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**ELECTRODE REACTION ORDERS,
TRANSFER COEFFICIENTS AND RATE
CONSTANTS
AMPLIFICATION OF DEFINITIONS AND
RECOMMENDATIONS FOR PUBLICATION OF
PARAMETERS**

(Recommendations 1979)

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Commission on Electrochemistry*

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AND RATE CONSTANTS

AMPLIFICATION OF DEFINITIONS AND RECOMMENDATIONS
FOR PUBLICATION OF PARAMETERS

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Electrode reaction rate constants and transfer coefficients have been defined in Appendix III of the Manual of Symbols and Terminology for Physicochemical Quantities and Units (Pure and Applied Chemistry, 37 (1974) 501). In that publication the aim was to provide general definitions in the simplest form. However, it is desirable that further amplification of these definitions should be given in view of the complications and confusions which exist in the literature. A summary of recommendations appears at the end of this document.

1. THE ELECTRODE REACTION

In most steady state electrochemical experiments the primary observation is the relationship between the current and the potential for a single electrode process. The term electrode process is used to describe the totality of changes occurring at or near a single electrode during the passage of current. At a given potential the current is controlled by the kinetics of a number of steps which include the transport of reactants to and from the interface and the interfacial reaction itself. The latter, which is called the electrode reaction, must always include at least one elementary step in which charge is transferred from one phase to the other, but may also involve purely chemical steps within the interfacial region. The charge transfer step, like the electrode reaction is normally written as if the electrons were the carrier of charge across the interface. Consequently this step is frequently referred to as an electron transfer step. Since charge can also be transferred by ions, the more general term charge transfer step is preferred.

The complete kinetic analysis of an electrode reaction would require the determination of the rate constants of each of its steps. Unless the reaction is simple this is a difficult problem almost certainly involving studies as a function of time or frequency. Even when they have used such techniques most studies of electrode reactions up to the present time have provided information on the kinetics of the electrode reaction as a whole and only rarely on its elementary steps. The aim of the present document is to make recommendations about the reporting of kinetic data for the electrode reaction as a whole, which are the quantities normally obtained from steady state studies, although these recommendations may also be used for the results of some time dependent studies.

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2. OBSERVABLE OR OPERATIONAL RATE CONSTANTS

The observable electrode reaction rate constant is the constant of proportionality expressing the dependence of the rate of the electrode reaction on the interfacial concentration of the chemical species involved in the reaction. It may be possible to determine this interfacial concentration directly, but more often it must be calculated using a model of the mass transport in the regions adjacent to the interface, as well as chemical reactions at the interface and in the adjoining phases, appropriate to the conditions of the experiment. (Note that the term interfacial concentration is used to denote the local volume concentration at the boundary of the diffusion layer towards the electrode, but not within the electrical double layer) (see 4.1 of Bulletin , Nomenclature for Transport Phenomena in Electrolytic Systems by N. Ibl, Pure and Applied Chemistry, in press). When these regions overlap one, method of applying these models is to vary the mass transport conditions (e.g. rotation speed, potential sweep speed) and then to extrapolate the observed total rate (= current) to a hypothetical state in which all processes in the cell other than the interfacial reaction are not perturbed from their equilibrium state. The great variety of methods for carrying out this procedure will not be discussed here as they are well described in modern text books. It may be noted, however, that many of these methods depend on previous knowledge (or assumption) about the order of the reaction. In some systems, especially when the interfacial reaction is slow, the perturbation from the equilibrium state of processes other than the interfacial reaction may actually be negligible. The dependence of the current on the bulk concentration may then be used directly.

The faradaic current density measures the rate of the interfacial reaction, the proportionality constant being the charge number of the reaction multiplied by the Faraday constant. Thus the study of the current as a function of the interfacial concentration of all reactants at a given potential is equivalent to the determination of the order of the reaction with respect to each reactant. The net rate is the difference between forward and reverse rates, i.e. the net current is the sum of cathodic and anodic partial currents. To simplify the analysis it is preferable to work at potentials sufficiently far from the equilibrium value such that one partial current may be neglected in comparison with the other. Under these conditions many, but by no means all, electrode reactions follow a simple rate law in which the interfacial concentrations of the reactants are raised to a power which is constant and usually integral. This is equivalent to the expressions 8.10.1 and 8.10.2 in Appendix III, i.e. for the anodic partial current

$$I_a = (n/\nu) F A k_{ox} \prod_1 c_1^{\nu_{1,a}} \quad 2.1$$

and for the cathodic partial current

$$I_c = -(n/\nu) F A k_{red} \prod_1 c_1^{\nu_{1,c}} \quad 2.2$$

Here n is the charge number of the electrode reaction as written and ν_1 is the order of reaction with respect to reactant i . In Appendix III the two concentration products are written as if they were identical. Here subscripts a and c have been added to the ν_1 to indicate that different orders of reaction with respect to each species will be observed in the anodic and cathodic reactions.

