

THE ELECTRODE POTENTIAL CONCEPT REVISITED

M. Luísa P. Leitão

Departamento de Química , Universidade de Coimbra, Portugal

ABSTRACT

The concepts of absolute and relative electrode potential and their relationship to the structure of the metal/electrolyte interface are presented. The necessity of distinguishing between electrode potential and electromotive force of a half-cell reaction, particularly in teaching, is highlighted. It is shown that electrode potential should be the concept recommended for defining the electrode interface potential drop.

KEY WORDS - Metal/electrolyte interface, electrode potential, electromotive force, galvanic cell

INTRODUCTION

It is always surprising the number of students even of advanced courses who have no sound knowledge of important basic everyday, chemical concepts. An apparent acquaintance with such concepts comes, very often, from routine applications which may mask the inability to understand the underlying scientific basis.

Many reasons can be ascribed to account for such situations for example: the lack of adaptation of teaching methodologies to the scientific level of the students leading to an incomplete understanding of the fundamental principles of the subject, more emphasis being placed on practical uses of the topics rather than on their fundamental bases, no links being given between the subjects taught, and lack of concern of teachers about a gradual development of the knowledge of the different topics. Whatever the reasons, it is important that teachers should pay attention to this sort of situations.

Concept of the electrode potential is a good example of a subject that the students rarely get familiar with and it is quite common to find graduates with a

very unsatisfactory understanding of important aspects of this area. Although this is a topic that has been exhaustively discussed, its presentation in articles, even in specialised textbooks, often does not help the reader to get correct ideas.

This article tries to call attention to the situation, in particular the need to be clear about terms, conventions and concepts when introducing the material. As the article is primarily aimed at undergraduate students, some of the details will already be familiar to specialists in this area.

STRUCTURAL ASPECTS OF THE METAL - ELECTROLYTE INTERFACE

Let us start by considering the interface formed when a piece of metal, M, is dipped into a solution of its metal ions, M^{z+} . Some ions can leave the metal phase and pass to the solution, whilst at same time some cations pass from the solution to the metal. The ions leaving the metal set up a negative charge on the surface while a positive charge is created as ions flow from the solution to the solid phase.

Increasing the metal/solution potential difference tends to equalize the rate of flow of ions between the two phases until equilibrium is finally achieved. The metal will then be positively or negatively charged relative to the solution phase according to the relative amount of matter transferred. The magnitude and sign of the electric charge on the metal depend on the nature of the system involved as well as on the ionic activity in the solution.

The electric charge set up on the metal surface will influence ion distribution in the surrounding solution, attracting ions of opposite charge and pushing out those of the same charge, thus giving rise to an electrochemical double layer, which extends from the surface into the solution over a distance of a few molecular diameters. The potential difference, $\Delta\psi$, caused by this charge is called the *outer potential*, or *Volta potential*. In polar solvents, there is a monolayer of oriented solvent molecules adsorbed at the surface, independent of the charge of the metal, giving rise to a potential drop called the *surface potential*, usually denoted by $\Delta\chi$. The potential difference $\Delta\phi$ between two points in the bulk of the two adjoined phases, the *inner* or *Galvani potential*, is the sum of the two kinds of potential just described¹

$$\Delta\phi = \Delta\psi + \Delta\chi \quad (1)$$

Whilst the outer potential can be measured or determined, it is difficult to determine the surface potential either experimentally or theoretically. Hence in principle, $\Delta\phi$, is not a measurable quantity.

In this context a simplified model of the electrochemical double layer is sufficient. Fig. 1 shows some features of the electrochemical double layer formed at an electrode interface²⁻⁴.

