactions arises from the fact that they involve transfer of charge across the interface between two conducting phases. This leads to the existence of a potential-dependent rate constant for such reactions. Experimentally[2] it is found that the rate constant is often dependent on the exponential of the potential. The first satisfactory interpretation of this from a kinetic point of view was given by Butler[3] followed by Erdey-Gruz and Volmer[4].

Simple Electrode Reactions

We define a simple electrode reaction as one which consists of only one elementary step. The best example is that of an electron transfer reaction in which a single electron is transferred[5] *e. g.*

$$V^{2+} = V^{3+} + e \tag{2—1}$$

We generalise this in the form

$$R = O + e \tag{2—2}$$

where R is the reduced form and O is the oxidized form. R and O need not necessarily be both in the same phase. It is preferable to write the reaction so that the electrons are on the right-hand side. The forward direction $(R \rightarrow O)$ then corresponds to a positive (anodic) current. The net rate of the reaction is then given in terms of current (using Faraday's laws) by

$$i = F \frac{d\xi}{dt} = F \overrightarrow{k} c_R - F \overleftarrow{k} c_O \qquad (2\text{—}3)$$

where ξ is the extent of reaction and $\overrightarrow{k}$, $\overleftarrow{k}$ are rate constant for the forward and reverse reactions, which include the activity coefficient factors.

We may now define the transfer coefficient α by

$$\frac{RT}{F} \left(\frac{\partial \ln \overleftarrow{k}}{\partial E} \right) = - \alpha \qquad (2\text{—}4)$$

noting that in general α may be dependent on the electrode potential E. If it is established on experimental or theoretical grounds, that α is independent of E over a particular range of E, then (2—4) may be integrated to obtain the familiar expression

$$\overleftarrow{k} = \overleftarrow{k}_0 \exp (- \alpha \, Ef) \qquad (2\text{—}5)$$

where k_0 is the integration constant and $f = F/RT$. We chose to define α as the cathodic transfer coefficient since this appears to be the majority usage.

At equilibrium it follows from thermodynamics that

$$\left(\frac{\partial \ln \overrightarrow{k}}{\partial E} \right)_{E_e} - \left(\frac{\partial \ln \overleftarrow{k}}{\partial E} \right)_{E_e} = f \qquad (2\text{—}6)$$

so that

$$\left(\frac{\partial \ln \overrightarrow{k}}{\partial E} \right)_{E_e} = (1 - \alpha) \, f \qquad (2\text{—}7)$$

At least in principle, by adjustment of c_O and c_R the equilibrium potential E_e can be established over the whole accessible potential range, so that provided $\overrightarrow{k}$ and $\overleftarrow{k}$ are independent of c_O and c_R, (2—6) may be extended to any value of the potential and the subscript e dropped.

$$(\partial \ln \overrightarrow{k}/\partial E)_E - (\partial \ln \overleftarrow{k}/\partial E)_E = f \qquad (2\text{—}8)$$

where the subscript E indicates that both derivatives are taken at the same value of E.

While the formal definition (2—4) of the transfer coefficient is satisfactory for the unambiguous description of an experiment, further dissection of the nature of α is helpful in the light of more detailed knowledge of the mechanism of an electrode reaction. Thus we may distinguish *intrinsic* effects from *environmental effects*. The *intrinsic* effect is the direct effect of the potential on the rate of the charge transfer reaction itself. The *environmental* effect is a secondary effect due to the fact that the structure of the electrode-solution interface is itself a function of the electrode potential.