The order of reaction ν_1 may be positive or negative and need not be integral. It is not necessarily equal to a stoichiometric number in the overall reaction. ν (without subscript) which was omitted in 8.10, is the stoichiometric number giving the number of identical activated complexes formed and destroyed in the completion of the overall reaction as formulated with charge number n (for further explanation see section 3). ν is a positive number. A is the area of the electrode-solution interface over which the reaction occurs uniformly. Experimental arrangements should ensure that the reaction occurs uniformly over the interface. The area A may be a geometrical area or a true area, but if the latter, the way in which this is determined must be clearly stated. Note that, under some conditions, the area available for the reaction may itself be dependent on the potential.

For some reactions it is not possible to find a simple rate law of the form of equations 2.1 and 2.2. These are complex reactions, often involving adsorbed species. It is not possible to assign a single overall rate constant to such a reaction. Further analysis into component reactions is necessary.

When the kinetics of the electrode reaction follow equation 2.1 and 2.2 the rate constant can be calculated directly from these equations at the potential of the electrode.

The characteristic feature of an electrode reaction, due to the transfer of charge associated with it, is the dependence of the rate constant on potential. This dependence is expressed by the transfer coefficient in the form

$$\alpha_c/\nu = -(RT/nF) (\partial \ln k_{\text{red}}/\partial E)_{T,p} \quad 2.3$$

for the cathodic reaction and

$$\alpha_a/\nu = (RT/nF) (\partial \ln k_{\text{ox}}/\partial E)_{T,p} \quad 2.4$$

and the quantities α_c/ν and α_a/ν may be considered as the observable transfer coefficients for the cathodic and anodic reactions respectively. If the interfacial reactant concentrations can be held constant experimentally as the potential of the electrode varies then the rate constants in 2.3 and 2.4 may be replaced by the partial currents and equations 8.11.1 and 8.11.2 of Appendix III are obtained. This replacement is valid if the rate law follows 2.1 and 2.2 and may also be valid for some more complex rate laws.

If it is found that the transfer coefficient is independent of potential E , then 2.3 and 2.4 may be integrated simply to obtain

$$k_{\text{red}} = k_{\text{red}}^0 \exp [-(\alpha_c nF/\nu RT) (E-E^0)] \quad 2.5$$

$$k_{\text{ox}} = k_{\text{ox}}^0 \exp [(\alpha_a nF/\nu RT) (E-E^0)] \quad 2.6$$

where k_{red}^0 and k_{ox}^0 are the rate constants at some standard potential E^0 . The only satisfactory standard potential which yields a standard rate constant without some arbitrary content is the conditional (formal) potential E_c^0 on the concentration scale of the electrode reaction whose kinetics are being studied. It follows from the equilibrium condition at this potential that there is a single standard rate constant for the cathodic and anodic reactions which is defined as k_c^0 in equations 8.12.1 and 8.12.2 of Appendix III.

Note that there is no justification for describing the coefficient of $(F/RT) (E-E^0)$ in the exponent of 2.5 and similar expressions as αn_a where n_a is 'the number of electrons transferred in the rate-determining reaction'. This description is misleading and may be incorrect; its use should be discontinued.

Equations 8.12.1 and 8.12.2 of Appendix III could be used even if the transfer coefficient is dependent on potential. This procedure is not recommended, but if it is used the result should not be called a conditional (or standard) rate constant. In this case it is preferable to quote the experimental rate constants as functions of potential.

When the interfacial reaction is fast compared to the rate of transport of reactant it may be impossible to make measurements sufficiently far from equilibrium that a single current component can be measured. The accessible quantity is then the slope of the total current with respect to potential at the equilibrium potential which is the effective conductance of the electrode. From 2.5 or 2.6, or more generally from irreversible thermodynamics, it can be shown that

$$(\partial I / \partial E)_{\eta=0} = I_0 nF / \nu RT \quad 2.7$$

where I_0 is the exchange current. From the concentration dependence of the exchange current it is possible to obtain some information about the orders of reaction and the transfer coefficient. Thus

$$(\partial \ln I_0 / \partial \ln c_B)_{c_i} = \{ \alpha_c \nu_{B,a} + \alpha_a \nu_{B,c} \} \quad 2.8$$

where $\nu_{B,c}$ and $\nu_{B,a}$ are the orders of the cathodic and anodic reactions respectively with respect to species B (see 2.1 and 2.2) c_B is the concentration of species B and c_i is the concentration of any other reactant. Note that, at equilibrium, the interfacial concentration is equal to the bulk concentration. In the general case it is not possible to disentangle these orders from the transfer coefficients and the stoichiometric number even though at a given potential, in particular the equilibrium potential,

