2.1

(English Text)
REPORT OF COMMISSION NO. 2

ELECTROCHEMICAL NOMENCLATURE AND DEFINITIONS

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THE following text 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 9th annual meeting held in Paris, France, in July 1957. It will serve as a basis for further work by the Commission. It should also be regarded as constituting the report for 1957 of the Sub-Commission of Electrochemical Symbols and Terminology of the Commission on Electrochemistry (presided over by M. Pourbaix, Brussels) of the International Union of Pure and Applied Chemistry (I.U.P.A.C.).

The personnel of Commission No. 2 of C.I.T.C.E. is at present the following: J. O'M. Bockris (University of Pennsylvania), E. Darmois (University of Paris), R. Defay (University of Brussels), T. P. Hoar (University of Cambridge), E. Lange (University of Erlangen), G. Milazzo (University of Rome), G. Valensi (University of Poitiers), P. Van Rysselberghe (Stanford University). In addition, G. Allard (University of Paris) has agreed to represent on Commission No. 2 of C.I.T.C.E., his colleagues of the I.U.P.A.C. Commission of Physical Chemical Symbols and Terminology (presided over by J. A. Christiansen, Copenhagen) and to act as a connecting link between the two Commissions concerning any question of common interest.

1. General definitions

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

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

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

A point charge q, deprived of any material support, is moved infinitely

* The *image force* is the electrostatic force between a charge and a conductor resulting from the electrostatic charges induced in the conductor by the charge under consideration. At a distance of 10^{-4} cm the contribution of image forces to the exit work (see *2.7*) of the electron or of a univalent ion is only about 10 calories per mole.

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 toward zero. During this process the electric and magnetic fields acting on the point charge are regarded as stationary.

1.4. The *electric tension* from a point 1 to a point 2 is equal to the electric potential at point 1 minus the electric potential at point 2.

1.5. The *electric potential difference* corresponding to an interval 1–2 is equal to the electric potential at point 2 minus the electric potential at point 1.

The electric potential difference is thus equal in absolute value, but of opposite sign to the tension*.

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 taken, in vacuum, immediately beyond 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.

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 of oriented dipoles requires a quantity of electric work which must be expended against the macroscopic coulombic forces. The work thus performed furnishes a measure of the *surface electric tension.*

This tension is positive when, across the superficial layer, the electric potential increases from the exterior to the interior of the phase.

2.3. The *inner electric potential* in a point of a phase is the sum of the outer electric potential and of the surface electric tension.

In other words, it is the potential which would be calculated in the theory of electrostatics from the macroscopic distribution of charge densities per unit volume or area and from the molecular polarizations per unit volume.

The inner electric potential is a quantity definable in principle, but not in general measurable.

2.4. (*a*) In an electrochemical system enclosing all the acting 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 by the 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 acting charges. In this differentiation, all the other numbers of moles, the temperature and the pressure 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

* The electric field E in a point is connected to the electric potential in this point by the well known relation $E = -\text{grad}\,\varphi$. In the case of a single space coordinate x we write $E = -\mathrm{d}\varphi/\mathrm{d}x$, or, when the field is uniform in the interval Δx, $E = -\Delta\varphi/\Delta x = U/\Delta x$, U representing the tension between the origin and the extremity of the interval Δx. The electric potential difference defined in *1.5* is thus equal to the increment $\Delta\varphi$ appearing in the last formula above.

minus the product of the molar charge of this constituent by the inner electric potential of this phase.

2.5 (*a*). In an electrochemical system enclosing all the acting charges the *electrochemical free energy* (of Helmholtz) is defined as the energy of the system minus the product of the absolute temperature by 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 electrochemical free energy of the system enclosing all the acting charges. In this differentiation, all the other numbers of moles, the temperature, the volumes of the phases and the geometric configuration of the system 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 minus the product of the molar charge of this constituent by the inner electric potential of the phase.

2.6 (*a*). In an electrochemical system enclosing all the acting charges the *electrochemical free enthalpy* of the system is defined as the sum of the electrochemical free energy of the system and of the product of the external pressure by 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 acting charges. In this differentiation, all the other numbers of moles, the temperature and the pressure 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 minus the product of the molar charge of this constituent by the inner electric potential of the 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 transfer one mole of this constituent from the interior of the phase, at the inner electric potential, to the exterior of the phase, at the outer electric potential (see definitions *2.1* and *2.3*)*.

2.8. The absolute value of the quotient of the exit work by the molar

* The exit work consists of a coulombic term $w_{ie}{}^{\alpha}=z_iF(\psi^{\alpha}-\varphi^{\alpha})=-z_iF\chi^{\alpha}$ and of a chemical term $w_{ie}{}^{\alpha}=\mu_{iS}-\mu_i{}^{\alpha}$, z_i being the number of faradays F per mole of constituent i, ψ^{α} the outer electric potential, φ^{α} the inner electric potential, χ^{α} the surface electric tension, μ_{iS} the chemical potential of consitutent i in the imaginary Schottky state, and $\mu_i{}^{\alpha}$ 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 one another such that the inter-ionic 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 $\tilde{\mu}_i{}^{\alpha}=\mu_i{}^{\alpha}+z_iF\varphi^{\alpha}$ with $\varphi^{\alpha}=\psi^{\alpha}+\chi^{\alpha}$. If Schottky's imaginary state is taken as corresponding to the zero of chemical potential, the exit work can be written in the following two forms: $w_i{}^{\alpha}=w_{ie}{}^{\alpha}+w_{ic}{}^{\alpha}=z_iF\psi^{\alpha}-\tilde{\mu}_i{}^{\alpha}=-z_iF\chi^{\alpha}-\mu_i{}^{\alpha}$. The exit work and tension are measurable quantities (see *2.8*).

charge of constituent i of phase α is the *exit electric tension* of this constituent from this phase.