The best known separation of type is that due to Frumkin[6], in which the effect of the diffuse part of the double layer is considered. Charge transfer is assumed to take place to or from a particle present at the outer Helmholtz plane (OHP). Equation (2—5) is replaced by

$$\overleftarrow{k} = \overleftarrow{k}_0 \exp - \alpha \, (E - \varphi_2) \, f \qquad (2\text{—}9)$$

where φ_2 is the potential in the OHP, and the concentration of the reacting particle in (2—3) is taken to be that in the OHP $c_{0,2}$

$$c_{0,2} = c_0 \exp(-z_0 \varphi_2 f) \tag{2—10}$$

Where z_0 is the charge (in atomic units) of the reacting particle. Calculation of rate constants and transfer coefficients using (2—3) and (2—4) is then said to yield apparent values while the *true* values are said to be obtained if (2—9) and (2—10) are taken into account (see for example refs. 7 and 8). In our present terminology (2—9) would describe the intrinsic effect of the potential while (2—10) describes the environmental effect.

Equations (2—9) and (2—10) have been found adequate to represent a number of systems[7,8] with the assumption that α is potential-independent and have also been used to detect a potential dependence of the *intrinsic* or *true* transfer coefficient[9]. The validity of this approach has been questioned from an apparently general thermodynamic viewpoint[10] but the difference in predictions between the Frumkin theory and that based on the Marcelin-De Donder equation appears to be due to the use of an incorrect analogy between chemical and electrochemical processes in the latter. A more rigorous derivation from the point of view of irreversible thermodynamics yields (for the same model) identical results to the Frumkin theory[11].

The problem of accounting for environmental effects in systems where the simple theory proposed by Frumkin breaks down has proved difficult. It has recently been proposed[12] that these effects can be expressed formally by factoring out from the rate constant, the activity coefficient of the activated complex ($\gamma_{\pm}$). Since this expresses the interaction of the activated complex with its environment, it may be potential dependent. Thus (2—3) is rewritten

$$i = (F \overrightarrow{k'}/\gamma_{\pm}) c_R - (F \overleftarrow{k'}/\gamma_{\pm}) c_O \tag{2—11}$$

The activity coefficients of the reactants in initial and final states are not potential dependent and therefore they are conveniently left implicit in the rate constants. Explicit expressions for $\gamma^{\pm}$ may be obtained from the adsorption isotherm obeyed by the particles adsorbed at the electrode surface. For example, if the activated complex and unreacting particles B, C *etc.* each replace one particle of solvent when they are adsorbed, a mixed Langmuir adsorption isotherm is obeyed and

$$\gamma_{\pm} = (1 - \Sigma_i \Theta_i)^{-1} \tag{2—12}$$

where the summation covers all particles except the solvent and Θ_i is the fraction of the surface covered by particles of species i. Some implications of this approach have been explored[12-14] both for simple and complex reactions.

According to equation (2—11) the observed transfer coefficient would be given by

$$\partial \ln (\overleftarrow{k'}/\gamma_{\pm})/\partial E = -\alpha f \tag{2—13}$$

and the *intrinsic* or *true* transfer coefficient by

$$\partial \ln \overleftarrow{k'}/\partial E = -\alpha_I f \tag{2—14}$$

while the *environmental* effect is given by

$$- \partial \ln \gamma_{\ddagger} / \partial E = - \alpha_E f \qquad (2\text{—}15)$$

Clearly

$$\alpha = \alpha_E + \alpha_I \qquad (2\text{—}16)$$

This type of division has been employed by Sluyters *et al.*[15,16], although not precisely in these terms, to account for the effect of specific adsorption on the $Zn(Hg)/Zn^{2+}$ reaction. They assumed α_I to be independent of potential while α_E was potential-dependent.

It is possible of course to express the Frumkin correction using this formalism by writing

$$\gamma_{\ddagger} = \exp\left[(z_e - \alpha)\, \varphi_2\, f\right] \qquad (2\text{—}17)$$

or

$$\alpha_E = (z_0 - \alpha)\, \partial\, \varphi_2 / \partial E \qquad (2\text{—}18)$$

Although we could increase the generality of the equations written in this section by applying them to a reaction

$$r\,R \leftrightharpoons o\,O + z e, \qquad (2\text{—}17)$$

it seems improbable that such a reaction could occur in a single elementary step unless perhaps when $r = o = 1$ and $z = 2$. Hence it seems preferable to pass on to reactions occurring in more than one elementary step.

