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NOMENCLATURE FOR TRANSPORT PHENOMENA IN ELECTROLYTIC SYSTEMS

(Recommendations 1979)

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SUMMARY

The document deals with the transport phenomena of importance to electrochemists and electrochemical engineers. In the absence of a report on mass transport at large, the first section presents general definitions of mass flux, of flux density and of phenomenological coefficients, as appearing in the relationships of irreversible thermodynamics, which express the proportionality between the driving forces and the fluxes. The main part is concerned with electrolytic systems, in particular with ideal dilute solutions. Mass transport by diffusion, by convection and by migration of ions under the influence of an electric field is considered. The diffusion coefficient of a species is distinguished from that of an electrolyte. A section is devoted to the transport of charges, including transport numbers, the flow of current through the solution and through the electrode, current efficiency, and current distribution. The report also discusses the precise meaning of concepts related to mass transport, such as the Nernst diffusion layer, mass transport control, interfacial concentrations, concentration overpotential, mass transport coefficients and diffusion potentials. However, the diffusion in solid electrolytes and surface diffusion are not treated.

Recommendations for symbols and definitions are given. In many cases, it is endeavoured to clarify by a brief discussion the concept itself.

INTRODUCTION

This document is an Appendix to the Manual of Symbols and Terminology for Physicochemical Quantities and Units[1,7]. It is to be used in conjunction with Appendix III to the above Manual (Electrochemical Nomenclature)[2]. Further documents with related definitions are:
a) Report on Electrode Reaction Orders etc.[3], b) Report on Terms, Symbols and Definitions for Electroanalytical Chemistry[4], c) Report on Conditional Diffusion Coefficients[5], d) I.E.C. (International Electrotechnical Commission) Vocabulary document 50-50 (1960) and I.S.O. (International Organization for Standardization) International Standard 2080 (1973) (definitions and vocabulary related to technical applications).

The following text includes the nomenclature on transport phenomena believed to be most important to electrochemists and electrochemical engineers. However, it is by no means complete and it is hoped that it will be supplemented in the future. Some definitions (section 1) are fairly general but the majority of them pertains to liquid solutions, in particular to ideal dilute solutions. The nomenclature proper to transport phenomena in solids and to surface diffusion is not included. Generally speaking, the nomenclature presented here is related to electrolytic systems; it is planned to integrate it eventually into a more general document on Transport Phenomena.

For each defined quantity the SI unit has been given. Whenever more convenient, multiples or submultiples are equally acceptable.

1. MASS TRANSPORT: GENERAL CASE

1.1 Flux density of species B (mol m^{-2} s^{-1}) $\mathbf{N}_B$, $\mathbf{J}_B$

We consider a multicomponent mixture of adequately defined species A,B,C,...*. The flux density $\mathbf{N}_B$ of a species B is a vector which indicates the direction in which the species moves and the amount of substance of B passing through a plane perpendicular to the vector, divided by time and by area. Sometimes the flux density is simply called flux. However, this is not consistent with the usage in vector theory.

The symbol $\mathbf{N}_B$ is preferred to $\mathbf{J}_B$ in the case of the flux density of a species. The use of $\mathbf{J}_B$ is suggested for the flux densities of other quantities such as heat, or as a generic symbol for any flux density.

1.2 Flux of species B (mol s^{-1}) $N_B^{\square}$

The flux of a species B is the amount of substance of B passing through an area A and divided by time:

$$N_B^{\square} = \int_0^A \mathbf{N}_B \cdot d\mathbf{A} \qquad\qquad\qquad [1]$$

$\mathbf{N}_B . d\mathbf{A}$ is a scalar product and $N_B^{\square}$ is thus a scalar quantity.

1.3 Velocity of species B (m s^{-1}) $\mathbf{v}_B$

The flux density is related to the velocity by the equation

$$\mathbf{N}_B = c_B \mathbf{v}_B \qquad\qquad\qquad [2]$$

The vector $\mathbf{v}_B$ is the macroscopic average velocity at which the species B moves (which is to be distinguished from the random molecular velocity) (see also 1.4 and 1.5), c_B is the concentration of species B (mol m^{-3}). Note that the velocity is defined with respect to a frame of reference.