The exit electric tension can be considered as the sum of two tensions, one corresponding to the chemical work of exit from the phase and another corresponding to the work done in crossing the barrier due to the surface electric tension. It is frequent practice to make use of an exit work expressed in volts obtained by dividing the exit work defined above by the molar charge expressed in coulombs. The use of our new definition of exit work and of that of exit electric tension is more correct from the dimensional point of view.

The above definition of the exit electric tension applies unambiguously to ions of any charge.

The exit work may be expressed in kilocalories, in joules or in faraday-volts for one mole of ion.

The exit electric tension is expressed in volts.

2.9 (*a*). The *electrochemical migration* or *electrochemical 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*.

The expression *electrochemical migration* will be used preferably when the difference between the values of the electrochemical potential is chiefly due to the difference of electric potential between the two regions, while the expression *electrochemical diffusion* will be used preferably when the difference between the values of the electrochemical potential is chiefly due to the difference of chemical potential between the two regions (typical case of polarography, for instance).

The *molar electrochemical force* applied to a charged constituent of a phase is equal to minus the gradient of the electrochemical potential of this constituent. The *electrochemical force per particle* is equal to this quantity divided by Avogadro's number.

(*b*). The *electric migration*, or more briefly the *migration* of a charged, non-dipolar 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 potentials of this constituent having the same value in these two regions.

The *molar electric force* applied to a charged, non-dipolar constituent of a phase is equal to minus the gradient of the electric potential (i.e. plus the electric field) multiplied by the molar charge of this constituent. The *electric force per particle* is equal to this quantity divided by Avogadro's number.

(*c*). The *chemical diffusion*, or more briefly the *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.

We can similarly define the diffusion of an ionic species in case the

* Definition *2.9* (*a*) also applies to dipolar constituent in a non-uniform field.

difference of electric potential between the two regions is equal to zero or is negligible. When this is not the case we are brought back to definition *2.9* (*a*).

The *molar chemical force* applied to a constituent of a phase is equal to minus the gradient of the chemical potential of this constituent. The *chemical force per particle* is equal to this quantity divided by Avogadro's number.

2.10. If the frictional resistance exerted on a particle by a given medium is assumed proportional to the velocity of this particle, we designate as *mobility* of this particle the stationary velocity which it acquires under the action of a unit force.

When the particle under consideration is charged, we designate more specially as *electric mobility* of this particle the stationary velocity which *it acquires under the action of a unit electric field.*

2.11. The *electric conductibility* of a system is the property of this system allowing the circulation of electric charges under the influence of an electric field.

2.12. Any phase endowed with electric conductibility is called a *conductor.*

A conductor is said to be *of the first class* or *electronic* when the mobile electric charges of this conductor are exclusively electrons. This is the case of pure metals.

A conductor is said to be *of the second class* or *ionic* when the mobile electric charges of this conductor are anions and cations.

An *electrolyte* is a pure substance able to exhibit conductibility of the second class in the solid, liquid or dissolved state.

A conductor is said to be *mixed* when the mobile electric charges of this conductor are simultaneously electrons and ions. Certain oxides and metallic salts are mixed conductors in the crystalline state.

2.13. The *conductance* of a system is the reciprocal of its electric resistance. It is thus the arithmetic value of the charge transmitted per unit time and under stationary conditions when an electric tension arithmetically equal to one unit is applied between the extremities of the system.

2.14. The *conductivity* of a phase is the conductance of a conductor cut out of this phase and having a length equal to one unit in the direction of the electric field and a cross-section with an area equal to one unit in a plane perpendicular to this field.

2.15. The *equivalent conductibility* of a solid, liquid or dissolved electrolyte is the quotient of its conductivity by its concentration expressed in gram-equivalents per unit volume.

In the case of an electrolyte completely dissociated into its ions this equivalent conductibility is equal to the product of the faraday by the sum of the electric mobilities of the anion and cation.

The *limiting equivalent conductibility* of an electrolyte is its equivalent conductibility at infinite dilution.

The *equivalent ionic conductibility* of an ion is equal to the product of the faraday by the electric mobility of this ion.

The *limiting electric mobility* of an ion is the value of its electric mobility in the solvent free of electrolytes.

The *limiting equivalent ionic conductibility* of an ion is equal to the product of the faraday by the limiting electric mobility of this ion.

2.16. The *molar conductibility* of a solid, liquid or dissolved electrolyte is the quotient of its conductivity by its concentration expressed in moles per unit volume. It is thus equal to the equivalent conductibility multiplied by the number of gram-equivalents constituting one mole of the electrolyte.

The *limiting molar conductibility* of an electrolyte is its molar conductibility at infinite dilution.

2.17. The *transference number* of an ionic species, present or considered as present in a system, is the quotient of the quantity of electricity transported by this ionic species in the course of its migration (see *2.9* (*b*)) by the total quantity of electricity transported by all charged species present or considered as present in the system.

A more detailed examination of the concept of transference number is beyond the scope of the present report.

2.18. The numerical values of the various quantities defined above in current usage in physical chemistry and electrochemistry are based upon a mixed system of units derived on the one hand from the C.G.S. system as far as geometric and kinematic quantities are concerned, and on the other hand from the practical (or Giorgi) system as far as work and electric quantities are concerned. Thus, lengths are expressed in cm, areas in cm^2, volumes in cm^3, velocities in $cm.sec^{-1}$, electric fields in $volt.cm^{-1}$, equivalent conductibilities in $ohm^{-1}.cm^2.equiv^{-1}$, molar conductibilities in $ohm^{-1}.cm^2.mole^{-1}$, forces in $joule.cm^{-1}$, mobilities in $cm^2.joule^{-1}.sec^{-1}$, electric mobilities in $cm^2.volt^{-1}.sec^{-1}$.

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 we also designate as *electrodes* certain electrochemical systems with two phases (or sometimes several phases). In the majority of cases one of these phases is a metallic conductor. In electrochemistry the word *electrode* applies particularly to metal–solution systems.

