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(English Text)

REPORT OF COMMISSION 2

ELECTROCHEMICAL NOMENCLATURE AND DEFINITIONS

PIERRE VAN RYSSELBERGHE, CHAIRMAN
Department of Chemistry, University of Oregon, Eugene

THE text below represents the state of advancement of the work of the Commission on Electrochemical Nomenclature and Definitions of C.I.T.C.E. at the conclusion of the 6th annual meeting held in Royaumont and Poitiers, France, in September 1954. It will serve as a basis for further work by the Commission and it will be submitted to the members of the Commission on Electrochemistry of the Physical Chemistry Section of the International Union of Pure and Applied Chemistry (I.U.P.A.C.) with the hope that this latter Commission will be able to make use of it for the formulation of recommendations at the July 1955 meeting of I.U.P.A.C. in Zurich, Switzerland.

The following authors have collaborated in the preparation of this report:

J. O'M. Bockris,	University of Pennsylvania;
R. Defay,	University of Brussels;
E. Lange,	University of Erlangen;
G. Valensi,	University of Poitiers;
P. Van Rysselberghe,	University of Oregon.

R. Piontelli of the Politecnico of Milan, who had participated in the early stages of the work, has been occasionally consulted.

1. *General Definitions*

1.1. Cation: A *cation* is a positively charged atom or grouping of atoms.

1.2. Anion: An *anion* is a negatively charged atom or grouping of atoms.

1.3. The *electric potential* in a vacuum and at a sufficient distance from all material systems (i.e. outside the effective range of image forces) is defined as follows:

A point charge q, deprived of any material support, is moved infinitely slowly from infinity to the point considered, the work expended in this process being w. The electric potential is the limit of the quotient w/q when q tends towards zero. During this process the electric and magnetic fields (acting on the point charge) are regarded as stationary.

1.4. The *electric potential difference* from a point A to a point B is equal to the electric potential at point A minus the electric potential at point B.

Note: In the French version of the present report the electric potential difference as defined here will be called *tension*, while in the German version it will be called *Spannung*.

2. *One-phase electrochemical systems*

2.1. The *outer electric potential* of a conducting phase, the bounding surface of which is uniform, is that defined in the classical theory of electricity and is taken, in vacuum, as the potential immediately outside the effective range of action of the image forces, i.e. at a distance of the order of 10^{-4} cm from the geometric exterior of the phase.

This quantity is measurable. At a distance of 10^{-4} cm the contribution of the image forces to the exit work (see *2.7*) of the electron or of a monovalent ion is only about 10 calories per mole.

2.2. To transfer a unit positive charge from the point at which the outer electric potential has been defined to a point in the bulk of the phase, the existence of a layer of charges and oriented dipoles requires a quantity of electric work which must be done against the coulombic forces. The work thus performed measures the *surface electric potential difference.*

2.3. The *inner electric potential* of the phase is the sum of the outer electric potential and of the surface electric potential difference.

This inner electric potential is also identical with that calculated by electrostatics from the macroscopic distribution of charge density per unit volume or unit surface and from the molecular polarization per unit volume. The inner electric potential is a quantity calculable in principle but not in general measurable.

2.4 (*a*). In an electrochemical system enclosing all the affective charges (i.e. all charges affecting the energy of the system) the *electrochemical enthalpy* is defined as the sum of the energy of the system and of the product of the external pressure and the total volume of the system.

(*b*). The *partial molar electrochemical enthalpy* of a constituent of a phase is the partial derivative, with respect to the number of moles of this constituent in this phase, of the electrochemical enthalpy of the system enclosing all the affective charges. In this differentiation the pressure, temperature and all other numbers of moles are kept constant.

(*c*). *The partial molar chemical enthalpy* of a constituent of a phase is equal to the electrochemical partial molar enthalpy of this constituent in this phase diminished by the product of the molar charge of this constituent and the inner electric potential of this phase.

2.5 (*a*). In an electrochemical system enclosing all the affective charges the *electrochemical free energy* (of Helmholtz) is defined as the energy of the system diminished by the product of temperature and the entropy of the system.