Complex Electrode Reactions with a Single Rate-determining Step

A number of attempts[17-23] have been made to describe in a general way an electrode reaction which occurs in more than one step. The problem consists of producing a treatment which is sufficiently realistic and general and yet not so cumbersome as to limit its use. Most of the published attempts can be criticised on one or more of these grounds. We propose here a treatment which avoids some of the restrictions and difficulties of an earlier version[17] and is more generally applicable. The principal object is to elucidate the significance of the experimental transfer coefficient but we hope that a wider use will be served.

Considerable simplification can be achieved by assuming that one particular elementary step is rate-determining, that is, the standard free energy of its activated complex is higher than that of any other configuration through which the system passes during the reaction. It is necessary of course to consider the elementary system of reacting particles as a whole throughout the course of the reaction even though some of them may not take part in the rate-determining reaction. Neglect of this fact has led to some inaccurate criticism of this type of approach in the past. Similarly it is incorrect to criticize conclusions based on the model of a single rate-determining step by reference to systems where a change in rate-determining step is assumed.
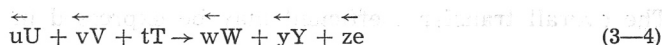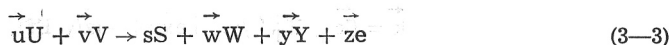
We assume that the overall reaction

$$u\,U + v\,V \rightarrow w\,W + y\,Y + z e \qquad (3\text{—}1)$$

has been established as the potential determining reaction at the electrode. Let the rate-determining reaction be

$$(s/v)\,S \rightarrow (t/v)\,T + (z^{\ddagger}/v)\,e \qquad (3\text{—}2)$$

and this reaction is assumed to occur v times for each unit reaction (3—1). Since (3—2) is an elementary reaction, we might expect (s/v), (t/v) and $(z^{\ddagger}/v)$

to be all unity. On the other hand an elementary surface reaction might well be bimolecular between two identical particles or two different particles. Hence S and T may be taken to represent not necessarily a single species. It turns out that the present formalism does not restrict the generality of this discussion. Finally, S and/or T may be identical with or include one of the reactants U, V, W, Y.

The intermediates S and T are formed in the general case by the reactions

$$\overrightarrow{u}U + \overrightarrow{v}V \rightarrow sS + \overrightarrow{w}W + \overrightarrow{y}Y + \overrightarrow{z}e \qquad (3\text{—}3)$$

$$\overleftarrow{u}U + \overleftarrow{v}V + tT \rightarrow \overleftarrow{w}W + \overleftarrow{y}Y + \overleftarrow{z}e \qquad (3\text{—}4)$$

where it is clear from the stoichiometry that

$$\overrightarrow{u} + \overleftarrow{u} = u$$

$$\overrightarrow{v} + \overleftarrow{v} = v$$

$$\overrightarrow{w} + \overleftarrow{w} = w \qquad (3\text{—}5)$$

$$\overrightarrow{y} + \overleftarrow{y} = y$$

$$\overrightarrow{z} + z^{\pm} + \overleftarrow{z} = z$$

The assumption of a single rate determining step has the advantage that we may assume with good approximation that (3—3) and (3—4) remain in equilibrium*. Hence the concentrations of S and T may be readily determined and substituted in the rate expression for reaction (3—2)

$$i = (zF/\nu)\,(d\xi/dt) = (zF/\nu)\,\overrightarrow{k}_{\pm}/\gamma_{\pm})\,(\gamma_S c_S)^{(s/\nu)} - (zF/\nu)\,\overleftarrow{k}_{\pm}/\gamma_{\pm})\,(\gamma_T c_T)^{t/\nu} \qquad (3\text{—}6)$$