3.2. With respect 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 of this report) possesses a *face of entry* and a *face of exit.*

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

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

3.5. The *Galvani electric tension* of a phase 1 with respect to a phase 2 is equal to the inner electric potential of phase 1 minus the inner electric potential of phase 2, when these two phases are in contact.

The *absolute electric tension* of an electrode is equal to the inner electric potential of the metal minus that of the solution. It is, therefore, a Galvani electric tension.

3.6. We shall assume that there exists in all interphase regions an *electro-*

chemical double layer, an expression 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–solution 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 differ from their values in the bulk of the metal; it extends to the point in the solution where the chemical potentials of the reactive species become equal to their values in the bulk of the solution.

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

On the solution side the double layer may 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 phase.

3.8. We recommend the adoption of the quantitative concept of *advancement of a reaction*:

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 stoichiometric equation, there has been formed a number of moles equal to the stoichiometric coefficient of this constituent, then the reaction has advanced by *one unit of advancement.*

Affinities and heats of reaction are then expressed, for instance, in calories .(unit of advancement)$^{-1}$, the reaction charges (see *3.9*) in coulombs.(unit of advancement)$^{-1}$, etc.

On the initiative of R. Piontelli the C.I.T.C.E. Commission on Electrochemical Nomenclature and Definitions has suggested that the unit of advancement be designated as the *Dedonder.*

The recent death of Professor Th. De Donder enables us to recommend the use of this designation to the competent Commissions of the International Union of Pure and Applied Chemistry (I.U.P.A.C.).

3.9. 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 unit, i.e. when it has occurred once from left to right.

The *number of charges transported* by an electrode reaction is the positive or negative number of charges expressed in faradays transported from phase 1 to phase 2 by the reaction when it has advanced by one unit.

The product zF of the denominator of the coefficient RT/zF of the Nernst formula is the reaction charge and the number z, positive or negative, is the number of charges transported.

3.10. The *electrochemical free enthalpy of an electrode reaction* is equal to the sum of the electrochemical potentials of the products of the reaction,

respectively multiplied by their stoichiometic coefficients, minus the sum of the electrochemical potentials of the reactants of the reaction, respectively multiplied by the absolute values of their stoichiometric coefficients.

3.11. The *electrochemical affinity of an electrode reaction* is the quantity defined in *3.10* taken with the minus sign.

At electrochemical equilibrium these two quantities are equal to zero.

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

3.13. The *chemical affinity of an electrode reaction* is the quantity defined in 3.12 taken with the minus sign.

3.14. If, for a given chemical and electric state of an electrode, we invert the left-hand and right-hand sides of the electrode reaction, without changing the numbering of the phases, the quotient of the electrochemical affinity of this electrode reaction by the corresponding reaction charge (as it has been defined in *3.9*) is invariant in sign.

It is indeed easily verified that an inversion such as $Me^{z+}(1) \rightarrow Me^{z+}(2)$ becoming $Me^{z+}(2) \rightarrow Me^{z+}(1)$ in the writing of the reaction of electrode $\underset{1}{Me}|\underset{2}{Me^{z+}}$ implies simultaneous changes of signs for the electrochemical affinity and for the reaction charge, the quotient of these two quantities being thus invariant in sign.

Like the electrochemical affinity itself, this quotient differs from zero only away from equilibrium. In the case of a simple electrode (see *3.19*) it will be called *electrochemical tension* of this electrode.

Let us note that, for an electric state of the electrode corresponding to a spontaneous reaction in the direction of oxidation (dissolution of a metal, formation of a halogen or of a salt from the corresponding anion, etc.), the electrochemical tension is positive for the metal–solution system and negative for the solution–metal system. For the same chemical state of the electrode, but for an electric state corresponding to a spontaneous reaction in the direction of reduction (deposition of a metal, formation of an anion from a halogen or from a salt, etc.), the electrochemical tension is negative for the metal–solution system and positive for the solution–metal system.

The electrochemical tension will be connected with the overtension (or overvoltage, or overpotential) in part 5 of this report.

3.15. If, for a given chemical state of an electrode, we invert the left-hand and right-hand sides of the electrode reaction, without changing the numbering of the phases, the quotient of the chemical affinity of this electrode reaction by the corresponding reaction charge (as it has been defined in *3.9*) is invariant in sign.

In the case of a simple electrode (see *3.19*) this quotient will be called *chemical tension* of the electrode.

The expression *chemical tension* is preferable to the designation *electromotive force* of the electrode, which would nevertheless conform with the current use of this appellation in electrochemical thermodynamics.

3.16. The *reversible* or *equilibrium Galvani tension* of a simple electrode (see *3.19*) is equal to minus the chemical tension of this electrode.

It is thus also equal to minus the chemical affinity of the electrode reaction divided by the reaction charge.

At equilibrium the sum chemical tension + electric tension is equal to zero.

Away from equilibrium the electric tension differs in absolute value from the chemical tension. The sum chemical tension + electric tension is then equal to the electrochemical tension defined in *3.14*, now different from zero.

3.17. The *chemical enthalpy of an electrode reaction* is equal to the sum of the partial molar chemical enthalpies of the products of the reaction, respectively multiplied by their stoichiometric coefficients, minus the sum of the partial molar chemical enthalpies of the reactants of the reaction, respectively multiplied by the absolute values of their stoichiometric coefficients.

3.18. The *chemical heat at constant pressure of an electrode reaction* is the quantity defined in *3.17* taken with the minus sign.

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

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

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

3.22. There is *chemical effect of the current* in the interphase region of an electrode when a material enrichment or depletion resulting from the electrode reaction is not compensated by electrochemical migration or diffusion (see *2.9* (*a*)).

At a metal–solution interphase there is in general chemical effect of the current, while at a metal 1–metal 2 interphase the current produces a mere change of environment for the electron and there is no chemical effect of the current.