(*b*). The *electrochemical potential* of a constituent of a phase is the partial derivative, with respect to the number of moles of this constituent in this phase, of the Helmholtz electrochemical free energy of the system enclosing all the affective charges. In this differentiation the temperature, the volumes of the phases, the geometric configuration of the system and all other numbers of moles are kept constant.

(*c*). The *chemical potential* of a constituent of a phase is equal to the electrochemical potential of this constituent in this phase diminished by the product of the molar charge of this constituent and the inner electric potential of the phase.

2.6 (*a*). In an electrochemical system enclosing all the affective charges the *electrochemical free enthalpy* of the system is the sum of the electrochemical free energy of the system and the product of the external pressure and the total volume of the system.

(*b*). The *partial molar electrochemical free enthalpy* of a constituent of a phase is the partial derivative, with respect to the number of moles of this constituent in this phase, of the electrochemical free enthalpy of the system enclosing all the affective charges. In this differentiation the pressure, temperature and all other numbers of moles are kept constant.

The partial molar electrochemical free enthalpy is identical with the *electrochemical potential* defined in *2.5* (*b*).

(*c*). The *partial molar chemical free enthalpy* of a constituent of a phase is equal to the partial molar electrochemical free enthalpy of this constituent in this phase diminished by the product of the molar charge of this constituent and the inner electric potential of this phase.

The partial molar chemical free enthalpy is identical with the *chemical potential* defined in *2.5* (*c*).

2.7. Consider a constituent of a conducting phase. The *exit work* of this constituent from this phase is the work which must be expended to take one mole of this constituent from the interior of the phase, where the electric potential is equal to the inner electric potential defined in *2.3*, to that distance from the phase where the electric potential is equal to the outer electric potential defined in *2.1*.*

2.8. The absolute value of the quotient of the exit work divided by the molar charge of constituent i of the phase α is the *exit electric potential difference* of this constituent from this phase.

The exit electric potential difference can be considered as the sum of two electric potential differences, one corresponding to the chemical work of

* The exit work is made up of a coulombic term

$$w_{ie}^{\alpha} = z_i F(\psi^{\alpha} - \varphi^{\alpha}) = -z_i F \chi^{\alpha}$$

and a chemical term

$$w_{ic}^{\alpha} = \mu_{iS} - \mu_i^{\alpha}$$

In these equations z_i is the number of faradays F per mole of the constituent i, ψ^{α} represents the outer electric potential, φ^{α} represents the inner electric potential, χ^{α} represents the surface electric potential difference, μ_{iS} represents the chemical potential of constituent i in the imaginary Schottky state, and μ_i^{α} represents the chemical potential of constituent i in the phase α.

To avoid any possible confusion, let us recall that Schottky's imaginary state is an ideal state in which the ions of constituent i are immobilized (i.e. deprived of their kinetic energy of translation) at a distance from each other such that the interionic forces can be considered as negligible, the internal degrees of freedom of the ions contributing each the energy corresponding to the statistical equilibrium for the given temperature.

The electrochemical potential of constituent i is given by

$$\tilde{\mu}_i^{\alpha} = \mu_i^{\alpha} + z_i F \varphi^{\alpha}$$

where

$$\varphi^{\alpha} = \psi^{\alpha} + \chi^{\alpha}$$

If Schottky's imaginary state is taken as corresponding to the zero of chemical potential, the exit work can be written in the two following forms:

$$w_i^{\alpha} = w_{ie}^{\alpha} + w_{ic}^{\alpha} = z_i F \psi^{\alpha} - \tilde{\mu}_i^{\alpha}$$
$$= -z_i F \chi^{\alpha} - \mu_i^{\alpha}$$

exit from the phase and another corresponding to the work done in crossing the barrier due to the surface electric potential difference.

It is frequent practice to make use of an exit work expressed in volts obtained by dividing the exit work defined above by the faraday. The use of our new definition of exit work and of that of exit electric potential difference is more correct from the dimensional point of view. The above definition of the exit electric potential difference applies unambiguously to ions of any charge. The exit work can be expressed in electron volts, in kilocalories, in joules or in faraday-volts per mole of ion. The exit electric potential difference is expressed in volts.