The equilibrium condition for (3—3) may be written

$$(\gamma_S c_S)^s = K_S \exp(zEf)\, c_U^{\overrightarrow{u}}\, c_V^{\overrightarrow{v}}\, c_W^{-\overrightarrow{w}}\, c_Y^{-\overrightarrow{y}} \qquad (3\text{—}7)$$

and similarly for (3—4)

$$(\gamma_T c_T)^t = K_T \exp(-zEf)\, c_W^{\overleftarrow{w}}\, c_Y^{\overleftarrow{y}}\, c_U^{-\overleftarrow{u}}\, c_V^{-\overleftarrow{v}} \qquad (3\text{—}8)$$

We note that this type of expression is obtained whatever the detailed nature of S and T may be. K_S and K_T are potential independent equilibrium constants which contain the activity coefficients of the reactants in their initial and final states. Thus, the full expression for the current becomes

$$i = (zF/\nu)\,\overrightarrow{k}_{\pm}\, K_S^{1/\nu}/\gamma_{\pm})\, \exp\{-(\overrightarrow{z}/\nu)\, Ef\}\,(c_U^{\overrightarrow{u}}\, c_V^{\overrightarrow{v}}\, c_W^{-\overrightarrow{w}}\, c_Y^{-\overrightarrow{y}})^{1/\nu} \qquad (3\text{—}9)$$

$$- (zF/\nu)\,\overleftarrow{k}_{\pm}\, K_T^{1/\nu}/\gamma_{\pm})\, \exp\{-(\overleftarrow{z}/\nu)\, Ef\}\,(c_W^{\overleftarrow{w}}\, c_Y^{\overleftarrow{y}}\, c_U^{-\overleftarrow{u}}\, c_V^{-\overleftarrow{v}})^{1/\nu}$$

Apart from the explicit dependence on potential which arises from (3—7) and (3—8) we note that the rate constants of the rate-determining step $\overrightarrow{k}_{\pm}$

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* Only one of these equilibrium conditions is necessary when the reaction as a whole is far from equilibrium.

and $\overleftarrow{k}_{\pm}$ and the activity coefficient $\gamma_{\pm}$ may be potential-dependent. It is convenient to define the intrinsic transfer coefficient of the rate-determining step (3—2) as

$$(z^{\ddagger}/v)\,\beta = -\,(\partial \ln \overleftarrow{k}_{\pm}\,)/\partial Ef \qquad (3\text{—}10)$$

Since the rate constant of the overall reaction is given by

$$\overleftarrow{k} = (\overleftarrow{k}_{\pm}\ K_T^{1/v}\,/\gamma_{\pm}\,)\exp\{-\,(\overleftarrow{z}/v)\ Ef\}, \qquad (3\text{—}11)$$

The overall transfer coefficient may be expressed in the form

$$\partial \ln \overleftarrow{k}/\partial E = -\,(z/v)\,\alpha\,f \qquad (3\text{—}12)$$

where

$$(z/v)\,\alpha\,f = (z^{\ddagger}/v)\,\beta\,f + (\overleftarrow{z}/v)\,f + \partial \ln \gamma_{\pm}/\partial E \qquad (3\text{—}13)$$

or

$$\alpha = (z^{\ddagger}\,\beta + \overleftarrow{z})/z + (v/z)\,\partial \ln \gamma_{\pm}/f\,\partial E \qquad (3\text{—}14)$$

Thus the *intrinsic* contribution is

$$\alpha_I = (z^{\ddagger}\,\beta + \overleftarrow{z})/z \qquad (3\text{—}15)$$

while the *environmental* contribution is

$$\alpha_E = (v/z)\,\partial \ln \gamma_{\pm}/f\,\partial E \qquad (3\text{—}16)$$

These expressions reduce to those derived in section 2 for a simple reaction by putting $z^{\ddagger} = 1$, $z = 0$, $z = 1$, $v = 1$. An equation for the transfer coefficient having the form of (3—14) except for the last term was quoted without proof some time ago[24].