4. Galvanic cells

4.1. Galvanic cells are series of conducting phases in contact two by two, one of which at least is an electrolyte (such that passage of the current results in chemical effect), the terminal phases being identical from the chemical and physical points of view, but not necessarily from the point of view of the inner electric potentials.

4.2. The identical (in the meaning defined in *4.1*) terminal phases of a galvanic cell are called its *poles* or *terminals*.

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

(*b*). In practical applications it is stated that there is *electrolysis* when the total chemical effect of the current (see *3.22*) flowing through the cell results from the consumption of electric energy, i.e. corresponds to an increase of the chemical free enthalpy of the cell. Such a galvanic cell may be called an *electrolytic cell*.

4.4. The *electric tension of a galvanic cell* is the electric tension of one pole with respect to the other. It is thus equal to the inner electric potential of the first pole minus that of the second.

In the diagrams of galvanic cells the various phases are written and

numbered in a definite order. The electric tension is taken from the first phase to the last.

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

4.5. The *cell reaction* is the chemical reaction, or, more generally, the material change in which the various constituents of the phases of the cell take part and which is bound up with the passage of the electric current.

Let us consider, for instance, the Daniell cell and let us represent it by the following diagram:

$$\begin{array}{c|c|c||c|c|c} \mathrm{Zn} & \mathrm{Zn^{2+}} & & \mathrm{Cu^{2+}} & \mathrm{Cu} & \mathrm{Zn} \\ 1 & 2 & & 3 & 4 & 1' \end{array}$$

The cell reaction corresponding to the passage of current from left to right is the following:

$$\mathrm{Zn}(1) + \mathrm{Cu^{2+}}(3) \rightarrow \mathrm{Zn^{2+}}(2) + \mathrm{Cu}(4)$$

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

The above reaction can be regarded as the sum or resultant of the following three electrode reactions:

$\mathrm{Zn}(1) \rightarrow \mathrm{Zn^{2+}}(2) + 2e^-(1)$	at the interphase 1/2,
$\mathrm{Cu^{2+}}(3) + 2e^-(4) \rightarrow \mathrm{Cu}(4)$	at the interphase 3/4,
$2e^-(1') \rightarrow 2e^-(4)$	at the interphase 4/1′.

We thus see why the electron does not appear in the cell reaction. It is, in fact, borrowed from, and restituted to the same chemical medium, the metal common to the two poles.

4.6. The *reaction charge* of the cell reaction, as well as the *number of charges transported* by the cell reaction, are defined as in *3.9*, the phases 1 and 2 becoming now the terminal phases 1 and 1′ of the cell.

4.7. The *electrochemical free enthalpy* of a cell reaction is equal to the sum of the electrochemical free enthalpies of the electrode reactions of which the cell reaction is the resultant (see *3.10* and *4.5*).

The *electrochemical affinity* of a cell reaction, equal to the latter quantity taken with the minus sign, is also equal to the sum of the electrochemical affinities of the electrode reactions of which the cell reaction is the resultant (see *3.11* and *4.5*).

$$-\Delta\tilde{G} = \tilde{A} = \mu^1_{\mathrm{Zn}} + \tilde{\mu}^3_{\mathrm{Cu^{2+}}} - \tilde{\mu}^2_{\mathrm{Zn^{2+}}} - \mu^4_{\mathrm{Cu}} + 2F(\varphi^1 - \varphi^{1'})$$

in which $\Delta\tilde{G}$ represents the electrochemical free enthalpy, $\tilde{A}$ the electrochemical affinity, μ a chemical potential, $\tilde{\mu}$ an electrochemical potential.

When the interphases 1/2, 3/4 and 4/1′ are all at electrochemical equilibrium, a situation which we shall consider as being the electrochemical

equilibrium of the cell, $\Delta\tilde{G}$ and $\tilde{A}$ are equal to zero and we have, in the case of our example, a cell tension said to be reversible and given by

$$U_{\text{rev.}} = (\varphi^1 - \varphi^{1'})_{\text{rev.}} = (\mu^2_{Zn^{2+}} + \mu^4_{Cu} - \mu^1_{Zn} - \mu^3_{Cu^{2+}})/2F + \varphi^2 - \varphi^3$$

The difference of electric potential $\varphi^2 - \varphi^3$ in the diffusion zone from liquid 2 to liquid 3 can sometimes be estimated and subtracted from the value $U_{\text{rev.}}$ of the above formula. It is also possible to diminish appreciably this difference of potential by interposing, between the two liquid phases, a concentrated solution of an electrolyte with ions of approximately the same mobility, for instance a saturated solution of potassium chloride. In the case of a galvanic cell with only one liquid phase the problem of the liquid junction obviously does not come up.

4.8. The *chemical free enthalpy* of a cell reaction is equal to the electrochemical free enthalpy of this cell reaction minus the sum of all terms of the form molar charge × inner electric potential.

The *chemical affinity* of a cell reaction, equal to the latter quantity taken with the minus sign, is also equal to the electrochemical affinity of this cell reaction minus the sum of all terms of the form molar charge × inner electric potential.

In the case of the example given in *4.5* we have:

$$-\Delta G = A = \mu^1_{Zn} + \mu^3_{Cu^{2+}} - \mu^2_{Zn^{2+}} - \mu^4_{Cu}$$

in which ΔG represents the chemical free enthalpy, A the chemical affinity.

At electrochemical equilibrium, i.e. at zero current, and neglecting the contribution $\varphi^2 - \varphi^3$ of the liquid junction or introducing an adequate correction, the reversible tension considered in *4.7* is written as

$$U_{\text{rev.}} = -A/2F$$

and we also have, in this case,

$$\tilde{A} = A + 2FU_{\text{rev.}} = 0$$

In general the *reversible tension* of a galvanic cell is equal to minus the chemical affinity of the cell reaction divided by the reaction charge.

