

**INTERNATIONAL UNION OF  
PURE AND APPLIED CHEMISTRY**  
DIVISION OF PHYSICAL CHEMISTRY

**MANUAL OF SYMBOLS AND  
TERMINOLOGY FOR  
PHYSICOCHEMICAL QUANTITIES  
AND UNITS**

**APPENDIX III**

**Electrochemical Nomenclature**

Recommendations approved 1973

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## CONTENTS

|   |     |
|---|-----|
| Introduction  | 503 |
| 1. General  | 504 |
| 2. Galvanic cells   | 504 |
| 3. Thermodynamics of a charged, simple phase                    | 506 |
| 4. Equilibrium between two charged, simple phases               | 507 |
| 5. Phenomena at electrode/electrolyte interfaces at equilibrium | 508 |
| 6. Activities in electrolytic solutions and related quantities  | 510 |
| 7. Transport properties of electrolytes                         | 511 |
| 8. Kinetics of reactions at electrodes                          | 512 |

## INTRODUCTION

The present document constitutes an Appendix to the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* [Butterworths: 1970 and *Pure Appl. Chem.*, 21, No. 1 (1970)] prepared by the Commission on Symbols, Terminology and Units in 1969. It consists of recommendations for usage of symbols and terminology in electrochemistry. These recommendations are by no means complete and it is hoped that they will be supplemented in the future. The Commission on Electrochemistry† has discussed these recommendations extensively and in its deliberations has been greatly helped by comments received from many other interested scientists. These comments revealed considerable differences of opinion and the recommendations presented here cannot reflect all preferences. However, the Commission hopes that these recommendations will be widely accepted and hence will serve to avoid some of the confusion which may exist as a result of different usages in electrochemistry.

### Units

In each recommendation the appropriate SI unit has been given. Multiples or submultiples of these units are equally acceptable and may frequently be preferred. For example, the SI unit of concentration is  $\text{mol m}^{-3}$  but concentrations are frequently expressed in  $\text{mol dm}^{-3}$  or  $\text{mol cm}^{-3}$  and different such submultiples may be convenient in different parts of electrochemistry.

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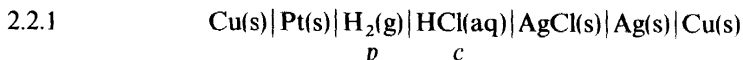
## 1. GENERAL

- 1.1 Faraday constant (SI unit  $C \text{ mol}^{-1}$ )  $F$   
is the product of the Avogadro constant and the charge of the proton (elementary charge).
- 1.2 Charge number of an ion B (number)  $z_B$   
positive for cations, negative for anions:  $z_B$  is the ratio of the charge carried by ion B to the charge carried by the proton.

## 2. GALVANIC CELLS

- 2.1 Charge number of the cell reaction (number)  $n(z)$   
is the stoichiometric number equal to the number of electrons transferred in the cell reaction as formulated.  $n$  is a positive number.
- 2.2 Electric potential difference of a galvanic cell  $E$   
(SI unit V) including the condition when current flows through the cell.  $E$  is the difference of electric potential between a metallic terminal attached to the right-hand electrode in the cell diagram and an identical metallic terminal attached to the left-hand electrode.

The galvanic cell is represented by a diagram. Thus, the chemical cell, consisting of an aqueous solution of hydrogen chloride (concentration  $c$ ), a platinum-hydrogen electrode (partial pressure of hydrogen:  $p$ ), and a silver-silver chloride electrode, both with copper terminals is represented by the diagram



A single vertical bar (|) should be used to represent a phase boundary, a dashed vertical bar (⋮) to represent a junction between miscible liquids, and double, dashed vertical bars (⋮⋮) to represent a liquid junction, in which the liquid junction potential has been assumed to be eliminated.

The value of  $E$  measured when the left-hand electrode is at virtual equilibrium, and hence acting as a reference electrode, may be called 'the potential of the (right-hand) electrode with respect to the (left-hand) reference electrode. This terminology should not be taken as implying that single electrode potentials are measurable.

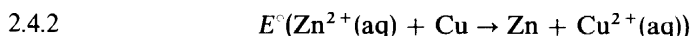
- 2.3 emf (electromotive force) of a galvanic cell (SI unit V)  $E_{MF}$   
is the limiting value of  $E$  when the current through the external circuit of the cell becomes zero, all local charge transfer equilibria across phase boundaries which are represented in the cell diagram (except at possible electrolyte-electrolyte junctions) and local chemical equilibria within phases being established.
- 2.4 Standard potential of the reaction in a chemical cell  $E^\circ$   
(SI unit V)  
is defined by

$$2.4.1 \quad E^\circ = -\Delta G^\circ / nF = (RT/nF) \ln K$$

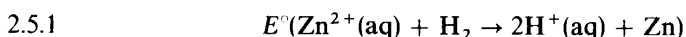
where  $\Delta G^\circ$  is the standard molar Gibbs energy change and  $K$  is the

equilibrium constant of the reaction.  $R$  is the gas constant and  $T$  the thermodynamic temperature.