1.4 Phenomenological coefficient of species B

$$(\text{mol}^2 \text{ J}^{-1} \text{m}^{-1} \text{s}^{-1}) \qquad\qquad\qquad L_{Bi}$$

In the following we will restrict ourselves to media which are isotropic with respect to mass transport (i.e. the transport coefficients are independent of direction). In the linear range (not too far from equilibrium), for uniform temperature and neglecting external fields such as the earth's gravitational field, the flux density of species B is related to the gradients of the electrochemical potentials of all species by the phenomenological equation:

$$\mathbf{N}_B - c_B \mathbf{v}_A = -\sum_{i \neq A} L_{Bi}^A \nabla \tilde{\mu}_i \qquad \text{with} \quad i = B,C.... \qquad [3]$$

where $\nabla \tilde{\mu}_i$ is the gradient of the electrochemical potential of species i. The proportionality factors L_{Bi}^A are called phenomenological coefficients. Their values depend on the frame of reference. The latter is taken here to move with the velocity $\mathbf{v}_A$ of species A, and hence

$$L_{Ai}^A = 0 \qquad\qquad\qquad [4]$$

Therefore, $\mathbf{N}_B - c_B \mathbf{v}_A = \mathbf{N}_B^A$ is the flux density of species B referred to a frame of reference moving at the velocity of species A, or more simply, the flux density referred to species A.

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* In principle a species is any grouping of particles, which is regarded as a separate entity. However, in practice, the species should be so defined that it can be determined analytically under the experimental conditions at hand and that its properties do not change appreciably during the time scale considered.

Note that in general the $\nabla \tilde{\mu}_i$ are not independent: They are linked through the Gibbs-Duhem equation. To produce unambiguous values of the phenomenological coefficients, $\nabla \tilde{\mu}_A$ has been omitted from the set of driving forces. This requires

$$L_{Bi}^{A} = 0 \quad \text{for} \quad i = A \qquad\qquad [5]$$

i.e. i = A is omitted from the sum in eq.[3].

The $\nabla \tilde{\mu}_i$ are generalized forces (in the sense of irreversible thermodynamics). The conjugate flux density is $\mathbf{N}_i - c_i \mathbf{v}_A$. For these conjugate forces and fluxes, we have

$$\sum_i (\mathbf{N}_i - c_i \mathbf{v}_A) \cdot \nabla \tilde{\mu}_i = T\dot{s} \qquad\qquad [6]$$

where $\dot{s}$ is the rate of local entropy production, i.e. the local rate of increase of the entropy density due to irreversible processes inside the volume element considered.

In eq.[3] L_{BB}^{A} (i = B) is the coefficient conjugated with species B. The L_{Bi}^{A} (i ≠ B) are coupling coefficients. The Onsager reciprocal law includes the statement that the matrix of the coupling coefficients is symmetric $(L_{Bi}^{A} = L_{iB}^{A})$. Generalized forces other than those in eq.[3] can influence the flux of species B (for instance, a temperature gradient). In the present context, the action of such forces is regarded as negligible. It is to be noted, however, that the influence of an electric field is included because of the relationship between $\tilde{\mu}_i$ and the electric potential ϕ.

1.5 Mass-average velocity (m s^{-1}) $\mathbf{v}_b$

Molar-average velocity (m s^{-1}) $\mathbf{v}_m$

Average velocities are often used as velocity of reference. They can be defined in different ways.

Mass-average velocity:

$$\mathbf{v}_b = \rho^{-1} \sum_i c_i M_i \mathbf{v}_i \qquad\qquad [7]$$

Molar average velocity:

$$\mathbf{v}_m = c_t^{-1} \sum_i c_i \mathbf{v}_i \qquad\qquad [8]$$

with $\quad c_t = \sum_i c_i \qquad\qquad [9]$

where M_i = molar mass, c_t = total concentration (mol m^{-3}), ρ = density of the solution (kg m^{-3}).

1.6 Friction coefficient of species B (kg s^{-1}m^{-3}) K_{Bi}

Interaction diffusion coefficient of species B (m^{2}s^{-1}) $\mathfrak{D}_{Bi}$

An alternative way of writing the phenomenological mass transport equation is as follows:

$$c_B \nabla \tilde{\mu}_B = \sum_i K_{Bi} (\mathbf{v}_i - \mathbf{v}_B) = RT \sum_i c_B c_i (c_t \mathfrak{D}_{Bi})^{-1} (\mathbf{v}_i - \mathbf{v}_B) \quad [10]$$

$c_B \nabla \tilde{\mu}_B$ is the force acting on species B, divided by volume. K_{Bi} is the coefficient of friction between species B and i. $\mathfrak{D}_{Bi}$ is the interaction diffusion coefficient (between species B and i). The number of independent equations [10] which can be written for a given system is equal to the number of species minus one.