Let us note that this relation is always valid, regardless of the direction in which the cell reaction is written: the inversion of this direction corresponds to a change of sign for both the chemical affinity and the reaction charge.

In general also, the zero electrochemical affinity corresponding to the case of electrochemical equilibrium is equal to the sum of the chemical affinity and of the product of the reaction charge by the reversible cell tension.

Away from equilibrium, i.e. with passage of current, the electrochemical affinity is equal to the sum of the chemical affinity and of the product of the reaction charge by the cell tension from which is subtracted the sum of the ohmic tensions establishing themselves from the first to the second face of each phase in the direction of their numbering.

4.9. As has been done in *3.14* for the case of an electrode reaction, we shall call the quotient, invariant in sign, of the electrochemical affinity of the cell reaction by the reaction charge the *electrochemical tension* of the cell.

In the case of the diagram of the Daniell cell chosen in *4.5* the electrochemical tension is positive (except in case the ratio of concentrations Cu^{2+}/Zn^{2+} were to be extremely small). In the case of the opposite diagram (Cu on the left, Zn on the right), the electrochemical tension would be negative. We thus see that a positive electrochemical tension represents the combined action of the chemical and electric forces tending to move, inside the cell, the positive charges in the direction 1, 2, 3 . . . 1′ of the numbering of the phases. At electrochemical equilibrium the chemical and electric forces balance each other and the electrochemical tension is equal to zero.

4.10. As has been done in *3.15* for the case of an electrode reaction, we shall call the quotient, invariant in sign, of the chemical affinity of the cell reaction by the reaction charge the *chemical tension* of the cell.

This chemical tension is identical with the quantity currently called *electromotive force* of the cell in the literature of physical chemistry, of thermodynamics and of electrochemistry. We consider the expression *chemical tension* as definitely preferable.

In the case of the diagram of the Daniell cell chosen in *4.5* the chemical tension is positive (except in case the ratio of concentrations Cu^{2+}/Zn^{2+} were to be extremely small). In the case of the opposite diagram (Cu on the left, Zn on the right), the chemical tension would be negative. We thus see that a positive chemical tension (or electromotive force) represents the action of the non-electric forces (i.e. the action of the chemical forces) tending to move, inside the cell, the positive charges in the direction 1, 2, 3 . . . 1′ of the numbering of the phases.

4.11. The *electric tension* of the cell is equal to the electrochemical tension minus the chemical tension*. At electrochemical equilibrium the electric tension is equal to minus the chemical tension.

In the case of the diagram of the Daniell cell chosen in *4.5* the electric tension is negative (except in case the ratio of concentrations Cu^{2+}/Zn^{2+} were to be extremely small). In the case of the opposite diagram (Cu on the left, Zn on the right), the electric tension would be positive. We may consider a positive electric tension as implying the existence of chemical forces tending to move, inside the cell, the positive charges in the direction opposite to that of the numbering of the phases, 1′, . . .3, 2, 1. The actual movement of the charges is due to the combined action of the electric and of the chemical forces, i.e. to the action of the electrochemical tension.

4.12. Let us go back to the case of the Daniell cell. It can be represented by one or the other of the following two diagrams:

$$(I)\ \begin{array}{c|c|c|c|c} Zn & Zn^{2+} & Cu^{2+} & Cu & Zn \\ 1 & 2 & 3 & 4 & 1' \end{array} \quad \text{or} \quad (II)\ \begin{array}{c|c|c|c|c} Cu & Cu^{2+} & Zn^{2+} & Zn & Cu \\ 1 & 2 & 3 & 4 & 1' \end{array}$$

The cell reaction can be written under one or the other of the following two forms:

$$(a)\ Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \quad \text{or} \quad (b)\ Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$$

* A correction should eventually be introduced for the ohmic tensions, as indicated in *4.8*. The difference electrochemical tension minus chemical tensions is equal to the electric tension minus the sum of the ohmic tensions establishing themselves from the first to the second face of each phase, in the direction of their numbering.

The numbers of charges transported are:

$$n_{Ia} = +2, \quad n_{IIa} = -2, \quad n_{Ib} = -2, \quad n_{IIb} = +2$$

The chemical affinities and chemical free enthalpies of reactions a and b are connected by the following relations:

$$A_a = -\Delta G_a = -A_b = +\Delta G_b$$

The chemical tension (or electromotive force) corresponding to diagram I is given by the four ratios

$$E_I = (+A_a)/(+2F) = (-\Delta G_a)/(+2F) = (+A_b)/(-2F) = (-\Delta G_b)/(-2F)$$

while the reversible electric tension corresponding to diagram I is given by the four ratios

$$U_{I\,\mathrm{rev.}} = (-A_a)/(+2F) = (+\Delta G_a)/(+2F) = (-A_b)/(-2F) = (+\Delta G_b)/(-2F)$$

The chemical tension (or electromotive force) corresponding to diagram II is given by the four ratios

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

while the reversible electric tension corresponding to diagram II is given by the four ratios

$$U_{II\,\mathrm{rev.}} = (-A_a)/(-2F) = (+\Delta G_a)/(-2F) = (-A_b)/(+2F) = (+\Delta G_b)/(+2F)$$

We do indeed verify that

$$U_{I\,\mathrm{rev.}} + E_I = 0 \quad \text{and} \quad U_{II\,\mathrm{rev.}} + E_{II} = 0$$

Away from equilibrium, but at given temperature, pressure and chemical composition, the chemical tension (or electromotive force) keeps the same value as at equilibrium, while the electric tension departs from its reversible or equilibrium value in a direction depending on the direction of the current passing through the cell. If the direction of the current is that corresponding to the spontaneous direction of the cell reaction, the absolute value of the electric tension is smaller than the absolute value of the reversible electric tension. If the direction of the current is that corresponding to the non-spontaneous direction of the cell reaction, the absolute value of the electric tension is greater than the absolute value of the reversible electric tension.