2.9 (*a*). *Electrochemical migration* or *diffusion* of a charged constituent of a phase is the displacement of this constituent from one region of the phase to another region of this same phase resulting from a difference between the values of the electrochemical potential of this constituent in these two regions.

(*b*). *Electric migration* or *diffusion* of a charged constituent of a phase is the displacement of this constituent from one region of the phase to another region of this same phase resulting from a difference between the values of the electric potential in these two regions, the chemical potential of this constituent having the same value in these two regions.

(*c*). *Chemical migration* or *diffusion* of a neutral constituent of a phase (for instance the simultaneous diffusion of the two ionic species produced by the dissociation of a neutral electrolyte species) is the displacement of this constituent from one region of the phase to another region of this same phase resulting from a difference between the values of the chemical potential of this neutral species in these two regions.

2.10. An *electrolyte* is a liquid or solid phase in which a difference between the values of electrochemical potential in two regions of this phase will cause at least one ionic species present in significant concentration to move detectably from one region towards the other.

3. *Two-phase electrochemical systems*

3.1. The literal meaning of the word *electrode* is: a metallic phase in contact with an electrolyte. By extension one also designates as *electrodes* certain electrochemical systems having two (or sometimes several) phases. In general one of these phases is a metallic conductor. In electrochemistry the word *electrode* applies particularly to metal-solution systems.

3.2. With reference to the conventional direction of the current (which is opposite to that of the movement of the electrons in the metallic phases), each phase of a cell (see Part *4*) possesses an *entry* and an *exit face*.

3.3. A metallic conductor in contact with an electrolyte functions as a *cathode* with respect to this electrolyte if its face of contact with the electrolyte is the entry face for the metal. Conversely, a metallic conductor in contact with an electrolyte functions as an *anode* with respect to this electrolyte if its face of contact with the solution is the exit face for the metal.

3.4. The *Volta electric potential difference* of a phase 1 with respect to a phase 2 is equal to the outer electric potential of phase 1 diminished by the outer electric potential of phase 2, when the two phases are in contact.

3.5. The *Galvani electric potential difference* of a phase 1 with respect to a

phase 2 is equal to the inner electric potential of phase 1 diminished by the inner electric potential of phase 2, when the two phases are in contact.

The *absolute electric potential difference of an electrode* is equal to the inner electric potential of the metal diminished by that of the electrolyte. It is, therefore, a Galvani electric potential difference.

3.6. We shall assume that there exists at all interfaces an *electrochemical double layer*, a term which we recommend for use in place of 'electric double layer' (and particularly in place of 'electrolytic double layer', an expression frequently employed in German).

The electrochemical double layer of a simple metal-electrolyte electrode in the absence of current starts, on the metal side, at the point where the chemical potentials of the ion and of the electron in the metal begin to vary from the values in the bulk of the metal; it extends to the point in the electrolyte where the chemical potentials of the reactive species in the solution become equal to their values in the bulk of the solution.

The thickness of the double layer may thus also depend on other constituents of the solution apart from those taking part in the electrode reaction.

On the solution side the double layer can be decomposed into two portions. That which is contiguous with the metal possesses some of the properties of adsorption layers and the standard chemical potentials of its constituents will in general be different from the corresponding standard chemical potentials in the bulk of the solution. The other portion, which is contiguous with the solution, is called *diffuse double layer* and the standard chemical potentials of its constituents are equal to the corresponding standard chemical potentials in the bulk of the solution.

3.7. An *electrode reaction* is a reaction involving the constituents of two phases in contact by which a transfer of charge takes place from the bulk of one phase to the bulk of the other.

3.8. The *electrochemical free enthalpy* of an electrode reaction is equal to the sum of the electrochemical potentials of the products of the reaction multiplied respectively by their stoicheiometric coefficients, diminished by the sum of the electrochemical potentials of the reactants of the reaction multiplied respectively by the absolute values of their stoicheiometric coefficients.

3.9. The *electrochemical affinity* of an electrode reaction is the quantity defined in *3.8* taken with a negative sign.

At electrochemical equilibrium these two quantities are equal to zero.

3.10. The *chemical free enthalpy* of an electrode reaction is derived from the chemical potentials in the same manner as the electrochemical free enthalpy of this reaction is derived from the electrochemical potentials of the products and reactants.