2. MASS TRANSPORT: APPROXIMATION OF IDEAL DILUTE SOLUTIONS

2.1 Diffusion coefficient of species B (m^{2}s^{-1}) $\mathcal{D}_B$

For a sufficiently dilute solution (for instance, an aqueous solution) the interaction diffusion coefficients $\mathfrak{D}_{Bi}$ and the phenomenological coupling coefficients L_{Bi} (i ≠ B) between the minor constituents can be regarded as negligibly small. Further, the concentration of the solvent is virtually equal to the total concentration c_t . Combination of eqs.[2] and [10] thus yields:

$$\mathbf{N}_B = -c_B \mathcal{D}_B (RT)^{-1} \nabla \tilde{\mu}_B + c_B \mathbf{v} \qquad [11]$$

$\mathbf{N}_B$ is the flux density of a minor constituent of the solution with respect to a fixed frame of reference. The flux density with respect to the solvent is:

$$\mathbf{N}_B - c_B \mathbf{v} = -c_B \mathcal{D}_B (RT)^{-1} \nabla \tilde{\mu}_B \qquad [12]$$

$\mathbf{v}$ is the velocity of the solvent. All the average velocities defined in 1.5 are now virtually equal to $\mathbf{v}$ which can thus be called the velocity of the fluid and written without subscript. Likewise, the second subscript can be omitted in writing the diffusion coefficient of species B since only the interaction with the solvent is of importance.

If the dilute solution behaves ideally (i.e. if the interactions between all the solute particles of the mixture can be neglected) the electrochemical potentials can be written in terms of concentrations:

$$\tilde{\mu}_B = \mu_B^o + RT \, \ell n \, (c_B / c_B^o) + z_B F \phi \qquad [13]$$

where ϕ is the electric potential at the point of the solution considered and z_B is the charge number of the species (positive for cations, negative for anions). $\tilde{\mu}_B$ is the electrochemical potential of species B, μ_B^o its standard value; c_B^o is the standard concentration (see Manual 1 p.40); R, T and F have their usual meaning[1].

For an ideal dilute solution eq.[11] thus can be written as

$$\mathbf{N}_B = -\mathcal{D}_B \nabla c_B - F(RT)^{-1} z_B c_B \mathcal{D}_B \nabla \phi + c_B \mathbf{v} \qquad [14]$$

The first term on the right hand side represents the transport by the molecular process of diffusion (diffusion flux density), the second one the transport owing to migration under the influence of the electric field (migration flux density) and the third one the transport by convection (convection flux density).*

$\mathcal{D}_B$ is the diffusion coefficient of species B in an ideal dilute solution. It is related to the electric mobility $u_B (m^2 V^{-1} s^{-1})$ by:

$$\mathcal{D}_B = u_B RT / |z_B| F \qquad [15]$$

In addition one has (except in the electric double layer) the electroneutrality condition

$$\sum_i z_i c_i = 0 \qquad [16]$$

Note that eq.[14] is also often used when $\nabla \tilde{\mu}$ is not the only acting force, i.e. when external forces, such as pressure differences, are acting on the fluid. $\mathbf{v}$ corresponds then to the field of hydrodynamic velocities, which is given, in principle, by the Navier-Stokes equation of hydrodynamics.

2.2 Rate of concentration change of species B (mol $m^{-3} s^{-1}$) $\partial c_B / \partial t$

The equation

$$\partial c_B / \partial t = \mathcal{D}_B \nabla^2 c_B + F(RT)^{-1} z_B \mathcal{D}_B \nabla \cdot (c_B \nabla \phi) - \mathbf{v} \cdot \nabla c_B + \sum_r v_{Br} \qquad [17]$$

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*In principle, the decomposition into a diffusion, migration and convection term is also possible in the case of a dilute but non-ideal solution (eq.[12]). However, the diffusion term must then be expressed in terms of activities (or concentrations and activity coefficients) instead of concentrations alone. In the case of ionic species this involves the problem of the individual ionic activities. The result is that the electric potential is not unambiguously given and a convention has to be used. The potential can be arbitrarily referred to one of the ionic species of the solution.

follows for an incompressible fluid ($\nabla.\mathbf{v} = 0$) from eq.[14] by making a mass balance for an infinitesimal volume element of the solution.*

v_{Br} is the amount of substance of B produced (or consumed) by the homogeneous reaction r divided by time and volume (see 1.1 of the Manual 1). The summation extends over all homogeneous reactions.