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

It is often considered as practical, once the positive pole of the cell has been explicitly designated, to use only the arithmetic value of the electromotive force of the cell or, as is then equivalent, that of its reversible electric tension.

4.13. It is easily proved that the electric tension $U = \varphi^1 - \varphi^{1'}$ of a galvanic cell 1, 2, 3, 4, 1', of which the metallic phase 4 is different from the chemically

identical metallic phases 1 and 1′, is equal to the electrochemical potential of the electron in phase 4 decreased by the electrochemical potential of the electron in phase 1 and divided by one faraday.

We have indeed:

$$U = \varphi^1 - \varphi^{1'} = (\tilde{\mu}_{e^-}^{1'} - \tilde{\mu}_{e^-}^{1})/F$$

since

$$\mu_{e^-}^{1} = \mu_{e^-}^{1'}$$

At the intermetallic contact 4/1′ we always have electrochemical equilibrium with respect to electron transfer and we thus have:

$$\tilde{\mu}_{e^-}^{1'} = \tilde{\mu}_{e^-}^{4}$$

It then follows that

$$U = (\tilde{\mu}_{e^-}^{4} - \tilde{\mu}_{e^-}^{1})/F$$

Let us now consider the passage of the electron from 4 to 1 through 1′ and a metallic wire connecting 1′ to 1. As in *3.14* we may define here an *electrochemical tension* equal to the quotient of the electrochemical affinity of this electron transfer by the reaction charge, here equal to minus one faraday. This electrochemical tension U' is equal to minus the electric tension U of the galvanic cell:

$$U' = (\tilde{\mu}_{e^-}^{4} - \tilde{\mu}_{e^-}^{1})/(-F) = -U$$

At electrochemical equilibrium this electrochemical tension U' is thus equal to the chemical tension (or electromotive force) of the cell, but U' remains equal to $-U$ away from equilibrium.

If the electrochemical tension U' is positive, electrons will pass from 1 to 4 through the wire and 1′. In other words, the positive current will pass from 4 to 1 through 1′ and the wire. The opposite will be the case when the electrochemical tension U' is negative.

4.14. The *relative electric tension of an electrode* is the electric tension of a galvanic cell consisting of the following phases: 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 electric tension from the first solution to the second being subtracted from the total electric tension of the cell.

This quantity is rigorously accessible to measurement in the exceptional 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 tension of the cell consisting of the following phases: the electrode under study, the metal of which consitutes the first pole, the solution of the reference electrode, the metal of the reference electrode, and finally the second pole of the same metal as that of the electrode under study.

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 tension. 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.

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

After specification of the type of concentration to be used (molarity, molality or mole fraction), a *standard state* is chosen for each dissolved constituent in such a manner that its chemical potential is then numerically equal to the constant of the linear relation which, at the same temperature and total 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.

4.16. The *standard electric tension of an electrode* (or *standard electrode potential*) is the equilibrium value of the relative electric tension of the electrode 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 value of a standard electrode potential depends on the unit chosen for concentrations and of the choice of the reference electrode. The difference between the electrode potentials of identical electrodes dipping in aqueous solutions of which one has a molarity m and the other a molality m with respect to a potential-determining constituent is of the order of a few tenths of a millivolt in the case of dilute aqueous solutions.

Knowledge of the standard electrode potential enables the electrode under consideration to be placed in the *electrochemical series* (or *series of tensions*).

4.17. 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.

A standard electrode potential is actually a combination of standard chemical potentials divided by the reaction charge and its value can be obtained rigorously by extrapolation to infinite dilution.

4.18. When the reference electrode is the standard hydrogen electrode the *relative electric tension of an electrode* defined in *4.14* is also called *relative electrode*

potential, or more briefly *electrode potential*. In the case of equilibrium this quantity is identical with that defined under the same name by the International Union of Pure and Applied Chemistry ((I.U.P.A.C.), Stockholm recommendations, 1953, text revised by the Commission of Electrochemistry at Madrid, 1956, and at Paris, 1957).

In the case of the $Zn|Zn^{2+}$ electrode, for instance, the *relative electric tension* is the electric tension of the cell

$$(I)\ \begin{array}{c|c|c|c|c|c|c} Zn & Zn^{2+} & H^+(a_{H^+}=1) & H_2(p_{H_2}=1), & Pt & Zn \\ 1 & 2 & 3 & 4 & & 1' \end{array}$$

while the *electrode potential* is defined in the I.U.P.A.C. recommendations as being the electromotive force of the cell

$$(II)\ \begin{array}{c|c|c|c|c|c|c} Pt, & H_2(p_{H_2}=1) & H^+(a_{H^+}=1) & Zn^{2+} & Zn & Pt \\ 1 & & 2 & 3 & 4 & 1' \end{array}$$

It is clear that at electrochemical equilibrium these two quantities are identical:

$$U_{I\,rev.} \equiv E_{II}$$

Away from equilibrium the electric tension and the electrode potential remain identical to each other but they are not any more equal to E_{II}.

Our definition of the relative electric tension automatically implies the use of the so-called 'European' signs (noble tensions positive, so-called 'reduction' potentials). The arrangement with the first pole attached to the reference electrode and the second pole consisting of the metal of the electrode under study, which is opposite to that described in *4.14*, would automatically lead to the use of the so-called 'American' signs (noble tensions negative, so-called 'oxidation' potentials).

4.19. The reversible or equilibrium values of the relative electric tensions with so-called 'European' signs are equal to the chemical affinities of the reactions (of cells *I* and *II* above, for instance) written in the direction of reduction, by 1/2 H_2 at $p_{H_2}=1$ atmosphere becoming H^+ at $a_{H^+}=1$, divided by one faraday:

$$1/2\ Zn^{2+} + 1/2\ H_2 \rightarrow 1/2\ Zn + H^+ \qquad A/F = U_{rev.\ Eur.}$$

The quantities improperly called 'reduction potentials' are thus *reduction affinities* referred to the unit of charge. In the practical system they are thus expressed in volts.