$$\alpha_a + \alpha_c = 1 \quad 2.9$$

However, in many reactions the situation is sufficiently simple that assumptions may legitimately be made about some of these parameters so that the values of ν , ν_i and α may be found. The conditional rate constant may be obtained from

$$I_0 = A(n/\nu) F k_c^0 \prod_i c_i^{\nu_i} \quad 2.10$$

where

$$\nu_i = \{ \alpha_c \nu_{i,a} + \alpha_a \nu_{i,c} \} \quad 2.11$$

3. THE STOICHIOMETRIC NUMBER ν

This quantity is introduced into the equations for the kinetics of complex reactions to allow for the possibility that the rate-determining step may occur more or less than once in the completion of the overall reaction as written. It is clear therefore that ν is arbitrary in the same way that n is arbitrary because it depends on the way in which one chooses to write the equation down. Thus, for example, it is possible to write



with $n = 2$, or



with $n = 1$ and it is well known that this choice leads to no ambiguity in the associated thermodynamics. If it is supposed that the rate determining step in this reaction is the proton transfer



then this reaction would occur twice ($\nu = 2$) in the completion of 3.1 or once ($\nu = 1$) in the completion of 3.2.

In general the quantity n/ν is not arbitrary and is a true characteristic of the reaction kinetics. This ratio is the charge number which always appears in the kinetic equations. In principle the use of ν could be avoided by choosing n so that ν is always unity but this requires more knowledge about the detailed kinetics of a complex reaction than is often available.

The stoichiometric number ν can be determined once n is chosen if a measurement of the current-potential curve can be made close to, and one far

from, equilibrium. The value of I_0 obtained from the latter is then used in equation 2.7 to obtain v_0 . A measurement of the current-potential curve on either side of equilibrium and far from it yields the same information. Both methods assume that the rate determining step is the same in the two regions of measurement. When measurements can be made only close to equilibrium it is not possible to find v_0 . However, fortunately most such fast reactions are simple.

4. RATE CONSTANTS FOR ELEMENTARY STEPS OR SIMPLE REACTIONS IN THE ABSENCE OF ADSORPTION

Such reactions follow the kinetic laws 2.1 and 2.2 with the concentration products taking rather simple forms. The orders of reaction v_i are integral and usually 1. Only one or two species appear in these products and no species appears in the product for both anodic and cathodic reaction. The stoichiometric number is unity if the reaction written is the elementary step.

The equations in Section 1 hence take a simple form and for a first order reaction reduce to those given in Appendix III.

There seems no good reason to recommend a special term for the transfer coefficient of an elementary step.

5. RATE CONSTANTS FOR ELEMENTARY STEPS IN THE PRESENCE OF ADSORPTION

When reactants or intermediates are adsorbed, the rate of reaction may no longer be related to the concentration by a simple law like 2.1 or 2.2. The deviation may be due to either entropic or energetic effects or both. Methods for treating these kinetics are at present so diverse and controversial that it is not possible to make general recommendations now.

The situation best understood is that where a reactant is non-specifically adsorbed in the outer Helmholtz plane (inner boundary of the diffuse layer). The effect of such adsorption on electrode kinetics is usually termed the 'Frumkin Effect'. Rate constants, transfer coefficients etc. corrected for this effect are frequently called 'true' rate constants etc. It would be preferable to describe them as 'corrected for the Frumkin Effect', but in any case, if such a correction is carried out, the basis on which it is made should be clearly described.

Physical and chemical adsorption on the electrode surface is usually described by means of an adsorption isotherm and kinetic equations compatible with various isotherms such as the Langmuir, Frumkin, Temkin etc. are known. Rate constants and transfer coefficients calculated on the basis of such an equation should be accompanied by a clear statement of the equation used as well as the evidence for the applicability of this equation.

Note that adsorption effects in electrode kinetics are often potential dependent and they may lead to kinetic parameters which depend on potential and reactant concentration in a complex way.

RECOMMENDATIONS FOR THE PUBLICATION OF PARAMETERS DERIVED FROM ELECTRODE KINETIC DATA

1. Corrections for mass transport and ohmic drop should be as accurate as possible and the method should be clearly described.
2. The conditions by which a steady state is achieved and the time required for this achievement should be described. For measurements in the non-steady state the nature of the time dependent parameters as well as their control or measurement should be described.
3. Potential and concentration dependence of rate should be studied and expressed in terms of a transfer coefficient and reaction orders respectively.

4. If the transfer coefficient is potential dependent, rate constants should be quoted at the potential of measurement.
5. If the transfer coefficient is independent of potential, the conditional rate constant at the equilibrium potential of the reaction being studied should be quoted. The range of potential over which a constant transfer coefficient is observed should be stated.
6. If the equilibrium potential of the reaction under study is not known, the rate constant should be quoted at the potential of measurement rather than at some arbitrary standard potential.
7. Any corrections to kinetic parameters due to adsorption should be clearly described. The term "true" rate constant is not recommended.