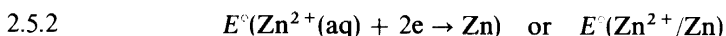
The reaction to which  $E^\circ$  refers should be clearly indicated, for example



2.5 Standard potential of an electrode reaction  $E^\circ$   
 (SI unit V) abbreviated as standard electrode potential is the value of the standard potential of a cell reaction when that reaction involves the oxidation of molecular hydrogen to solvated protons, for example

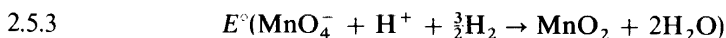


This may be abbreviated

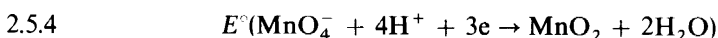


but the order of these symbols should not be reversed.

Similarly



may be abbreviated



or



This quantity is distinguished from that defined in 2.4 only by the nature of the reaction indicated.

In some non-aqueous solvents it is necessary to use a standard reaction (which should be specified) other than the oxidation of molecular hydrogen. No general choice of standard reaction is possible and it is not appropriate to make a recommendation for all non-aqueous solvents at this time.

2.6 Potential of a cell reaction (SI unit V)  $E_{\text{cell}}$   
 is given by

$$2.6.1 \quad E_{\text{cell}} = E^\circ - (RT/nF) \sum_i v_i \ln a_i$$

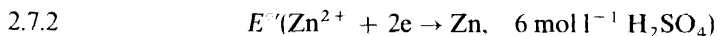
where  $a_i$  are the activities of the species taking part in the cell reaction and  $v_i$  are the stoichiometric numbers of these species in the equation written for the cell reaction.  $v_i$  is taken as positive for species appearing on the right-hand side of the equation and negative for those on the left-hand side. The composition variable on which the definition of the activity is based should always be stated.

2.7 Conditional (formal) potential (SI unit V)  $E_c^\circ$   
 is related to  $E_{\text{cell}}$  by an equation analogous to 2.6.1 with the activity replaced by any composition variable (to be indicated by a subscript). For example

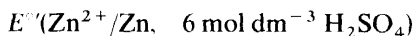
$$2.7.1 \quad E_{\text{cell}} = E_c^\circ - (RT/nF) \sum_i v_i \ln c_i$$

Often the concentration of a reactant is fixed by the composition of the medium and is consequently omitted from the sum.

The electrode reaction considered *and* the medium should be clearly specified, for example



or



### 3. THERMODYNAMICS OF A CHARGED, SIMPLE PHASE

3.1 Electrochemical potential of species B in phase  $\beta$   $\tilde{\mu}_B^\beta$   
(SI unit J mol<sup>-1</sup>) is given by

$$3.1.1 \quad \tilde{\mu}_B^\beta = (\partial U / \partial n_B^\beta)_{S, V, n_c, \dots}$$

where  $U$  is the total internal energy (including the energy of the external field) of the specified system,  $n_B^\beta$  is the amount of B in phase  $\beta$ ,  $S$  is the total entropy and  $V$  the volume of the specified system.  $n_c, \dots$  indicates the amounts of all other components in the system.

The system consists of phase  $\beta$  together with other phases which may or may not be in equilibrium with each other. It includes all the relevant charges.

3.2 Outer electric potential of phase  $\beta$  (SI unit V)  $\psi^\beta$   
is the electrostatic potential of phase  $\beta$  due to the total electric charge of the phase. It may be calculated from classical electrostatics knowing the charge distribution on the phase under consideration.

3.3 Inner electric potential of phase  $\beta$  (SI unit V)  $\phi^\beta$   
is the electrostatic potential within phase  $\beta$  related to the electric field strength  $E$  in the interior of the phase by  $-\nabla\phi = E$ . The inner potential can be calculated from a model of the phase.

3.4 Surface electric potential (SI unit V)  $\chi^\beta$   
is given by

$$3.4.1 \quad \chi^\beta = \phi^\beta - \psi^\beta$$

$\chi^\beta$  may be regarded as the part of  $\phi^\beta$  due to a dipolar distribution of charge at the surface of  $\beta$ .

3.5 Chemical potential of species B in phase  $\beta$   $\mu_B^\beta$   
(SI unit J mol<sup>-1</sup>) is defined by

$$3.5.1 \quad \mu_B^\beta = \tilde{\mu}_B^\beta - z_B F \psi^\beta$$

For an uncharged species ( $z_B = 0$ ) the electrochemical potential is equal to the chemical potential.