2.3 Diffusion coefficient of an electrolyte (m^2s^{-1}) $\mathcal{D}$

The potential ϕ can be eliminated from eq.[17] in two limiting cases.

a) An ionic species B is present in very small amount as compared to other ionic species in the solution (supporting electrolyte). The migration term in eq.[17] (i.e. $F(RT)^{-1} z_B \mathcal{D}_B \nabla.(c_B \nabla \phi)$) is then negligible as compared to the convection and diffusion terms, when eq.[17] is written for species B.

b) The solution contains a binary electrolyte such as $CuSO_4$ (i.e. two ionic species only). The potential ϕ can then be eliminated from eq.[17] by means of the electroneutrality condition [16]. This yields the equation

$$\partial c_B / \partial t = \mathcal{D} \nabla^2 c_B - \mathbf{v}.\nabla c_B \qquad [18]$$

where $\mathcal{D}$ is the diffusion coefficient of the neutral electrolyte which is linked with the ionic diffusion coefficients $\mathcal{D}_+$ and $\mathcal{D}_-$ through the equation

$$\mathcal{D} = \frac{(z_+ - z_-) \mathcal{D}_+ \mathcal{D}_-}{z_+ \mathcal{D}_+ - z_- \mathcal{D}_-} \qquad [19]$$

The + and - signs refer to the cation and the anion, respectively, $\mathcal{D}_+$ and $\mathcal{D}_-$ being defined by eq.[14] (with B = + or -).

2.4 Average diffusion coefficient (m^2s^{-1}) $\bar{\mathcal{D}}$

Strictly speaking, eqs.[14] to [19] are valid only for ideal dilute solutions and $\mathcal{D}$ is then independent of concentration and ionic strength. In practice, however, the equations are often applied as a first approximation to systems which more or less depart from ideal behaviour. The error involved can then often be reduced by using an effective diffusion coefficient determined experimentally for the concentrations under consideration (the value of $\mathcal{D}$ being calculated formally from the experimental data by means of equations applying to ideal dilute solutions).

If the concentration changes substantially over the diffusion path it is suggested to use an average value of the diffusion coefficient over the concentration range involved in the calculation of quantities of practical interest such as the limiting current. Experimental diffusion coefficients employed in such computations should inasmuch as possible have been determined under conditions similar to those for which the calculation is made. For instance, if the limiting current is to be calculated for a cell with channel flow it is preferable to use a diffusion coefficient determined by measuring the limiting current with a rotating disk, rather than by the method of the porous cup.

3. CHARGE TRANSPORT

3.1 Current density of a species B in solution (A m^{-2}) j_B

The current density j_B of a species B in a given point of the solution is obtained by multiplying the flux density of that species at the given point by the Faraday constant and by the charge number z_B of the species:

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*
Eq.[17] is the fundamental equation of mass transport whose integration (usually in a more or less simplified form) ultimately yields the main quantities of practical interest, such as the limiting current. The calculation requires the knowledge of the field of the fluid velocity which can be deduced from the laws of hydrodynamics. The quantities related to these laws have not been defined by IUPAC so far. However, it would be beyond the scope of this appendix to deal with the terminology and symbols of purely hydrodynamic quantities.

$$\mathbf{j}_B = z_B F \mathbf{N}_B \qquad\qquad [20]$$

$\mathbf{j}_B$ is a vector which indicates the direction in which the charges transported by the species B flow and which gives the number of these charges going through a plane oriented perpendicular to the vector, divided by time and by area.

The current density of a species B relative to a frame of reference moving at velocity $\mathbf{v}$ is

$$\mathbf{j}_B^A = z_B F (\mathbf{N}_B - c_B \mathbf{v}_A) = z_B F \mathbf{N}_B^A \qquad\qquad [20']$$

The total current density $\mathbf{j}$ is given by

$$\mathbf{j} = \sum_i \mathbf{j}_i \qquad\qquad [21]$$

3.2 Transport number of species B $\qquad\qquad t_B$

From eq.[3] follows that in the absence of concentration gradients the current densities $\mathbf{j}_B$ all have the same direction given by the vector $\nabla\phi$. The transport number of species B is then defined by:

$$t_B = |\mathbf{j}_B| / |\mathbf{j}| \qquad\qquad [22]$$

It represents the fraction of the total current transported by species B in the absence of gradients of concentration. The value of t_B depends on the frame of reference. For instance, if the velocity of species A has been selected as reference velocity the transport number of B is given by the equation (which follows from eqs.[3],[13],[20'],[21] and [22]):

$$t_B^A = |\mathbf{j}_B^A| / |\mathbf{j}| = z_B \sum_{i \neq A} z_i L_{Bi}^A / \sum_{i \neq A} \sum_{j \neq A} z_i z_j L_{ij}^A \qquad\qquad [23]$$

where the quantity $\sum_{i \neq A} \sum_{j \neq A} z_i z_j L_{ij}^A$ is equal to κ/F^2 (with κ = conductivity) and is independent of the reference velocity.