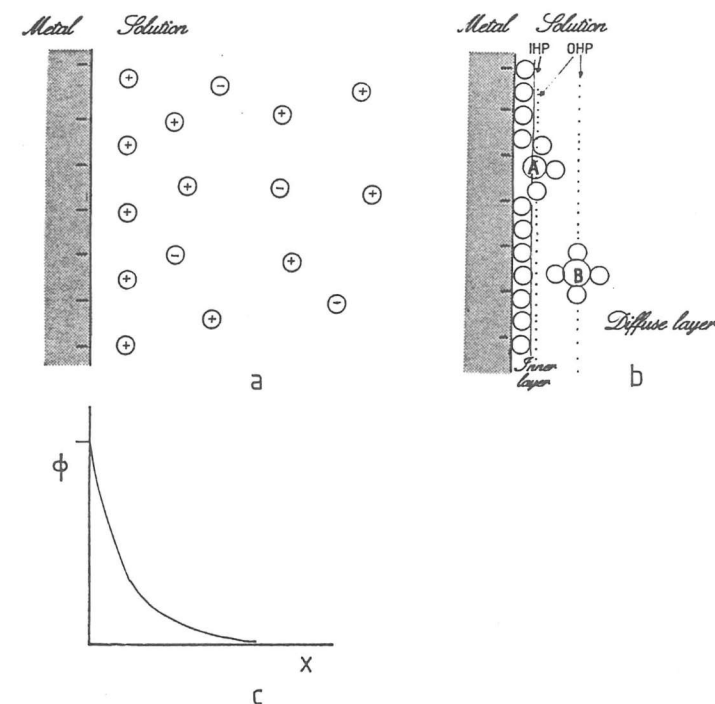


Fig 1. Electrochemical double layer. a) The Stern model for the metal/electrolyte solution interface; b) Two possibilities for the distance of closest approach: ion A is strongly adsorbed, losing some hydration water, and penetrating into the inner region; ion B is not so strongly adsorbed, keeping its hydration shell, and not penetrating into the inner region; c) Electric potential vs distance at an electrode interface.

An equation relating the electrode potential to the nature of the electrochemical system and to ion activity in solution can easily be obtained from thermodynamics.

The variation of the Gibbs energy on adding dn_i moles of a charged species to a phase α is given by

$$dG(\alpha) = -S(\alpha) dT + V(\alpha) dP + \mu_i(\alpha) dn_i + z_i \phi(\alpha) dn_i \quad (2)$$

$\mu_i(\alpha)$ is the chemical potential of the species in the phase α , z_i the ionic charge, $\phi(\alpha)$ the Galvani potential of the phase α ; other symbols have their normal meaning. The last term of the right-hand side of equation (2) is the electrical energy introduced into the phase due to the mass increment dn_i . Thus, in electrochemical systems an electrostatic energy term should be added to the normal chemical potential that can be done by using the *electrochemical potential* which contains both the "chemical" and "electrical" contribution. The electrochemical potential, $\tilde{\mu}_i$, introduced initially by Guggenheim, is defined by the following equation⁵

$$\tilde{\mu}_i = \mu_i + z_i F \phi \quad (3)$$

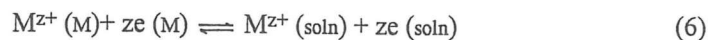
Equation (2) can then be written in the following form

$$dG(\alpha) = -S(\alpha) dT + V(\alpha) dP + \tilde{\mu}_i(\alpha) dn_i \quad (4)$$

At constant T and P, the equilibrium condition between two phases is expressed by

$$\tilde{\mu}_i(\alpha) = \tilde{\mu}_i(\beta) \quad (5)$$

For the reversible metal/solution interface under consideration, equation (5) yields



The equilibrium conditions may be formulated by one of the following equations

$$\tilde{\mu}_{M^{z+}}(M) = \tilde{\mu}_{M^{z+}}(\text{soln}) \quad (6a)$$

or

$$\tilde{\mu}_e(M) = \tilde{\mu}_e(\text{soln}) \quad (6b)$$

Although electrons are not intrinsic components of a solution they can exist in this phase upon contact with, for example, a metal, and provide charges of opposite sign to ensure electroneutrality. In certain polar solvents solvated electrons can even be stabilized⁶.