3.6 Real potential of species B in phase  $\beta$   $\gamma_B^\beta$   
(SI unit J mol<sup>-1</sup>) is defined as

$$3.6.1 \quad \gamma_B^\beta = \tilde{\mu}_B^\beta - z_B F \psi^\beta$$

Since  $\psi^\beta$  is zero when the charge on the phase  $\beta$  is zero, the real

potential may be regarded as the value of the electrochemical potential of the uncharged phase.

The best known example of the real potential is the electronic work function which is equal to  $-z_e^M$ , where e stands for the electron and M is a metal.

#### 4. EQUILIBRIUM BETWEEN TWO CHARGED, SIMPLE PHASES

4.1 The general condition of equilibrium of a species B between phases  $\alpha$  and  $\beta$  is

$$4.1.1 \quad \tilde{\mu}_B^\alpha = \tilde{\mu}_B^\beta$$

4.2 Volta potential difference (SI unit V)  $\Delta_x^\beta \psi$

$$4.2.1 \quad \Delta_x^\beta \psi = \psi^\beta - \psi^\alpha$$

This is an electric potential difference due to the electric charge on  $\alpha$  and on  $\beta$ . It is measurable or calculable by classical electrostatics from the charge distribution.

The value of the Volta potential difference between two phases  $\alpha$  and  $\beta$  between which there is equilibrium of species B is given by

$$4.2.2 \quad \Delta_x^\beta \psi = (z_B^\alpha - z_B^\beta)/z_B F$$

This particular value of the Volta potential difference is usually called the contact potential and this expression is a generalization of the well-known relation between contact potentials of metals and the difference of their electronic work functions. Note that the experimental measurement of contact potentials is not usually done under these conditions but with zero charge on  $\alpha$  and  $\beta$ . If  $\chi^\alpha$  and  $\chi^\beta$  are independent of charge between these two conditions the same quantity is obtained.

4.3 Galvani potential difference (SI unit V)  $\Delta_x^\beta \phi$

$$4.3.1 \quad \Delta_x^\beta \phi = \phi^\beta - \phi^\alpha$$

This is an electric potential difference between points in the bulk of the two phases. It is measurable only when the two phases have identical composition, for example in the measurement of the potential difference between two copper wires using a potentiometer.

It may be convenient to regard the Galvani potential difference between two phases in contact as due to two effects: the orientation of dipoles in the interface between them  $g_\alpha^\beta$  (dipole) and the separation of independently mobile charged species across this phase boundary  $g_\alpha^\beta$  (ion). This is somewhat analogous to the separation of  $\phi$  into  $\psi$  and  $\chi$ . The analogy breaks down because at a free surface, it appears that under accessible experimental conditions there is little or no dependence of  $\chi$  on  $\psi$ . On the other hand, many examples of interfaces are known where the dipole contribution to  $\Delta\phi$  is highly dependent on the ionic contribution. Hence it is desirable to emphasize this distinction by using different symbols:

$$4.3.2 \quad \Delta_x^\beta \phi = g_\alpha^\beta(\text{ion}) + g_\alpha^\beta(\text{dipole})$$

4.4 Medium effect on ionic species  $B$  due to transfer from solvent  $S_1$  to solvent  $S_2$  (number) is defined by  $\gamma_{S_1}^{S_2}(B)$

$$4.4.1 \quad RT \ln \gamma_{S_1}^{S_2}(B) = \mu_B^{0,S_2} - \mu_B^{0,S_1}$$

where  $R$  is the gas constant,  $T$  is the thermodynamic temperature and  $\mu_B^{0,S_i}$  is the standard chemical potential of  $B$  in solvent  $S_i$  (where  $i = 1$  or  $2$ ), the reference states being the same in both solvents  $\gamma_{S_1}^{S_2}(B)$  is not an exactly measurable quantity.

## 5. PHENOMENA AT ELECTRODE/ELECTROLYTE INTERFACES AT EQUILIBRIUM

5.1 Electric charge divided by area of an interface (electrode)  $Q$   
(SI unit  $C m^{-2}$ )

is given by Lippmann's equation

$$5.1.1 \quad (\partial \gamma / \partial E)_{T,p,\mu_i,\dots} = -Q$$

where  $\gamma$  is the interfacial tension,  $E$  is the potential of the electrode with respect to any convenient reference electrode and  $\mu_{i,\dots}$  indicates a set of chemical potentials which is held constant. The choice of these chemical potentials must be specified.  $T$  is the thermodynamic temperature and  $p$  the external pressure.