3.11. The *chemical affinity* of an electrode reaction is the quantity defined in *3.10* taken with a negative sign.

3.12. We propose the adoption of a *unit of advancement of a reaction* called the *dedonder* and defined as follows:

When, from a given initial state, a reaction has progressed in such a manner that, for each constituent on the right-hand side of the stoicheiometric equation, there has been formed a number of moles equal to the stoicheiometric coefficient of this constituent, then the reaction has advanced by one dedonder.

Affinities and heats of reaction are then expressed in calories . dedonder^{-1}, the reaction charges (see *3.13*) in coulombs . dedonder^{-1}, etc.

3.13. The *reaction charge* of an electrode reaction is the charge transported from phase 1 to phase 2 by the reaction when it has advanced by one dedonder, i.e. when it has occurred once from left to right.

The *number of charges transported* by an electrode reaction is the number of positive faradays transported from phase 1 to phase 2 by the reaction when the latter has advanced by one dedonder. This number can be positive or negative.

The product nF in the denominator of the coefficient RT/nF of the Nernst equation is the reaction charge and the number n, positive or negative, is the number of charges transported.

3.14. The *reversible* or *equilibrium Galvani electric potential difference* of a simple electrode (see *3.17*) is equal to minus the chemical affinity of the electrode reaction divided by the reaction charge.

3.15. The *chemical enthalpy* of an electrode reaction is the sum of the partial molar chemical enthalpies of the products of the reaction multiplied respectively by their stoicheiometric coefficients, diminished by the sum of the partial molar chemical enthalpies of the reactants of the reaction multiplied respectively by the absolute values of their stoicheiometric coefficients.

3.16. The *chemical heat at constant pressure* of an electrode reaction is the quantity defined in *3.15* taken with a negative sign.

3.17. A *simple electrode* is an electrode at which only one electrode reaction occurs.

3.18. A *polyelectrode* or *multiple electrode* is an electrode at which several electrode reactions occur simultaneously.

3.19. The *exchange current density at equilibrium*, for a given electrode reaction, is the absolute value of the current density corresponding to the equal and opposite velocities of the anodic and cathodic transformations.

3.20. Electrolysis is the process occurring at the phase boundary of an electrode when a qualitative and/or quantitative change of composition resulting from the electrode reaction is not compensated by migration.

4. Galvanic cells

4.1. Galvanic cells are series of conducting phases, in contact two by two, at least one of which is an electrolyte (such that, upon passage of current, electrolysis takes place), the terminal phases being chemically identical with one another but not having necessarily the same inner electric potential.

4.2. The identical extremities of a galvanic cell are called its *poles* or *terminals*.

4.3. A *battery* (or *element*) is a practical form of realization of a galvanic cell used to generate current.

4.4. The *electric potential difference of a galvanic cell* is the electric potential of one pole with respect to the other, i.e. it is equal to the inner electric potential of the first pole diminished by that of the second.

In the schematic representation of a cell the different phases are written and numbered in a definite order. The electric potential difference is taken from the first phase to the last.

If the phases are numbered as follows: 1, 2, 3, . . . 1′, the phases 1 and 1′ being of the same metal and constituting the poles of the galvanic cell, the electric potential difference of the cell is the difference $\varphi^1 - \varphi^{1'}$ between the inner electric potentials of the phases 1 and 1′.

4.5. The *cell reaction* is the chemical reaction, or, in a general way, the material change which the various constituents of the cell take part in and which is connected with the passage of current.

When the electric current changes its direction, the cell reaction also changes its direction.

4.6. The *reaction charge* of the cell reaction, and also the number of charges transported by the cell reaction are defined as in *3.13*, the phases 1 and 2 becoming now the terminal poles 1 and 1′ of the cell.

4.7. The *chemical affinity* of the cell reaction has the following important property: it is equal to the electric work which is done reversibly by the cell reaction on the external circuit when the reaction has advanced by one dedonder.

4.8. The above definitions lead to the following relation: the reversible electric potential difference of the cell is equal to minus the chemical affinity of the cell reaction divided by the reaction charge.