Similarly, the reversible or equilibrium values of the relative electric tensions with so-called 'American' signs are equal to the chemical affinities of the reactions (of cells I and II above for instance) written in the direction of oxidation, by H^+ at $a_{H^+}=1$ becoming 1/2 H_2 at $p_{H2}=1$ atmosphere, divided by one faraday:

$$1/2\ Zn + H^+ \rightarrow 1/2\ Zn^{2+} + 1/2\ H_2 \qquad A/F = U_{rev.,\ Amer.}$$

The quantities improperly called 'oxidation potentials' are thus *oxidation affinities* referred to the unit of charge. In the practical system they are thus expressed in volts.

5. Kinetics of electrode reactions and polarization phenomena

5.1. At a *simple electrode* (see *3.19*) 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 *3.21*).

5.2. At a *polyelectrode* (see *3.20*) 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.

The total or partial currents are positive when the positive charges corresponding to these currents move in the direction given by the numbering of the phases.

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 is known (from measurements 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* 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 concentrations of the reacting species (concentrations in the bulk of the solution or concentrations in certain superficial layers according to cases) raised to the powers required by the order of the reaction.

The units will be related as follows:

$$\begin{aligned}\text{Current density} &= (\text{charge per unit of advancement or reaction charge}) \times (\text{advancement}) \times (\text{length})^{-2} \times (\text{time})^{-1},\\ &= (\text{charge}) \times (\text{length})^{-2} \times (\text{time})^{-1}.\\ \text{Reaction rate density} &= (\text{advancement}) \times (\text{length})^{-2} \times (\text{time})^{-1}\\ &= (\text{reaction rate constant}) \times (\text{concentration})^{n}.\end{aligned}$$

At given temperature and pressure these electrochemical reaction rate constants depend on the Galvani electric tensions at the interphase regions at which these reactions take place. They include the activity coefficients of the reacting species and of the activated complex, and, therefore, they are not necessarily independent of composition.

The above does not apply to reactions controlled by diffusion.

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

and the reaction itself is said to be cathodic. When this electrode reaction transfers a negative charge to the metal of the electrode, the corresponding current is designated as *anodic* and the reaction itself is said to be anodic.

In the same manner we may speak of the *cathodic component* and of the *anodic component* of an electrode reaction. For instance, if we consider the forward and reverse components (see *5.1*) of a cathodic reaction, the forward component will be cathodic and the reverse component anodic.

In metal–solution systems (metal = phase 1, solution = phase 2) anodic or partial anodic currents are positive, cathodic or partial cathodic 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 to 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 tensions or potentials (and of electric tensions of galvanic cells) from their values at zero net current.

Polarization is said to be *anodic* when the electrode tension is higher than its value at zero current (the electrode being considered as a metal–solution system).

Polarization is said to be *cathodic* when the electrode tension is lower than its value at zero current (the electrode being considered as a metal–solution system).

This electrochemical polarization should not be confused with the polarization of dielectrics.

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

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

Similarly, after interruption of the stationary current, it is possible to determine, for the instant of interruption, the slope of the curve representing the decrease of the electrode tension 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 *overtension* (or *overvoltage*, or *overpotential*) of this reaction on this electrode, at a given instant, is equal to the electrode tension under current minus the reversible electrode tension corresponding to this reaction.

As has been explained in *4.14*, the electric tension of an electrode is obtained by measuring the electric tension of a cell, which we shall call

tensiometric cell to distinguish it from that which is the seat of the current, where the electrode under study corresponds to the left-hand phases 1/2 and the reference electrode to the right-hand phases 3/4 of this tensiometric cell. The electrode under study is thus always a metal–solution system in the tensiometric cell. Consequently, any overtension of this electrode due to an anodic polarization will be positive, and any overtension of this electrode due to a cathodic polarization will be negative (see *5.8*).

If the electrode under study is also the left-hand electrode 1/2 of the cell which is the seat of the current, its electrochemical tension, defined in *3.14*, being equal to the electric tension 1/2 minus the reversible value of this electric tension (equal to minus its chemical tension or electromotive force), is identical with the overtension of this electrode, in magnitude and in sign.

If, on the contrary, the electrode under study is the right-hand electrode 3/4 of the cell which is the seat of the current, its electrochemical tension, defined in *3.14*, being equal to the electric tension 3/4 minus the reversible value of this electric tension, is equal in absolute value to the overtension, but is of opposite sign to the overtension.

We thus have two types of quantities to express quantitatively the polarization of an electrode: the overtension, which is always positive in the case of an anodic polarization and always negative in the case of a cathodic polarization, and the electrochemical tension, which is positive in the case of an anodic polarization of a metal–solution electrode and in that of a cathodic polarization of a solution–metal electrode, and negative in the case of a cathodic polarization of a metal–solution electrode and in that of an anodic polarization of a solution–metal electrode, the two quantities, overtension and electrochemical tension being thus always identical in absolute values.*

5.11. If several electrode reactions with distinct values of their reversible electrode tensions occur simultaneously at the same electrode, the electric tension of this electrode is called *mixed electrode tension.*

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

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

5.13. The quotient of the overtension by the current or partial current density corresponding to the reaction is called *overtension resistance per unit area.*

5.14. The quotient of the excess tension by the current density is called *excess tension resistance per unit area.*

5.15. The *differential resistance per unit area* of an electrode reaction is the

* The last four paragraphs of *5.10* represent a personal contribution of the chairman, P. Van Rysselberghe. It has been found impossible to reach complete agreement between all members of the Commission within the available deadlines. It should also be noted that the various uses of the word 'tension' in the present report exactly correspond to the uses of the same word in the French text and to the German word 'Spannung' and should be regarded as suggestions made by the chairman with the approval of at least a few members of the Commission.

derivative of the stationary overtension of that reaction with respect to the corresponding current or partial current density.