If the cell in which  $E$  is measured is represented by a conventional diagram (cf. 2.2) with the interface under study forming part of the right-hand electrode, then  $Q$  as given by 5.1.1 is the charge on the right-hand side of the interface in the diagram (for a metallic electrode this would be the charge on the metal).

$Q$  may also be regarded as the quantity of electricity which must be supplied to the interface at thermodynamic equilibrium when its area is increased by unit amount while  $T, p, E$  and the set of chemical potentials  $\mu_{i,\dots}$  are maintained constant.

At an interface where no charged species can cross the boundary between the two phases (ideal polarized electrode)  $Q$  has a unique value. On the other hand, when charge can cross the interface (non-polarizable electrode)  $Q$  no longer has a unique value, but depends upon the choice of components whose chemical potentials are held constant in the above definition ( $\mu_{i,\dots}$ ).

The experimental measurement and the theoretical definition of the interfacial tension of a solid electrode is still controversial although the charge  $Q$  is measurable.

5.2 Free charge density on the interface (SI unit  $C m^{-2}$ )  $\sigma$

is the physical charge density believed to occur on either side of the electrical double layer. It depends upon the model assumed for the interface. In an ideal polarized electrode  $Q = \sigma$  if all the components of the interface retain the charges that they have in the adjoining bulk phases. However, if partial charge transfer takes place,  $\sigma$  will differ from  $Q$  whether the interface is ideally polarized or not.

In the discussion of models of the double layer, superscripts to  $\sigma$  may be used to denote the location of the charge, e.g.  $\sigma^M$  the charge



MANUAL OF SYMBOLS AND TERMINOLOGY

on the metal,  $\sigma^d$  the charge on the diffuse layer: subscripts may be used to denote the species contributing the charge, e.g.  $\sigma_+^s$  the charge on the solution side of the double layer due to cations.

- 5.3 Potential at the point of zero charge (pzc) (SI unit V)  $E_{Q=0}, E_{\sigma=0}$   
 is the value of the electric potential of the electrode at which one of the charges defined above is zero. The reference electrode against which this is measured should always be clearly stated. It is also important to define the type of charge (see  $Q$  and  $\sigma$  in 5.1 and 5.2) which vanishes at the pzc. Except for the simple ideal polarized electrode, each electrode may have more than one pzc. The concentration of the solution should also be specified as well as the nature of the electrode.

- 5.4 Potential difference with respect to the potential of zero charge (SI unit V)  $E_{pzc}$

5.4.1 
$$E_{pzc} = E - E_{\sigma=0}$$

where the pzc is that for the given electrode in the absence of specific adsorption (other than that of the solvent). Specific adsorption is adsorption which cannot be accounted for by diffuse layer theory.

- 5.5 Differential capacitance divided by the area of the electrode (SI unit  $F m^{-2}$ )  $C$   
 is given by

5.5.1 
$$C = (\partial Q / \partial E)_{T, \mu_i, \dots}$$

Various types of differential capacitance corresponding to the charges defined in 5.1 and 5.2 may be defined. Capacities of parts of the double layer may be denoted by superscripts, while components of the capacity contributed by particular species may be indicated by subscripts. As defined here the capacity is an equilibrium property. The differential capacity may also be defined under non-equilibrium conditions. Measured capacities may be dependent on the frequency used. This may be indicated in brackets, e.g.  $C(f = 100 \text{ Hz})$  or  $C(\omega = 2\pi \times 100 \text{ s}^{-1})$ .

- 5.6 Integral capacitance divided by the area of the electrode (SI unit  $F m^{-2}$ )  $K$

5.6.1 
$$K = Q / (E - E_{Q=0})$$

Integral capacities are related to differential capacities by

5.6.2 
$$K = (E - E_{Q=0})^{-1} \int_{E_{Q=0}}^E C \, dE$$

Integral capacities may also be determined between two potentials neither of which is the potential of zero charge.

- 5.7 Area of the interface (SI unit  $m^2$ )  $A$   
 In all measurements it is desirable that quantities like the charge and the capacity be related to unit, true, surface area of the interface. While this is relatively simple for a liquid-liquid interface, there are great difficulties when one phase is solid. In any report of these quantities it is essential to give a clear statement as to whether they refer to the true or the apparent (geometric) area and, especially if the former is used, precisely how it was measured.