When the coupling coefficients L_{Bi}^A ($i \neq B$) are negligible (as is the case for sufficiently dilute solutions) eq.[3], in the absence of concentration gradients, reduces to:

$$\mathbf{N}_B^A = \mathbf{N}_B - c_B \mathbf{v}_A = -z_B F L_B^A \nabla\phi \qquad\qquad [24]$$

or
$$\mathbf{v}_B^A = \mathbf{v}_B - \mathbf{v}_A = -z_B F c_B^{-1} L_B^A \nabla\phi \qquad\qquad [25]$$

and
$$|\mathbf{v}_B^A| = |-u_B^A \nabla\phi| \qquad\qquad [26]$$

where
$$u_B^A = |z_B| F c_B^{-1} L_B^A \qquad\qquad [27]$$

is the electric mobility of species B referred to the reference velocity $\mathbf{v}_A$. Eq.[23] then reduces to

$$t_B^A = |z_B| u_B^A c_B / \sum_{i \neq A} |z_i| u_i^A c_i \qquad\qquad [28]$$

In the case of dilute solutions the velocity of a neutral solvent A is usually taken as reference velocity. Eq.[24] can then be simply rewritten as

$$t_B = |z_B| u_B c_B / \sum_i |z_i| u_i c_i \qquad\qquad [29]$$

This is identical with the definition of t_B given in 7.6 of Appendix III[2]. Note that the mobility u_B as defined in Appendix III[2] is a positive quantity. However, when using u_B in transport relationships such as eq.[26] it may be more convenient to define u_B as an algebraic quantity. In that case, the vertical bars have to be deleted from eqs.[15],[26],[27] [28] and [29].

Note also that the phenomenological coefficient appearing in eqs.[24] and [25] has been written as L_B^A although it is, in fact, the conjugated coefficient L_{BB}^A. However, the second index may be dropped without ambiguity because all coupling coefficients have been regarded as negligible.

A difficulty arises in the application of the above definition of the transport number when one is considering as a species an ensemble of particles which do not have the same charge number. The definition has then to be modified in an appropriate manner. Let us take as example Cd in an iodide solution, which contains the ions Cd^{2+}, CdI_3^-, I^- etc. We can determine analytically only the <u>overall</u> concentration of cadmium or iodine, which we call a constituent C of the system: $c_{Cd} = c_{Cd2+} + c_{CdI_3^-} + \ldots$ and $c_I = c_{I^-} + 3c_{CdI_3^-} + \ldots$
(more generally, $c_C = \sum_i \nu_i c_i$, where ν_i is the number of moles of the considered constituent present in one mole of i). The transport number of constituent C is defined as:

$$t_C = |j_C^0|/j, \qquad \text{with} \qquad j_C^0 = z_C F \sum_i \nu_i N_i$$

where z_C is taken as being the charge number of the uncomplexed ionic constituent. In the above example we have:

if   C = Cd $z_C = +2$ and $j_{Cd}^0 = 2F(N_{Cd^{2+}} + N_{CdI_3^-} + \ldots)$

C = I $z_C = -1$ and $j_I^0 = -F(N_{I^-} + 3N_{CdI_3^-} + \ldots)$

Note that with the above definition the transport number may possibly be negative or larger than one.

3.3   Electrode current density (c.d.)(A m^{-2}) j

We restrict ourselves to the case that the charging current is negligible. In the case of a single electrode reaction the c.d. j of the electric current flowing through the electrode is related to the flux density of a species B by the equation:

$$j = n \nu_B^{-1} F(N_B)_e \qquad\qquad [30]$$

where $(N_B)_e$ is the normal component of the vector N_B at the electrode-solution interface, n is the charge number of the electrode reaction, ν_B the stoichiometric number of species B. The ratio n/ν_B is to be taken as positive if the species B is consumed in a cathodic reaction or produced in an anodic reaction. Otherwise it is to be taken as negative. With the convention that the normal distance vector points into the electrolytic solution, a cathodic current is then negative, an anodic current positive.