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

5.16. The *activation overtension* of an electrode reaction taking place at a simple electrode is the overtension defined in *5.10* when the rate of this electrode reaction is controlled exclusively by an electrochemical step (i.e. neither by diffusion nor by non-reactional resistances).

5.17. When the activation overtension 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 under the form $RT/\alpha F$, the parameter α is called *transfer coefficient.*

We have $\alpha = \beta n/\gamma$ in which β is a symmetry coefficient, n is the number of charges transported (see *3.9*) and γ is the number of occurrences of the rate-determining step corresponding to one occurrence of the over-all reaction.

5.18. The *electrochemical free enthalpy of activation* of an electrode reaction at a certain electrode tension is the electrochemical free enthalpy of activation at equilibrium plus the product of the following three factors: the overtension, the transfer coefficient and the faraday.

This definition and the following 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 electrode tension is the electrochemical enthalpy of activation of this reaction at equilibrium plus 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 electrode tension as at equilibrium.

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

5.21. The *concentration overtension* of an electrode reaction taking place at a simple electrode is the overtension 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 overtension reached with time under any condition of agitation is called the *stationary concentration overtension.*

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 overtension* of an electrode reaction taking place at a simple electrode is the overtension 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 overtension is often due to a resistant layer on the electrode surface.

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

5.24. A *simple electrode* is said to be *reversible* when any overtension, however small it may be, is accompanied by a total current *different from zero.*

If, on the contrary, a small overtension produces no current, the electrode is said to be *indifferent.*

In practice, the distinction between a reversible and an indifferent electrode is gradual and depends on the minimum or detectable values of the overtension and of the current densities.

From the kinetic point of view the determination of the exchange currents at equilibrium makes possible the estimation of the degree of reversibility of an electrode: the greater the exchange currents, the closer is the electrode to reversibility.

From the thermodynamic point of view a reversible simple electrode is an electrode for which the state of electrochemical equilibrium is a state of true equilibrium, whereas an indifferent simple electrode is an electrode capable of remaining in a state of non-equilibrium.

We should note that, as soon as the density of the total current becomes different from zero, the reversible electrode becomes the seat of *irreversible phenomena,* as is the case with any system evolving outside of its state of equilibrium.

5.25. With a *multiple electrode* reversibility must be examined with respect to every one of the reactions which are possible at that electrode.

A *multiple electrode* is *reversible with respect to one electrode reaction* when, its electric tension being brought to a value slightly different from the equilibrium tension of this reaction, the reaction is made to advance with a velocity *different from zero.*

A multiple electrode may be *reversible* with respect to one reaction and *indifferent* with respect to another reaction. For instance, a polished platinum electrode dipping in a solution containing the ions H^+, Fe^{2+}, Fe^{3+} ... may be reversible with respect to the reaction $Fe^{2+} \rightarrow Fe^{3+} + e^-$, and indifferent with respect to the reaction $2H^+ + 2e^- \rightarrow H_2$.

Finally, a multiple electrode may be indifferent with respect to all the reactions which are ultimately possible at that electrode.

5.26. The electric tension of a simple electrode at which the density of an anodic polarization current is equal to the sensitivity of its own measurement (for instance 10^{-8} ampere/cm^2) may be called *oxidation tension* for the specified sensitivity.

The electric tension of a simple electrode at which the density of a cathodic polarization current is equal to the sensitivity of its own measurement (for instance 10^{-8} ampere/cm^2) may be called *reduction tension* for the specified sensitivity.

In the case of a simple indifferent electrode (see 5.24) the oxidation tension so defined is higher and the reduction tension so defined is lower than the theoretical reversible tension of this simple electrode.

In the limiting case of a reversible simple electrode (see 5.24) the oxidation and reduction tensions corresponding to a minimum detectable current

coincide. Their common value is then the *oxidation-reduction tension* or *redox tension*, which is thus a reversible or equilibrium tension.

These definitions also apply to each of the reactions of a multiple electrode.

6. Corrosion

A group of definitions pertaining to corrosion in its relations with electrochemistry, adopted provisionally at Madrid in 1956 and revised at Paris in 1957, will form the object of a separate report after agreement will have been obtained with the members of C.I.T.C.E. specially concerned with corrosion.

Earlier stages of the present report have been published or distributed as follows:

2nd meeting, Milan, September 1950: *Proceedings of the 2nd meeting of C.I.T.C.E.*, Tamburini, Milan, 1951, p. 315 (in French).

3rd meeting, Bern, August 1951: *Proceedings of the 3rd meeting of C.I.T.C.E.*, Manfredi, Milan, 1952, p. 409 (in French).

4th meeting, London and Cambridge, September 1952: multigraphed (in English and French).

5th meeting, Stockholm, August 1953: multigraphed (in English and French). German translation by E. Lange: *Z. Elektrochem.*, 58 (1954) 530

6th meeting, Royaumont and Poitiers, September 1954: *Proceedings of the 6th meeting of C.I.T.C.E.*, Butterworths, London, 1955, p. 20 (in English and French). Japanese translation by G. Okamoto and M. Nagayama, *J. Electrochem. Soc. Japan*, 23 (1955) 465.

7th meeting, Lindau, July 1955: multigraphed (in English and French). Comments by G. Valensi: *Proceedings of the 7th meeting of C.I.T.C.E.*, Butterworths, London, 1957, p. 163 (in English).

8th meeting, Madrid, September 1956. *Proceedings of the 8th meeting of C.I.T.C.E.*, Butterworths, London, 1958, p. 18 (in English and French). Portuguese translation by I. Jordan: *Boletim do Departamento de Química*, Escola Politécnica da Universidade de São Paulo, no. 6, (1957) p. 1.