Applying (3) to equation (6a) or (6b), an expression for Galvani potential difference is obtained

$$\phi(M) - \phi(\text{soln}) = \Delta_S^M \phi = \frac{1}{zF} [\mu_{M^{z+}}(\text{soln}) - \mu_{M^{z+}}(M)] \quad (7a)$$

$$\Delta_S^M \phi = \frac{1}{zF} [\mu_e(M) - \mu_e(\text{soln})] \quad (7b)$$

To see how $\Delta_S^M \phi$ depends on the ion activity in solution let us take equation (7a). Bearing in mind the equilibrium between atoms and ions, an equilibrium inside the metal may be considered, which can be written as

$$\mu_{M^{z+}}(M) = \mu_M(M) + z \mu_e(M) \quad (8)$$

Expression (7a) is then written in the form

$$\Delta_S^M \phi = \frac{1}{zF} [\mu_{z+}(\text{soln}) - \mu_M(M) + z \mu_e(M)] \quad (9)$$

The chemical potential of a given component is related to its activity, a_i , by the general equation

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (10)$$

μ_i^0 is the standard chemical potential *i.e.* the state corresponding to $a_i = 1$.

Introducing the activity coefficient into (10), the equation becomes

$$\mu_i = \mu_i^0 + RT \ln c_i + RT \ln \gamma_i \quad (10a)$$

where c_i is the concentration and γ_i the activity coefficient. To find μ_i^0 we need to adopt a *reference state*, *i.e.* the state corresponding to $\gamma_i = 1$, and in a next step to define a *standard state*, $a_i = 1$.

For the metal phase, the concentration can be expressed in atom mole fraction and for the reference state the pure metal is commonly considered. In such conditions as $a_i = x_i$ γ_i standard and reference states are coincident. μ_M in equation (9) is then reduced to the chemical potential of pure metal, $\mu_M^0(M)$ and $\mu_e(M) = 0$.

For ions in solution the reference state commonly adopted is infinite dilution and the concentration is usually expressed in the molality scale. Thus, the standard state is defined by $m_i = 1$ and $\gamma_i = 1$, which corresponds to a fictitious situation, with a solution following Henry's law at molality equal to one (Fig. 2).

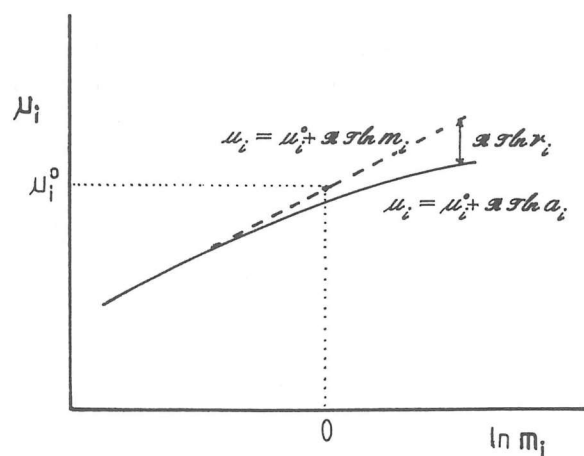


Fig. 2. The standard chemical potential for an ion in solution when the reference state is the solution at limiting null concentration.

With the symbols defined as above, the chemical potential of M^{z+} in solution is given by

$$\mu_{M^{z+}}(\text{soln}) = \mu_{M^{z+}}^0(\text{soln}) + RT \ln a_{M^{z+}}(\text{soln}) \quad (11)$$

Introducing the chemical potential of M^{z+} given by (11) into (9), the metal/solution potential difference is given as

$$\Delta_S^M \phi = \frac{1}{ZF} [\mu_{M^{z+}}^0(\text{soln}) - \mu_{M^{z+}}^0(M)] + \frac{RT}{ZF} \ln a_{M^{z+}}(\text{soln}) \quad (12)$$

If $\Delta_S^M \phi$ could be determined, it would give a straightforward physical description of the interface, and be a very useful property. However this is not possible, and so cannot be used in measuring the metal/solution potential drop.

ELECTRODE POTENTIAL

It is not possible to measure directly a metal/solution potential difference because the terminal of the measuring instrument would inevitably produce a new interface as soon as dipped into the solution, and form a cell consisting of the electrode under study and the potentiometer terminal. The reading would then be the electromotive force of that cell instead the electrode potential of interest. An alternative method is to compare the metal/solution interface with another interface taken as reference. The electrode potential reference universally adopted is the Standard Hydrogen Electrode, SHE, consisting of a piece of an inert metal, such as platinum, dipped into a solution saturated with hydrogen, $f_{H_2} = 1$ and $a_{H^+} = 1$. The electrode potential is determined from the electromotive force of the cell formed by the actual electrode and SHE.