Note that the electrode c.d. is a scalar (in contrast to the c.d. of a species in the solution which is a vector).*

In the approximation of the ideal dilute solution the flux density at the interface (where the fluid velocity v relative to the interface is zero) is given by
in case a of 2.3

$$(N_B)_e = -D_B \left(\frac{dc_B}{dy}\right)_{y=0} \qquad\qquad [33]$$

in case b of 2.3

$$(N_B)_e = -D\left(\frac{dc_B}{dy}\right)_{y=0} + j t_B / z_B F \qquad\qquad [34]$$

where y refers to a coordinate axis perpendicular to the interface and pointing into the solution. In eq.[34] B refers to the cation or to the anion of the binary electrolyte.

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*
In general, the current dI flowing through an electrode surface element of area dA is given by the scalar product of the vector dA representing the surface element and of the vector N_B (taken at the interface, at the point considered):

$$dI = n\nu_B^{-1} F(N_B)_e \cdot dA \qquad\qquad [31]$$

and the electrode c.d. at the point considered is

$$j = dI/dA \qquad\qquad [32]$$

3.4 Average and local current density (A m^{-2}) j_x

Eq.[90] (or [92]) yields in principle the c.d. at a given point x of the interface (local value). This may vary along the interface. We have then to distinguish between a local value j_x and an average c.d., the latter being defined by

$$j \;=\; A^{-1} \int_A j_x \, dA \qquad\qquad [35]$$

where A is the electrode area* and dA an infinitesimal surface element.

In cases where it is desirable to distinguish between local and average values it is recommended to use the subscript x to denote the local c.d.

The overall electrode current is

$$I \;=\; jA \qquad\qquad [36]$$

3.5 Current distribution; Wagner number Wa

The ratio j_x/j is called the relative local c.d. The current distribution is described by the function $j_x/j = f(x)$ (or, more generally, $j_x/j = f(x,y,z)$) where x or (x,y,z) are the coordinates of the points of the electrode-solution interface.

The primary current distribution is that which establishes itself when the influence of overpotential is negligible.

The secondary current distribution is that which establishes itself when the influence of overpotential cannot be neglected but concentration overpotential (see 4.5) is negligible. The secondary distribution is often described in terms of dimensionless numbers of the form

$$Wa \;=\; \kappa \, (d\eta/dj)/\ell \qquad\qquad [37]$$

where κ is the conductivity of the solution, $d\eta/dj$ the slope of the overpotential-current curve under the above conditions and ℓ a characteristic length of the system, for instance the radius of a disc electrode. Wa is Wagner number. It is a quantity which determines the throwing power and characterizes the equalizing influence of overpotential on the current distribution. In electroplating the throwing power is qualitatively defined as "the ability of a solution to deposit metal uniformly upon a cathode of irregular shape" (IEC vocabulary: Group 50 section 50 definition 50-30-020).

The tertiary current distribution is that which establishes itself when the influence of overpotential (including concentration overpotential) cannot be neglected.

3.6 Current efficiency (number) ε_k

If several reactions take place simultaneously at the electrode a partial c.d. j_k can be assigned to each reaction. It is given by the stoichiometry of the reaction and by the amount of substance of B reacting (per unit time and per unit electrode area) in the reaction considered. The current efficiency of reaction k, ε_k is defined as the ratio of j_k to the total c.d.:

$$\varepsilon_k \;=\; j_k \,/\, \sum_m j_m \qquad\qquad [38]$$

Note that ε_k may be larger than one if cathodic and anodic reactions take place simultaneously at the same electrode. However, ε_k still gives correctly the product yield, which is the quantity of industrial interest. The product yield is the amount of substance of B produced per unit charge and is equal to $\varepsilon_k \, \nu_{B,k} \,/\, n_k F$ (in the absence of a chemical reaction which is consecutive to the electrode reaction and which consumes or produces species B). n_k is the charge number of electrode reaction k.

Note that in the case of simultaneous electrode reactions the distribution of the partial

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*
 Note it may be necessary to specify the kind of electrode area used in eq.[35] and [36] (projected electrode area or area taking into account roughness, see 5.7 of Appendix III^2).

c.d. j_k may be different from that of the total c.d., i.e. the function $(j_k)_x / j = f_k (x)$
may be different from $j_x / j = f(x)$ (see 3.5). In electroplating the term "metal distribu-
tion" is sometimes used to designate the distribution $f_k(x)$ of the partial c.d. for metal
deposition.