At equilibrium the net current is zero and from (3—9) and (3—11) we can write the exchange current as

$$\overleftrightarrow{i} = zF\overrightarrow{k}_e\,(c\,\overrightarrow{\underset{U}{c^u}}\ \ \overrightarrow{\underset{V}{c^v}}\ \ \overrightarrow{\underset{W}{c^{-w}}}\ \ \overrightarrow{\underset{Y}{c^{-y}}})^{1/v} \qquad (3\text{—}17)$$

where the subscript e denotes the value at equilibrium whence

$$(\partial \ln \overleftrightarrow{i}/\partial \ln c_i)_{c \neq c_i} = (\partial \ln \overrightarrow{k}_e/\partial \ln c_i)_{c \neq c_i} + \overrightarrow{v}_i/v \qquad (3\text{—}18)$$

where $\overrightarrow{v}_i$ is the forward order with respect to species i and c_i is its concentration. (3—18) can be made more explicit by writing

$$(\partial \ln \overrightarrow{k}/\partial \ln c_i)_{c \neq c_i} = (\partial \ln \overrightarrow{k}/\partial E)_{E_e}\,(\partial E_e/\partial \ln c_i) = (z/v)\,(1-\alpha)\,f\,(-\,v_i/zf) \qquad (3\text{—}19)$$

making use of the Nernst equation where v_i is the stoichiometric coefficient of species i in the overall reaction (3—1). Combining (3—18) and (3—19) we have[25]

$$(\partial \ln \overleftrightarrow{i}/\partial \ln c_i)_{c \neq c_i} = \{\overrightarrow{v}_i - (1-\alpha)\,v_i\}/v \qquad (3\text{—}20)$$

or taking into account (3—5) this may be written in the more symmetrical form

$$(\partial \ln \overleftrightarrow{i}/\partial \ln c_i)_{c \neq c_i} = \{\alpha \overrightarrow{v_i} - (1 - \alpha) \overleftarrow{v_i}\}/v \qquad (3\text{—}21)$$

$$= \overleftrightarrow{v_i}/v \qquad (3\text{—}22)$$

If all the $\overleftrightarrow{v_i}$ are constant over the accessible range (3—22) may be written in the integral form

$$\overleftrightarrow{i} = (zF/v) \, \overleftrightarrow{k} \, (c_U^{\overleftrightarrow{u}} \, c_V^{\overleftrightarrow{v}} \, c_W^{-\overleftrightarrow{w}} \, c_Y^{-\overleftrightarrow{y}})^{1/v} \qquad (3\text{—}23)$$

where $\overleftrightarrow{k}$ is the standard rate constant.

An alternative method of obtaining this information from the exchange current is by use of the coefficient[25]

$$(\partial \ln \overleftrightarrow{i}/f\partial E_e)_{c \neq c_i} = (\partial \ln \overrightarrow{k}/f\partial E)_{E_e} + (\overrightarrow{v_i}/v)(\partial \ln c_i/f\partial E_e)_{c \neq c_i}$$

$$= (1 - \alpha) \, z/v - \overrightarrow{zv_i}/v_i \, v \qquad (3\text{—}24)$$

In the general case the coefficients (3—21) and (3—24) are expressed in terms of the three unknown parameters $\overrightarrow{v_i}$, v and α, which cannot therefore be obtained without other information, e. g. at potentials away from equilibrium.