## 6. ACTIVITIES IN ELECTROLYTIC SOLUTIONS AND RELATED QUANTITIES

6.1 Mean activity of electrolyte B in solution (number) is given by  $a_{\pm}$

$$6.1.1 \quad a_{\pm} = \exp[(\mu_B - \mu_B^{\circ})/vRT]$$

where  $\mu_B$  is the chemical potential of the solute B in a solution containing B and other species. The nature of B must be clearly stated: it is taken as a group of ions of two kinds carrying an equal number of positive and negative charges, e.g.  $\text{Na}^+ + \text{NO}_3^-$  or  $\text{Ba}^{2+} + 2\text{Cl}^-$  or  $2\text{Al}^{3+} + 3\text{SO}_4^{2-}$ .  $v$  is the total number of ions making up the group, i.e. 2, 3 and 5 respectively in the above examples.  $\mu_B^{\circ}$  is the chemical potential of B in its standard state, usually the hypothetical ideal solution of concentration  $1 \text{ mol kg}^{-1}$  and at the same temperature and pressure as the solution under consideration. The mole must be defined in a way consistent with the group of ions considered above, that is in the third example a mole of aluminium sulphate would consist of  $2 \text{ mol Al}^{3+} + 3 \text{ mol SO}_4^{2-}$ .

6.2 Stoichiometric mean molal activity coefficient (practical activity coefficient) of electrolyte B (number) is given by  $\gamma_{\pm}$

$$6.2.1 \quad \gamma_{\pm} = a_{\pm}/(v_+^{v_+} v_-^{v_-})^{1/2} (m_B/m^{\pm})$$

where  $m_B$  is the molality of B,  $m^{\pm} = 1 \text{ mol kg}^{-1}$ ,  $v_+$  is the number of cations and  $v_-$  the number of anions in the chosen group B which is taken as the electrolyte.

$$6.2.2 \quad v = v_+ + v_-$$

The term stoichiometric in the above definitions is used because these definitions are based on the total molality of the solution.

Other types of activity and activity coefficient may be defined in terms of other concentration variables.

6.3 Osmotic coefficient of solvent substance in an electrolytic solution (number)  $\phi$  is given by

$$6.3.1 \quad \phi = (\mu_A^* - \mu_A)/RTM_A \sum_i m_i$$

where  $\mu_A$  is the chemical potential of solvent A in the solution containing molality  $m_i$  of ionic species  $i$ ,  $\mu_A^*$  is the chemical potential of pure A at the same temperature and pressure and  $M_A$  is the molar mass of A.

Other types of osmotic coefficient may be defined in terms of other concentration variables.

6.4 Partial molar enthalpy of substance B (SI unit  $\text{J mol}^{-1}$ )  $H_B$  is given by

$$6.4.1 \quad H_B = -T^2 \{ \partial(\mu_B/T) / \partial T \}_{p, m_i}$$

$$6.4.2 \quad H_B = H_B^{\circ} - vRT^2 (\partial \ln \gamma_{\pm} / \partial T)_{p, m_i}$$

where  $H_B$  is the partial molar enthalpy of B when the activity of B is unity.

Note that at infinite dilution  $\gamma_{\pm} = 1$  at all temperatures so that the partial molar enthalpy of B in an infinitely dilute solution is

$$6.4.3 \quad H_{\text{B}}^{\infty} = H_{\text{B}}^{\circ}$$

6.5 Relative partial molar enthalpy of substance B (SI unit  $\text{J mol}^{-1}$ ) is given by  $L_{\text{B}}$

$$6.5.1 \quad L_{\text{B}} = H_{\text{B}} - H_{\text{B}}^{\circ}$$

or

$$6.5.2 \quad L_{\text{B}} = -vRT^2(\partial \ln \gamma_{\pm} / \partial T)_{p,m_i}$$

Analogous definitions of relative partial molar enthalpies may be made using mole fraction as the concentration variable, but not with concentration because the composition of a solution of fixed concentration varies with the temperature.

6.6 Partial molar heat capacity at constant pressure (SI unit  $\text{J K}^{-1} \text{mol}^{-1}$ ) is given by  $C_{p,\text{B}}$

$$6.6.1 \quad C_{p,\text{B}} = (\partial H_{\text{B}} / \partial T)_{p,m_i}$$

or

$$6.6.2 \quad C_{p,\text{B}} = C_{p,\text{B}}^{\circ} - vR \left( T^2 \frac{\partial^2 \ln \gamma_{\pm}}{\partial T^2} + 2T \frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{p,m_i}$$

where  $C_{p,\text{B}}^{\circ}$  is the partial molar heat capacity at constant pressure when the activity of B is unity. Note that the partial molar heat capacity of B at infinite dilution is

$$6.6.3 \quad C_{p,\text{B}}^{\infty} = C_{p,\text{B}}^{\circ}$$

6.7 Relative molar heat capacity at constant pressure of substance B (SI unit  $\text{J K}^{-1} \text{mol}^{-1}$ ) is given by  $J_{\text{B}}$

$$6.7.1 \quad J_{\text{B}} = C_{p,\text{B}} - C_{p,\text{B}}^{\circ}$$

or

$$6.7.2 \quad J_{\text{B}} = -vR \left( T^2 \frac{\partial^2 \ln \gamma_{\pm}}{\partial T^2} + 2T \frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{p,m_i}$$

## 7. TRANSPORT PROPERTIES OF ELECTROLYTES

7.1 Electric mobility of species B (SI unit  $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ )  $u_{\text{B}}$   
is the magnitude of the velocity of migration of B divided by the magnitude of the electric field strength. The frame of reference to which the velocity is referred must be specified.