Note that this relation is valid regardless of the direction in which the cell reaction is written, the reversal of the reaction implying a change of sign of both the affinity and the reaction charge. Nevertheless, for the needs of thermodynamics, the Commission on Electrochemistry of the International Union of Pure and Applied Chemistry (I.U.P.A.C.), in conjunction with the Commission on Physical Chemical Symbols and Terminology, has recommended (Stockholm, 1953) that the cell corresponding to a given reaction be written down in the direction making the reaction charge positive.

4.9. It is useful to consider the quotient of the chemical affinity divided by the reaction charge, in magnitude and sign, as the *electrotromotive force* of the cell.

The reversible electric potential difference of the cell is equal, but of opposite sign to its electromotive force.

4.10. Let us consider for example the Daniell cell and let us number its phases as follows:

Cu	Cu^{2+}	Zn^{2+}	Zn	Cu
1	2	3	4	1′

The electric potential difference of the cell is $\varphi^1 - \varphi^{1'}$. At equilibrium the potential difference $\varphi^{1'} - \varphi^1$ is the *electromotive force* of the cell.

Neglecting diffusion phenomena we may write the cell reaction as

(*a*) $$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+},$$

the chemical affinity A_a being such that $A_a = -\Delta G_a$, and the reaction charge being $n_a = -2$, or as

(*b*) $$Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn,$$

the chemical affinity A_b being such that $A_b = -\Delta G_b$ (with $A_b = -A_a$, $\Delta G_b = -\Delta G_a$), and the reaction charge being $n_b = +2$.

We have, from both ways of writing the cell reaction:

Reversible electric potential difference =

$$\frac{-A_a}{-2F} = \frac{-(-\Delta G_a)}{-2F} = \frac{-A_b}{+2F} = \frac{-(-\Delta G_b)}{+2F}$$

Electromotive force =

$$\frac{+A_a}{-2F} = \frac{+(-\Delta G_a)}{-2F} = \frac{+A_b}{+2F} = \frac{+(-\Delta G_b)}{+2F}$$

We thus have:

Reversible electric potential difference = − electromotive force,

or Reversible electric potential difference + electromotive force = 0.

At electrochemical equilibrium there are indeed two forces or tensions which are equal and opposite: an electric force ('tension' in French, 'Spannung' in German) and a chemical force, the latter corresponding to the electromotive force.

Let us note that a positive electromotive force indicates that the chemical affinity of the cell reaction tends to transport positive charges from left to right inside the cell.

4.11. The above relations between electric potential difference or electromotive force on the one hand and chemical affinity or chemical free enthalpy of the cell reaction on the other hand satisfy the electrochemical requirement that, to a particular schematic representation of a galvanic cell, one should be able to associate two directions of the cell reaction corresponding to the two possible directions of the electric current.

4.12. From the point of view of chemical thermodynamics this situation may be simplified through the fact that chemical reactions are then written in one particular direction and that one has to associate an electric potential difference to the chemical affinity corresponding to this direction. Between the two possible ways of formulating this association the I.U.P.A.C. Commissions (see *4.8*) have implicitly selected the following:

$$\text{Electromotive force} = \frac{\text{chemical affinity of the cell reaction}}{\text{absolute value of the reaction charge}}$$

and hence:

$$\text{Reversible electric potential difference} = -\frac{\text{chemical affinity of the cell reaction}}{\text{absolute value of the reaction charge}}$$

These formulas may be regarded as corresponding to a schematic representation of a galvanic cell such that, when the cell reaction is actually taking place from left to right as written, the reaction charge flowing in the cell from left to right (i.e. in the direction of the numbering of the phases: 1, 2, 3, . . . 1′) be positive (see *4.8*).

4.13. The *relative electric potential difference of an electrode* is the electric potential difference of a galvanic cell comprising successively: the metal of the electrode under study and its solution, the solution and the metal of the reference electrode, and finally, a terminal pole of the same metal as that of the electrode under study, the liquid junctions involving electric potential

differences which are subtracted from the total electric potential difference of the cell.

This quantity is rigorously accessible to measurement in the unusual case in which the reference electrode is in contact with the same electrolyte as the electrode under study. It is then equal to the electric potential difference of the cell defined by the electrode under study, the metal of which forms the first pole, the solution belonging to the reference electrode, the metal of the reference electrode, and finally the second pole identical with the first metal.