At potentials far from equilibrium one of the terms on the right-hand side of (3—6) becomes negligible compared with the other. At constant composition then the ratio α/v is readily obtained from the slope of the Tafel plot. If the Tafel plot is found experimentally to be linear, then a reliable value of the exchange current can be found by extrapolation and used to find the stoichiometric number v from[17]

$$v = zf \, \overleftrightarrow{i} \, (\partial E/\partial i)_{E_e} \qquad (3\text{—}25)$$

but this route clearly depends on an accurate extrapolation, which, if α is not independent of potential, requires reliable knowledge of its potential-dependence. Similar information is required for the other methods by which v may be determined[17,26]. The importance of determining v even when measurements can be made away from the equilibrium potential is clear from (3—9) and (3—12) since from these it is apparent that the potential — and concentration — dependence of the current yield α/v and v_i/v. This problem may be overcome by chemical intuition or by setting up possible reaction schemes and using these to predict the experimental coefficients. However, even with a moderately complex reaction there may be a great multiplicity of possible mechanisms[22].

An important conclusion from this method of treating complex reactions is that the non-ideality of the intermediate states in the reaction plays no direct part except for that of the activated complex expressed by $\gamma_{\neq}$. However, it must be recognised that the value of $\gamma_{\neq}$ may depend on the presence of intermediates at the electrode surface. Hence there may well be an indirect effect of concentrations of intermediates on the kinetics. Under such circumstances it may be of considerable importance to know whether parts of the reaction sequence can be considered approximately to be in equilibrium and if not to solve the detailed system of rate equations. For this reason it is difficult to give a general treatment of a reaction sequence in which there

is no single rate-determining reaction. Particular reaction sequences or even some particular types of reaction sequences can readily be discussed using the principles outined here together with the steady state or other appropriate hypothesis.

The Significance of the Transfer Coefficient

In the light of the above treatment we can make the following suggestions:

1. It is important to distinguish between the transfer coefficient of the overall reaction and that of an elementary reaction.

2. We suggest that the cathodic transfer coefficient of the overall reaction is given the symbol α. It is closely related to experimental measurements; for example when the potential is far from the equilibrium potential on the cathodic side (cf. 3—12)

$$\alpha = -\,(v/zf)\,(\partial \ln |\,i\,| /\partial E)_{c_i} \qquad (4—1)$$

3. We suggest that the cathodic transfer coefficient of an elementary step is given the symbol β. This is the quantity which has often been termed the symmetry factor. It has been pointed out by Bauer[1] that such terminology has misleading connotations.

4. In a complex electrode reaction the transfer coefficient of a unique rate-determining step can be obtained from the equation

$$\alpha = (z \mp \beta + \overleftarrow{z})/z + (v/z)\,\partial \ln \gamma_{\mp}/f\,\partial E \qquad (3—14)$$

but this requires a knowledge of the position of the rate-determining step in the sequence, i. e. $\overleftarrow{z}$ as well as of the environmental effects on the activated complex i. e. $\gamma_{\mp}$.

5. In a simple reaction

$$\alpha = \beta + \partial \ln \gamma_{\mp}/f\,\partial E \qquad (4—2)$$

and β is more easily obtained though environmental effects must still be known.

6. Quantum mechanical theories of electrode reactions are concerned with elementary reactions and consequently in favourable cases will predict values of β. Thus this type of theory should provide an understanding of β whereas an understanding of α depends on a knowledge of the reaction sequence, the environment of the activated complex as well as the value of β.

The Transfer Coefficient of an Elementary Step

When the concept of the transfer coefficient was first introduced[3,4] it was assumed to be a constant largely on the basis of experimental results on the evolution of hydrogen. Frumkin's work[6,27] showed that potential dependence of the observed transfer coefficient could arise from environmental effects. Although it was difficult to explain[28] the constancy of β this concept was retained. More recently discussion of the potential dependence of β has been revived[29,30]. General arguments show that[31,32] it must be potential-dependent. However, the practical importance of this is not yet fully established.