7.2 Conductivity (formerly called specific conductance)  $\kappa(\sigma)$   
(SI unit  $\text{S m}^{-1}$   $\{\Omega^{-1} \text{m}^{-1}\}$ ) is the reciprocal of the resistivity.

7.3 Cell constant of a conductivity cell (SI unit  $\text{m}^{-1}$ )  $K_{\text{cell}}$

$$7.3.1 \quad K_{\text{cell}} = \kappa R$$

## ELECTROCHEMICAL NOMENCLATURE

where  $R$  is the measured resistance of the cell

7.4 Molar conductivity of an electrolyte (SI unit  $\text{S m}^2 \text{mol}^{-1}$ )  $\Lambda$   
 { $\Omega^{-1} \text{m}^2 \text{mol}^{-1}$ }}

7.4.1  $\Lambda = \kappa/c$

where  $c$  is the concentration. The formula unit whose concentration is  $c$  must be specified and should be given in brackets, for example



The symbol  $\Lambda$  has also been used for the quantity  $\kappa/v_+z_+c$  where  $v_+$  is the number of cations of charge number  $z_+$  produced in the dissociation of a salt 'molecule' of a given type (cf. 6.1 and 6.2). This quantity has been called the equivalent conductivity. Whatever it is called, its SI unit is the same as that for the molar conductivity. It is recommended that the use of the equivalent conductivity be discontinued.

7.5 Ionic conductivity of ionic species B (SI unit  $\text{S m}^2 \text{mol}^{-1}$ )  $\lambda_B$   
 { $\Omega^{-1} \text{m}^2 \text{mol}^{-1}$ }}

7.5.1  $\lambda_B = |z_B| F u_B$

$z_B$  here is the charge number of the ionic species B. In most current practice it is taken as unity, i.e. ionic conductivity is taken as that of species such as  $\text{Na}^+$ ,  $\frac{1}{2}\text{Ca}^{2+}$ ,  $\frac{1}{3}\text{La}^{3+}$  etc. To avoid ambiguity the species considered should be clearly stated, e.g. as  $\lambda(\frac{1}{2}\text{Ca}^{2+})$ .

7.6 Transport number of the ionic species B (number) in an electrolytic solution  $t_B$

7.6.1  $t_B = |z_B| u_B c_B / \sum_i |z_i| u_i c_i$

where  $c_i$  is the actual concentration of ionic species  $i$  in the solution.

## 8. KINETICS OF REACTIONS AT ELECTRODES

8.1 Electric current (SI unit A)  $I_a$   
 A current (of positive electricity) passing from the electrode into the electrolyte is taken as positive.

An electrode at which a net positive current flows is called an *anode*. The chemical reaction which predominates at an anode is an *oxidation*.

An electrode at which a net negative current flows is called a *cathode*. The chemical reaction which predominates at a cathode is a *reduction*.

This convention is recommended so that, for example, the effective resistance of an electrode interface is positive under normal conditions. The opposite convention is widely used particularly in the electro-analytical literature.

8.2 Partial anodic (cathodic) current of a reaction  $I_a(I_c)$   
 (SI unit A). When a single electrochemical reaction occurs at an electrode (i.e. all other electrochemical reactions may be neglected)

8.2.1  $I = I_a + I_c$

$I_a$  being positive and  $I_c$  negative. When more than one reaction is significant the reactions may be numbered and the numbers used as subscripts:  $I_{1,a}$ ,  $I_{1,c}$ ,  $I_{2,a}$ , etc. Then

$$8.2.2 \quad I = \sum_i I_{i,a} + \sum_i I_{i,c}$$

8.3 Exchange current of an electrode reaction (SI unit A)  $I_0$   
is the common value of the anodic and cathodic partial currents when that reaction is at equilibrium

$$8.3.1 \quad I_0 = I_a = -I_c$$

For an electrode at equilibrium at which only one reaction is significant  $I = 0$ . When more than one reaction is significant at a given electrode, subscripts to  $I_0$  may be used to distinguish exchange currents.  $I$  is not usually zero when only one of these reactions is at equilibrium.

8.3 Limiting current (SI unit A)  $I_l$

Under usual conditions the steady-state current/potential characteristic has a positive slope. In some circumstances this slope decreases until it becomes approximately zero. This 'plateau' on the characteristic is the limiting current. It arises because the concentration of a reacting species at the electrode approaches zero as a result of the rate of diffusion, convection, chemical reaction in solution or at the interface or of combinations of these effects. A plateau following a region of negative slope in the current/potential characteristic cannot in general be defined as a limiting current.