When the reference electrode is not in contact with the same electrolyte as the electrode under study, it is possible to obtain an approximate value (to within a few millivolts) of the relative electric potential difference. This is carried out with an arrangement similar to that described above, except that, between the two liquid phases, one places a concentrated solution of an electrolyte consisting of anions and cations of approximately the same mobility, for example a saturated solution of potassium chloride, in order to reduce as much as possible the contributions of the liquid junctions.

It may be noted that the definition of relative electric potential difference given above automatically implies the use of electrode potential differences of the type referred to as 'European' (the noble electrode potential differences being positive), sometimes called 'reduction potentials'. The opposite arrangement (first pole attached to the reference electrode, second pole is the metal of the electrode under study) would lead immediately to the use of electrode potential differences of the type referred to as 'American' (noble electrode potential differences negative), sometimes called 'oxidation potentials'.

4.14. An *ideal dilute solution* is defined as a solution such that, when the temperature and pressure are constant, the chemical potential of each dissolved constituent varies linearly with the natural logarithm of its molar concentration (or of its molality or of its mol fraction), the coefficient of the logarithmic term being equal to the product of the perfect gas constant and the absolute temperature.

After having stated which concentration unit is to be used, a standard state is chosen for each dissolved constituent such that the chemical potential of each dissolved constituent is then numerically equal to the constant of the linear relation which, at the same temperature and pressure, defines the ideality of the solution at infinite dilution with respect to that constituent.

This type of standard state is that most commonly adopted in the electrochemistry of aqueous solutions, where it is used in terms of molarities or preferably of molalities.

4.15. The *standard electric potential difference of an electrode* (or *standard electrode potential*) is the equilibrium value of the relative electric potential difference of the electrode (or relative electrode potential) when the dissolved constituents taking part in the electrode reaction are all in their standard states, the solid constituents are in their pure states, and the gaseous constituents are at fugacities equal to one atmosphere.

In practice it is generally assumed that all gaseous constituents are perfect gases and that their fugacities can then be identified with their partial pressures.

The numerical values of standard electrode potentials depend on the units employed for concentrations and on the choice of the reference electrode. The difference between the electrode potentials of identical electrodes dipping in aqueous solutions of which one has a molality m and the other a molarity m with respect to a potential-determining constituent is of the order of a few tenths of a millivolt in the case of dilute solutions.

Knowledge of the standard electrode potential enables the electrode under consideration to be placed in the electrochemical series.

4.16. The reference electrode which is most commonly used is the *standard hydrogen electrode*. This is a reversible hydrogen electrode in which the hydrogen ion is in its standard state and the hydrogen gas is at a fugacity of one atmosphere.

It follows that the standard electrode potential of the hydrogen electrode is equal to zero at all temperatures. The standard electrode potential of some other electrode can be determined with a precision, which may reach one hundredth of a millivolt, in a cell with a single solution in which one electrode is that under study and the other is either a hydrogen electrode or another reversible electrode previously studied.

Standard electrode potentials are actually combinations of standard chemical potentials divided by the reaction charge and their values can be obtained rigorously by extrapolation to infinite dilution.

4.17. Let us note that, when the reference electrode is the standard hydrogen electrode, our *relative electrode potentials* (see *4.13* and *4.15*) become identical with the quantities of the same name (also designated in brief as *electrode potentials*) defined in the recommendations of the I.U.P.A.C. Commissions (see *Comptes Rendus de la Dix-Septième Conférence*, Stockholm, 1953, pp. 82–83).

In the case of the $Zn|Zn^{2+}$ electrode for example, the *relative electrode potential*, or in brief the *electrode potential* is the electric potential difference of the cell

Zn	Zn^{2+}	$H^+(a_{H^+}=1)$	$H_2(p_{H_2}=1)$, Pt	Zn
1	2	3	4	1′

while for the I.U.P.A.C. Commissions this *electrode potential* is the electromotive force of the cell

Pt, $H_2(p_{H_2}=1)$	$H^+(a_{H^+}=1)$	Zn^{2+}	Zn	Pt
1	2	3	4	1′

5. Electrode kinetics and polarization phenomena

5.1. At a *simple electrode* (see *3.17*) the current corresponding to the electrode reaction is the difference between the absolute values of a *forward* and of a *reverse* current.