Theories of the elementary electrode reaction may be put into two groups: one-dimensional theories and poly-dimensional theories. One-dimensional theories[33] are developed from the model of a triatomic gas reaction where the atoms are constrained to be co-linear. Potential energy-distance curves of more or less complex shape (e. g. Morse curves) can be assumed and the transfer coefficient is given by the relative slope of the two curves at the intersection. Such a model gives an excellent qualitative account of the Brønsted relation[34] but cannot give a realistic account of a reaction in a condensed phase.

The poly-dimensional theories[35-37] make a more or less crude attempt to treat the reactants and their surrounding as a whole. They have so far been restricted to the harmonic approximation and consequently yield a transfer coefficient which is 0.5 when the elementary reaction is at equilibrium and which varies linearly with potential. The simplest physical interpretation[35-36] of the transfer coefficient provided by these theories is that a hypothetical transfer of this fraction of a unit charge would yield a reactant in equilibrium with the environment which is most favourable for the charge transfer.

It should be noted that the treatment of the reactants and their surroundings in the poly-dimensional theories is concerned with the intrinsic potential dependence of the rate and does not include the effects defined above as environmental and expressed through $\gamma_{\pm}$. However, in a given electrode reaction it may be a matter of considerable difficulty to establish the division of an observed potential-dependence of the transfer coefficient between intrinsic and environmental effects. In a recent attempt at this[9] the reaction

$$Cr^{2+} \to Cr^{3+} + e$$
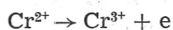
was studied and the environmental effects were assumed to be given by the simple Frumkin theory. The intrinsic transfer coefficient was then found to be potential-dependent in a manner consistent with the proposed poly-dimensional theories[35,36] for which this type of electron exchange reaction provide the closest example in reality. More recent experimental work on the same reaction[38] has shown that this conclusion was not as firmly established as it was originally thought. It appears from this analysis that experimental work of exceptionally high accuracy is necessary before definite proof is obtained concerning the potential-dependence of the transfer coefficient of simple redox reactions.

Finally, it should be noted that the proposed distinction between intrinsic and environmental effects must be essentially arbitrary. For some electrode reactions it is relatively easy to make a clear distinction but for others it may be difficult. An example of the latter may be found in the simple redox reactions like the chromium reaction discussed above. In such reactions the solvation shell plays an essential rôle in the activation process and the interaction of the central ion with it determines the value of the transfer coefficient. Hence it seems that this part of the environment must be considered as contributing to the intrinsic transfer coefficient. On the other hand if a reaction of this type is carried out in a mixed solvent system, change of the solvent might reasonably be expected to modify the environmental transfer coefficient. A possible solution to this problem is to regard the latter as arising only from the potential-dependence of the composition of the solvation

shell of the activated complex. Such an effect could occur in a mixed solvent. It is evident that the exact division between intrinsic and environmental effects will have to be discussed in terms of the model adopted for a particular system.

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IZVOD

Koeficijent prijenosa u elektrodnim reakcijama

R. Parsons

Kada je koeficijent prijenosa bio originalno uveden u teoriju elektrokemijskih reakcija smatran je konstantom ponajviše na osnovi eksperimentalnih podataka izlučivanja hidrogena. Frumkinov rad pokazao je da potencijalna ovisnost koeficijenta prijenosa proizlazi iz utjecaja okoline na elektrodnu reakciju. Kao rezultat teoretskih razmatranja predlaže se, da se razlikuje koeficijent prijenosa sveukupne reakcije od koeficijenta prijenosa elementarnog koraka u reakcijskom slijedu. Za koeficijent prijenosa katodičkog dijela sveukupne reakcije treba zadržati simbol α. Taj se koeficijent sastoji iz *intrinzičnog* ili pravog dijela α_I, i *environmentalnog* dijela α_E. Za katodički dio koeficijenta prijenosa elementarnog koraka elektrokemijske reakcije treba uzimati simbol β. Ukratko se razmatraju i posljedice primjene jedno-, kao i više dimenzionalnih teorija elektrodnih reakcija na predskazivanje intrinzičnih i environmentalnih efekata.

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