4. CONCEPTS AND QUANTITIES RELATED TO CHARGE AND MASS TRANSPORT

4.1 Interfacial concentration (mol m^{-3}) c_e

The interfacial concentration $c_{B,e}$ (or simply c_e) of a species B is the concentration of
that species at the boundary of the electric   double layer facing the solution, i.e. just
outside of the region where the departures from the electroneutrality of the solution are
significant.* This concept is mainly used in the usual case where the thickness of the elec-
tric   double layer is very small as compared to that of the diffusion layer (see 4.2). It
is often calculated from theory or derived from measurements of the limiting current, for
instance by means of equations [41] or [42] , k_d being related to the limiting current (see
8.5 of Appendix III).

4.2 Thickness of diffusion layer (m) δ

The diffusion layer (also called concentration boundary layer) is the region in the vicinity
of an electrode where the concentrations are different from their value in the bulk solu-
tion. The definition of the thickness of the diffusion layer is arbitrary because the con-
centration approaches asymptotically the value c_o in the bulk solution (see diagram).

a) This thickness can be defined as the distance from the electrode where the ratio
$(c - c_e)/(c_o - c_e)$ reaches a given value. If this ratio is selected as, say, 0.99 the
corresponding thickness of the diffusion layer is denoted by $\delta_{0.99}$.

b) Nernst's diffusion layer is a fictitious layer corresponding to the dotted straight
lines of the diagram which shows the concentration profile along the direction perpendicu-
lar to the electrode surface. The thickness δ of this layer is called the effective (or
equivalent) thickness of the diffusion layer. Its definition is apparent from the figure.
It is the thickness which the diffusion layer would have if the concentration profile were
a straight line coinciding with the tangent to the true concentration profile at the inter-
face, and that straight line were extended up to the point where the bulk concentration is
reached. δ has a formal significance only (cf. 8.6 of Appendix III[2]). It is simply another
way of writing the mass transfer coefficient k_d defined in 4.6 (in terms of a "resistivity"
instead of a "conductivity").

distance from the electrode y

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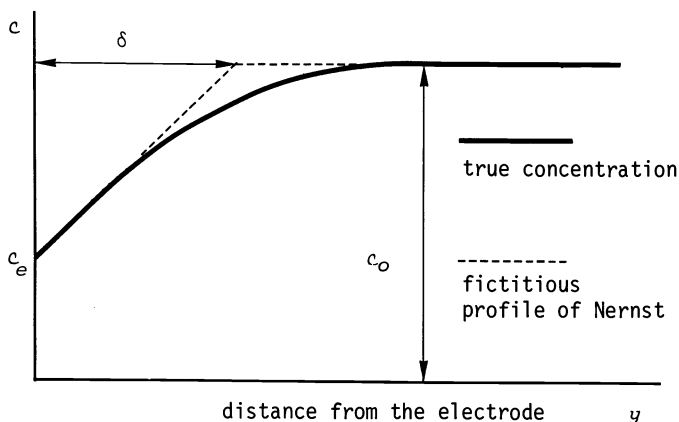
*
 A similar remark applies to the significance of the flux density at the interface, $(N_B)_e$.
In principle there are fluxes in the electric double layer. However, most equations used in
electrolytic mass transport calculations imply the electroneutrality of the solution. The
subscript e in $(N_B)_e$ then means "at the outer edge of the diffuse double layer."

If there are ℓ species in the solution there are, in principle, ℓ diffusion layer thicknesses. However, in the case of ionic species, because of the electroneutrality condition, there are only $\ell-1$ independent diffusion layers. If a distinction between the various species is made it is recommended to denote the thickness of the diffusion layer of species B by the subscript B.

If the term $\sum_r v_{Br}$ of eq.[17] is not negligible, i.e. if the considered species is taking part in a homogeneous chemical reaction going on in the diffusion layer the latter can be called the reaction layer. Note that the reaction may take place in a part of the diffusion layer only. One may then, in principle, distinguish for the same system between a reaction layer and a diffusion layer.

The thickness of the reaction layer can be characterized by a length δ_r which must be properly defined in the context of its use.

4.3 Transport control

The term "transport control" refers to conditions where, in a controlled-potential experiment the electrode current, and in a controlled-current experiment the electrode potential, is solely determined by the rate of mass transport to (or away from) the electrode. For instance, the current measured in a controlled-potential experiment is then called a transport controlled current.