At electrochemical equilibrium the forward and the reverse current are equal to each other. Their common value is the *exchange current* (see *3.19*).

5.2. At a *polyelectrode* (see *3.18*) the partial current corresponding to each electrode reaction is the difference between the absolute values of a *forward partial* and of a *reverse partial current.*

The sum of the partial currents is equal to the total current.

5.3. The *apparent current density* of an electrode reaction occurring at a simple electrode or the *apparent partial current density* of an electrode reaction occurring at a polyelectrode is the current or partial current corresponding to the reaction divided by the apparent area of the electrode surface at which the reaction takes place.

In some cases the true surface area available to the electrode reaction will be known (through the measurement of the *roughness factor*). In such cases the exact current density is obtainable.

In what follows we shall consider current densities without specifying whether they are apparent or exact.

5.4. The *velocity of an electrode reaction per unit area of electrode surface* or *electrochemical reaction rate density* is equal to the current or partial current density of this reaction divided by the reaction charge.

5.5. The *electrochemical reaction rate constant* of the forward or of the reverse component of an electrode reaction is the electrochemical reaction rate density of that forward or reverse component divided by the bulk concentration of the reactants raised to the powers required by the order of the reaction.

The dimensional relations are as follows:

Current density: $(\text{charge}) \times (\text{length})^{-2} \times (\text{time})^{-1}$,

Reaction rate density: $(\text{length})^{-2} \times (\text{time})^{-1}$

$= (\text{reaction rate constant}) \times (\text{concentration})^{n}$

$= (\text{reaction rate constant}) \times (\text{length})^{-3n}$,

Reaction rate constant: $(\text{length})^{3n-2} \times (\text{time})^{-1}$

$= (\text{concentration})^{-(n-1)} \times (\text{length}) \times (\text{time})^{-1}$.

If, for example, this forward or reverse component of the electrode reaction is of the first order, we have:

$$\text{Reaction rate constant: } (\text{length}) \times (\text{time})^{-1}.$$

At given temperature and pressure these electrochemical rate constants depend on the Galvani electric potential difference at the phase boundary at which the reaction takes place. They include the activity coefficients of the reactants and of the activated complex and, therefore, are not necessarily independent of composition. Note: the above does not apply to diffusion controlled reactions.

5.6. When a given electrode reaction transfers a positive charge to the metal of the electrode, the corresponding net current is designated as *cathodic*. When this electrode reaction transfers a negative charge to the metal of the electrode, the corresponding net current is designated as *anodic*.

In metal–solution systems (metal = phase 1, solution = phase 2) anodic currents or partial currents are positive, cathodic current or partial currents are negative. The opposite would hold in solution–metal systems.

5.7. The *electrochemical double layer* of a simple metal–solution electrode which carries a net current also includes a diffusion layer. This diffusion layer begins at the point where the standard chemical potentials of all species taking part in the electrode reaction have become equal to those in

the bulk of the solution, and extends outward to the point where the chemical potentials of all species taking part in the electrode reaction have become equal to those in the bulk of the solution.

This definition of the electrochemical double layer with net current flow is thus analogous with that given in *3.6* for the case of absence of net current.

5.8. Polarization is the general name given to the phenomena associated with the departure of electrode potentials (or of the electric potential differences of galvanic cells) from their values at a net current of zero.

This electrochemical polarization must be distinguished from dielectric polarization.

5.9. When, in a polarization experiment, one plots graphically the electrode potential as a function of the charge density (i.e. the integral of the product of the current density by the differential of time), the initial slope (i.e. at time zero) can be determined from the curve thus obtained. This slope measures the *initial polarizability per unit area.*

The reciprocal of this quantity is the *initial polarization capacity per unit area.*

Similarly, after interrupting the stationary current, it is possible to determine, at the instant of interruption, the slope of the curve representing the decrease of electrode potential as a function of the charge density which would be transported in the same time by the stationary current, and thus to deduce an *initial* (*decreasing*) *polarization capacity per unit area.*

5.10. When, at a given current density, an electrode is the seat of a certain single electrode reaction, the *overpotential* (or *overvoltage*) of this reaction on this electrode at a given instant is equal to the electrode potential under current diminished by the reversible electrode potential corresponding to this reaction.