8.5 Heterogeneous diffusion rate constant (SI unit  $\text{m s}^{-1}$ )  $k_d$

$$8.5.1 \quad k_d = I_l/nFcA$$

where the limiting current  $I_l$  is assumed to be due to the diffusion of a species of concentration  $c$  and of diffusion coefficient  $D$ .  $n$  is the charge number of the cell reaction written so that the stoichiometric coefficient of this species is unity.  $A$  is usually taken as the geometric area of the electrode.

8.6 Diffusion layer thickness (SI unit m)  $\delta$

$$8.6.1 \quad \delta = D/k_d = nFDcA/I_l$$

where the symbols are subject to the same conditions as described in 8.5.  $\delta$  has a purely formal significance.

8.7 Mean current density (SI unit  $\text{A m}^{-2}$ )  $j$

$$8.7.1 \quad j = I/A$$

Other current densities may be similarly defined in terms of the currents defined in 8.2 to 8.4. The nature of the area used in this calculation must be clearly stated (see 5.7). In interpreting the mean current density it is important to know whether the current is uniformly distributed over the electrode interface.

8.8 Mixed potential (SI unit V)  $E_{\text{mix}}$   
is the value of the potential of a given electrode with respect to a suitable reference electrode when appreciable contributions to the

total anodic and/or cathodic partial currents are made by species belonging to two or more different couples, but the total current is zero, i.e.

$$8.8.1 \quad I = \sum_i I_i = 0 \quad (I_i \neq 0)$$

where  $I_i$  is the partial current of reaction  $i$

$$8.8.2 \quad I_i = I_{i,a} + I_{i,c}$$

and the summation in 8.8.1 contains appreciable contributions from at least two reactions.

8.9 Overpotential (SI unit V)  $\eta$   
 is the deviation of the potential of an electrode from its equilibrium value required to cause a given current to flow through the electrode.

Consider a cell with a current  $I$  flowing in the external circuit from the cathode C to the anode A. The measured potential difference  $E(A/C)$  of A with respect to C can be considered to comprise three components: one associated with processes at the anode, one associated with processes at the cathode and one associated with the conduction of current through the bulk electrolyte, connections to the electrodes, etc. This third component is related to the bulk resistivity: hence, it may be expressed as  $IR_{\text{cell}}$ , where  $R_{\text{cell}}$  is the total resistance of the cell excluding resistances due to slow processes at the electrodes.

Measurements are frequently made with a third electrode R, the reference electrode, in the cell. This electrode has a known, invariant, electrode potential and measurements are made under conditions such that a negligible current passes through it. Let the anode A be the electrode under study, i.e. A is the *test* (indicator) electrode and the cathode C is the *auxiliary* (counter) electrode. Then the measured potential of A with respect to R,  $E$  contains no component associated with the processes at the auxiliary electrode. It also contains less of the  $IR$  component than  $E(A/C)$ . The remaining contribution from this source is  $I\Delta R$  where  $\Delta R$  is the uncompensated resistance. The value of  $\Delta R$  can be minimized, but not reduced to zero, by suitable cell design.

The measured quantity  $E$  also includes the contribution of the equilibrium potential difference across the reference electrode. This may be eliminated by considering the difference between the measured potential difference when the current is  $I$ ,  $E(I)$  and its value  $E(0)$  when the current is zero and the reaction at electrode A is at equilibrium. The difference  $E(I) - E(0)$  is characteristic of electrode A only but still includes  $I\Delta R$ . The quantity characteristic of the slow processes at electrode A is

$$8.9.1 \quad \eta = E(I) - E(0) - I\Delta R$$

and is the overpotential.

Note that, if the reference electrode E is of the same type as the test electrode, but at equilibrium,  $E(0) = 0$  and the measured potential difference is equal to  $\eta + I\Delta R$ .

Sometimes it is possible to express  $\eta$  as a sum of contributions from

different stages in the overall electrode reaction, but this is not always valid, for example when the different stages are interdependent.

- 8.10 Electrode reaction rate constants  $k_{\text{ox}}, k_{\text{red}}$   
 for the oxidizing (anodic) and reducing (cathodic) reactions respectively. (SI units  $\text{m s}^{-1}$  for a first order reaction:  $\text{mol}^{1-\Sigma} \text{m}^{3\Sigma-1} \text{s}^{-1}$  for a reaction of overall order  $\Sigma$ ). The rate constants are related to the partial currents by

$$8.10.1 \quad k_{\text{ox}} = I_a/nFA \prod_i c_i^{v_i}$$

$$8.10.2 \quad k_{\text{red}} = I_c/nFA \prod_i c_i^{v_i}$$

where the product  $\prod_i c_i^{v_i}$  includes all the species  $i$  which take part in the given partial reaction,  $c_i$  is the volume concentration of species  $i$  and  $v_i$  is the order of the reaction with respect to species  $i$ . 8.10.1 and 8.10.2 are not general definitions since not all reaction rates can be expressed in this form. For example the rate of a multistep reaction or a reaction involving adsorbed species may not be expressible in this form.