Under conditions of transport control there is no influence of the kinetics of a reaction taking place at the electrode or in the volume of the solution. Except in the case of the limiting current, this implies that the electrode reaction and homogeneous reactions, if present, are virtually at equilibrium (in spite of the current flow).

If the influence of the migration term in eq.[14] is negligible the term transport control may (but need not) be replaced by the term diffusion control.

If the measured quantity is determined <u>both</u> by the mass transport rate and by the kinetics of a reaction the term mixed control is to be used instead of the term transport (or diffusion) control.

4.4 Diffusion potential (V) $\Delta\phi_d$

For an ideal dilute solution follows from eq.[14], [20] and [21]:

$$\mathbf{j} = -F\sum_i \mathcal{D}_i\, z_i \nabla c_i - F^2 (RT)^{-1} \sum_i z_i^2 \mathcal{D}_i\, c_i \nabla \phi \qquad [39]$$

for $\mathbf{j} = 0$

$$\nabla\phi = \frac{RT\sum_i \mathcal{D}_i\, z_i \nabla c_i}{F\sum_i z_i^2 \mathcal{D}_i\, c_i} \qquad [40]$$

The integral of $\nabla\phi$ across the boundary between two regions of different concentrations is called the diffusion potential, $\Delta\phi_d$.

4.5 Concentration overpotential (V) η_c

The concentration overpotential of an electrode reaction at c.d. j is basically the difference in equilibrium potentials across the diffusion layer. More precisely, it is the potential of a reference electrode (of the same electrode reaction as the working electrode) with the interfacial concentrations which establish themselves at c.d. j, relative to the potential of a similar reference electrode with the concentraions of the bulk solution. From such a measured potential difference, with c.d. flowing, one needs to subtract the ohmic potential drop prevailing between the two electrodes.

Because of the difficulties of measurement one frequently calculates the concentration overpotential as the open circuit potential of a concentration cell where the electrodes are both equilibrated with respect to the given electrode reaction. One compartment of the concentration cell has the bulk solution concentrations, and the other compartment has the concentrations which would have established themselves at the interface of the working electrode. The junction used in the calculation should approximate the concentration profiles existing in the diffusion layer.

When no homogeneous reaction takes place in the diffusion layer the concentration overpotential may be called transport overpotential.

4.6 Mass transfer coefficient* (m s^{-1}) k_d

It is recommended to call mass transfer coefficient the heterogeneous diffusion rate constant k_d defined in 8.5 of Appendix III[2] for the case of the limiting current. A more general definition in terms of the electrode c.d's is:

$$k_d = jv/nF(c_e - c_o) \quad \text{case a of section 2.3} \qquad [41]$$

$$k_d = jv(1 - t_B nv^{-1} z_B^{-1})/nF(c_e - c_o) \quad \text{case b of section 2.3} \quad [42]$$

Depending upon whether local or average values of j are used in eq.[41] or [42] local or average mass transfer coefficients are obtained.

Note that eqs.[41] and [42] can also be written as:

$$k_d = \mathcal{D}_B/\delta \qquad [43]$$

In general, $\mathcal{D}_B$ as well as δ, and therefore also k_d, depend on the species considered. In cases where it is important to distinguish between the mass transfer coefficients of various species it is recommended to give a second index to the symbol k_d (for instance, $(k_d)_B$) to denote the mass transfer coefficient of species B.

4.7 Sherwood number Sh

The mass transport problem in electrolysis is usually approximated by one of the two limiting cases mentioned in 2.3. It is then essentially the same as in physical chemistry or chemical engineering at large and the same dimensionless groups can be used. The Sherwood number Sh (also called Nusselt number for mass transfer[1,6]) is defined as

$$Sh = k_d \ell/\mathcal{D} \qquad \text{(case a of section 2.3)} \qquad [44]$$

$$\text{or} \quad Sh = k_d \ell/\mathcal{D} \qquad \text{(case b of section 2.3)} \qquad [45]$$

where ℓ is a characteristic length, for instance the radius of a disc electrode.

Depending upon whether local or average values of k_d are used in eqs.[44] or [45] local or average Sherwood numbers are obtained. It is recommended to denote by subscript x local values of the Sherwood number or of the mass transfer coefficient.

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*   In the present text a distinction is made between mass transport and mass transfer. Mass transport is used to describe the movement of a species in a homogeneous phase, whereas mass transfer is used for the removal, at the interface, of a species from a homogeneous phase. Of course, the rate of the latter is equal to that of the mass transport in the homogeneous phase immediately adjacent to the interface.

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