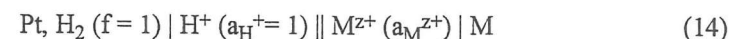
According to a general convention, the electromotive force of a galvanic cell, E , is equal to the potential of the right-hand terminal minus that of the left-hand side in open circuit.

$$E = \varepsilon_R - \varepsilon_L \quad (13)$$

It must be noted that the convention has nothing to do with the way that the cell is assembled in the laboratory but rather with its representation in a diagram.

According to the above conventions, $E > 0$ when the electrons are generated at the interface of the electrode on the left and flow through the external circuit towards the right. The polarity of electrode on the left is (-) and that of the right is (+). Inside the solution, positive ions move from left to right and negative ions in the opposite direction.

In order to have $\varepsilon(M, M^{z+}) = E$, SHE should be on the left and the electrode under study on the right in the cell diagram. Thus the cell should be depicted as



The double bar means that no liquid junction exists, or if there is any, the corresponding diffusion potential is negligible.

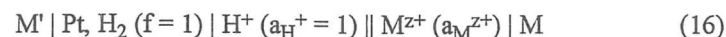
The electromotive force of (14) is

$$E = \varepsilon(M, M^{z+}) - \varepsilon^{\circ}(\text{SHE}) \quad (15)$$

As $\varepsilon^{\circ}(\text{SHE})$ is made equal to zero, $\varepsilon(M, M^{z+}) = E$ both in magnitude and in sign. Equation (15) defines the *relative electrode potential*, normally just called the *electrode potential*.

The electromotive force of a cell in whose diagram the left-hand side is SHE and the right-hand side is the actual electrode may be called *electromotive force of the half-cell*. Thus, the *electrode* is identified with the half-cell and the electrode potential with the electromotive force of the half-cell, provided this is defined as above. The *electrode* is frequently understood as the piece of the metal dipped into a half-cell^{4,7}.

In real cells, electronic conductors are employed for connecting the terminals to the measuring instrument. At least one piece of metal is required for connecting the reference electrode terminal to the potentiometer. This can best be accomplished using a piece of metal M, so that both terminals have the same composition. Thus, instead of the cell described above, the electrode potential determination is carried out with the following cell



The prime denotes the difference in the electrical state of the metal M at the two terminals.

When two dissimilar metals are in contact a potential drop is generated once the electrons are free to move from one metal to the other. Equalizing the electrochemical potentials of the electron in both phases we obtain for $\Delta\phi$ at the boundary of the two adjoined metals

$$\Delta_{\text{M}}^{\text{Pt}}\phi = \mu_e(\text{Pt}) - \mu_e(\text{M}) \quad (17)$$

It is worth noting that E for cell (15) is in reality the sum of three Galvani potential differences

$$E = \Delta_{\text{S}}^{\text{M}}\phi + \Delta_{\text{Pt}}^{\text{S}}\phi + \Delta_{\text{M}}^{\text{Pt}}\phi \quad (18)$$

Equation (18) can be arranged as follows:

$$E = [\Delta_{\text{S}}^{\text{M}}\phi + \mu_e(\text{M})] - [\Delta_{\text{S}}^{\text{Pt}}\phi + \mu_e(\text{Pt})]$$

We can arbitrarily consider $\varepsilon(M, M^{z+})$ to be given by the first term of the right-hand side of the equation, making the second term equal to zero. Obviously the electrode potential is still unambiguously given by equation (15).

Tables of standard potentials for a large number of electrodes defined by equation (15) are available. Negative values mean that species are stronger reducing agents than hydrogen and positive values are assigned to the species more strongly oxidizing than H^+ .