For an electrode reaction



which is first order in each direction

$$8.10.4 \quad k_{\text{ox}} = I_a/nFA c_{\text{red}}$$

$$8.10.5 \quad k_{\text{red}} = -I_c/nFA c_{\text{ox}}$$

and

$$8.10.6 \quad I = AnF(k_{\text{ox}} c_{\text{red}} - k_{\text{red}} c_{\text{ox}})$$

Here  $c_{\text{ox}}$  and  $c_{\text{red}}$  are the volume concentrations of Ox and Red respectively at the site of the reaction (at the electrode surface).

- 8.11 Cathodic transfer coefficient (number)  $\alpha_c$   
 For a reaction with a single rate-determining step

$$8.11.1 \quad \alpha_c/v = -(RT/nF) (\partial \ln |I_c| / \partial E)_{T,p,c_i, \dots}$$

where  $R$  is the gas constant and  $T$  is the thermodynamic temperature.  $v$  is the stoichiometric number giving the number of identical activated complexes formed and destroyed in the completion of the overall reaction as formulated with the transfer of  $n$  electrons. The corresponding anodic transfer coefficient is

$$8.11.2 \quad \alpha_a/v = (RT/nF) (\partial \ln I_a / \partial E)_{T,p,c_i, \dots}$$

In 8.11.1 and 8.11.2  $I_a$  and  $I_c$  are the partial kinetic currents, i.e. the currents which would flow if mass transport were infinitely fast.

If the mechanism of the reaction is unknown it is preferable to report the experimental quantities  $\alpha_c/v$  or  $\alpha_a/v$ . An unsubscripted  $\alpha$  should be used only for a cathodic transfer coefficient.

- 8.12 Conditional rate constant of an electrode reaction  $k^*$   
 (SI unit, same as  $k_{\text{ox}}, k_{\text{red}}$ )

is the value of the electrode reaction rate constant at the conditional (formal) potential of the electrode reaction (see 2.7). When  $\alpha$  the transfer coefficient is independent of potential.

$$8.12.1 \quad k_c^o = k_{ox}/\exp[\alpha_a(E - E_c^o) nF/vRT]$$

$$8.12.2 \quad = k_{red}/\exp[-\alpha_c(E - E_c^o) nF/vRT]$$

Similar rate constants can be defined using activities in place of concentrations in 8.10.1 and 8.10.2 and the standard electrode potential in place of the conditional potential in 8.12.1 and 8.12.2 This type of rate constant would be called the standard rate constant of the electrode reaction.

$$8.13 \quad \text{Mean exchange current density (SI unit A m}^{-2}\text{)} \quad j_0$$

$$8.13.1 \quad j_0 = I_0/A$$

When the electrode reaction is first order in each direction

$$8.13.2 \quad j_0 = nFk_c^o c_{ox}^{\alpha_a} c_{red}^{\alpha_c}$$

Note that, at equilibrium

$$8.13.3 \quad \alpha_a + \alpha_c = 1$$

$$8.14 \quad \text{Energy of activation of an electrode reaction at the equilibrium potential (SI unit J mol}^{-1}\text{)} \quad U^\ddagger$$

$$8.14.1 \quad U^\ddagger = -R(\partial \ln I_0 / \partial T^{-1})_{p, c_i, \dots}$$

$$8.15 \quad \text{Energy of activation of an electrode reaction at any overpotential } \eta \text{ (SI unit J mol}^{-1}\text{)} \quad U^\ddagger(\eta)$$

$$8.15.1 \quad U_a^\ddagger(\eta) = -R(\partial \ln I_a / \partial T^{-1})_{p, \eta, c_i, \dots}$$

$$8.15.2 \quad U_c^\ddagger(\eta) = -R(\partial \ln |I_c| / \partial T^{-1})_{p, \eta, c_i, \dots}$$

It is also possible to define energies of activation at constant potential  $E$  with respect to some reference electrode. However, these quantities include a contribution either from the temperature coefficient of the reference electrode potential, if the reference electrode is at the same temperature as the test electrode; or from the non-isothermal junctions in the cell, if the reference electrode is held at a constant temperature. The energies of activation defined in (8.14.1), (8.15.1) and (8.15.2) are therefore to be preferred since they depend only on the properties of the test electrode.