5.11. If several electrode reactions, which have distinct values of their reversible electrode potentials, occur simultaneously at the same electrode, the electrode potential is called *mixed electrode potential.*

In many cases the reactions taking place at an electrode are unknown. The difference between the mixed electrode potential under current and the mixed electrode potential at a net current of zero is called *excess electrode potential.*

5.12. When an electrode is the seat of several simultaneous electrode reactions, it is possible to evaluate an *overpotential* (or *overvoltage*) with respect to the reversible electrode potential of each reaction. This is possible even in the absence of a net current.

5.13. The quotient of the overpotential (or overvoltage) divided by the current or partial current density corresponding to the reaction is called *overpotential* (or *overvoltage*) *resistance per unit area.*

5.14. The quotient of the excess electrode potential divided by the current density is the *excess electrode potential resistance per unit area.*

5.15. The *differential resistance per unit area* of an electrode reaction is the derivative of the stationary overpotential (or overvoltage) of that reaction with respect to the corresponding current or partial current density.

The limit of this derivative when the current tends towards zero is the *differential resistance per unit area at zero current.*

5.16. The *activation overpotential* (or *overvoltage*) of an electrode reaction taking place at a simple electrode is the overpotential (or overvoltage)

defined in *5.10* when the electrochemical reaction rate of this electrode reaction is controlled exclusively by an electrochemical step (i.e. not by diffusion or non-reactional resistances).

5.17. When the activation overpotential (or overvoltage) of an electrode reaction is represented as a function of the natural logarithm of the current density, the relation is often linear at sufficiently large values of the current density (at which the reverse component of the reaction is negligible) and is designated as *Tafel's law*: $\eta = a + b \ln I$.

When the value of b is written as $RT/\alpha F$, the parameter α is called the *transfer coefficient.*

5.18. The *electrochemical free enthalpy of activation* of an electrode reaction at a certain Galvani potential difference is the electrochemical free enthalpy of activation at equilibrium increased by the product of the following three factors: the overpotential (or overvoltage), the transfer coefficient, and the charge involved in one dedonder of the rate determining step.

This definition and the following one imply the applicability of Tafel's law.

5.19. When the temperature dependence of the transfer coefficient is negligible, the *electrochemical enthalpy of activation* of an electrode reaction at a certain Galvani potential difference is the electrochemical enthalpy of activation of this reaction at equilibrium increased by the same product as that defined in *5.18.*

5.20. When the temperature dependence of the transfer coefficient is negligible, the *electrochemical entropy of activation* of an electrode reaction has the same value at any Galvani potential difference as at equilibrium.

The correction to be introduced in the two last definitions when the temperature dependence of the transfer coefficient is not negligible is easily derived from simple thermodynamic reasoning.

5.21. The *concentration overpotential* (or *overvoltage*) of an electrode reaction taking place at a simple electrode is the overpotential (or overvoltage) defined in *5.10* when the rate of the electrode reaction is controlled exclusively by the diffusion of the reacting species.

The maximum value of the concentration overpotential (or overvoltage) reached with time under any given condition of agitation is called the *stationary concentration overpotential* (or *overvoltage*).

5.22. The *limiting current* of an electrode reaction taking place at a simple electrode is the maximum value of the diffusion controlled current corresponding to that reaction.

5.23. The *resistance overpotential* (or *overvoltage*) of an electrode reaction taking place at a simple electrode is the overpotential (or overvoltage) defined in *5.10* when the rate of the electrode reaction is controlled exclusively by the resistance of the electrochemical double layer defined in *5.7.*

The resistance overpotential (or overvoltage) is often due to a resistant layer on the electrode surface.

In general the measured overpotential (or overvoltage) of an electrode reaction includes all three types of overpotential (or overvoltage). In certain cases it is possible to eliminate, at least approximately, two of the three types of overpotential.

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