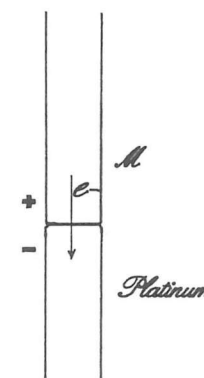


Fig. 3. Electric potential drop at the metal M/platinum boundary

ABSOLUTE ELECTRODE POTENTIAL

The majority of electrochemical processes are interpreted in terms of relative electrode potentials for chemical reactions resulting from electron transfer from one of the substances behaving as an electron donor and the other as an acceptor. Thus, only the difference in the electrode potential of the couples involved is required. However, as well as having relative values for electrode potentials, it is also makes sense to consider their absolute values. It is not just for logical reasons only that the absolute electrode potential concept is required. It is worthwhile to remember that the relative electrode potential lacks structural meaning because in making $\varepsilon^{\circ}(\text{SHE}) = 0$ a purely arbitrary convention is introduced. To interpret research data in some fields of electrochemistry and solid-state physics, values of absolute potentials are necessary. Therefore, for theoretical and practical reasons the concept of absolute potential is important, as has been discussed by many authors⁸⁻¹⁵.

One of the problems concerning the absolute value of electrode potentials is the reference level chosen. Much discussion has arisen around this subject. The absolute potential may be defined as that corresponding to the work involved in

taking an electron from the bulk of the metal to a convenient reference state, which may be the "free" electron in solution, the inner potential of the solution, a point in vacuum close to the surface of the solution or any other state which seems to be convenient. Whilst, obviously, a second interface as reference state for the concept of absolute electrode potential is ruled out, the most convenient reference level, as well as the applicability of the term, are still open questions.

A second point to bear in mind when working out an expression for the absolute potential is that it should be calculable from available results for processes related to the interface.

For some authors, $\Delta_S^M \phi$ is regarded as an absolute potential, whereas some others disagree. As this does not involve any a second interface it could be considered as a possible candidate. However, its reference is the solution which then makes it dependent on the nature of the solution.

Adopting as reference a point in a vacuum close to the solution surface, Trasatti¹⁶ derived the following equation for the absolute electrode potential

$$\varepsilon_M(\text{abs}) = \Delta_S^M \phi - \frac{\mu_e(M)}{F} + \chi_s \quad (19)$$

Introducing the electron work function, Φ , in eq (19), this can be written as

$$\varepsilon_M(\text{abs}) = \Phi_M + \Delta_S^M \psi \quad (20)$$

Φ_M is the *electron work function*, that is, the minimum energy required to extract electrons from the metal and $\Delta_S^M \psi$ is the metal/solution Volta potential.

An estimate of $\varepsilon(M, M^{z+})_{\text{abs}}$ can be obtained using (20), or from thermodynamic quantities related to the processes which take place at the electrode interface. The Gibbs energy corresponding to the electrochemical reaction $M \rightleftharpoons M^{z+} + ze$ can be calculated from the following thermodynamic cycle

$$\Delta_{\text{el}}^{\circ} G = \Delta_{\text{at}}^{\circ} G + \Delta_{\text{ion}}^{\circ} G + \Delta_{\text{hyd}}^{\circ} G + \mu_e(\text{Pt}) \quad (21)$$

Subscripts "el", "at", "ion" e "hyd" mean electrochemical, atomization, ionization and hydration process, respectively.

From $\Delta_{\text{el}}^{\circ} G$ the electrode potential is obtained

$$\varepsilon^{\circ}(M, M^{z+})_{\text{abs}} = (1/zF) \Delta_{\text{el}}^{\circ} G \quad (22)$$

If the value of $\varepsilon_{\text{SHE}}^{\circ}(\text{abs})$ could be calculated, an absolute electrode potential scale can be established. Trasatti obtained a value for SHE ($4,44 \pm 0,02$) V, a figure which is within the range of those estimated by other authors¹⁶⁻¹⁹. The relation between the relative and the absolute electrode potential scale is therefore

$$\varepsilon^{\circ}(\text{abs}) = \varepsilon^{\circ}(\text{rel}) + 4,44 \text{ V} \quad (23)$$

The use of an absolute electrode potential is restricted to specific cases. Since the uncertainty of 20 mV ascribed to $\varepsilon_{\text{SHE}}^{\circ}(\text{abs})$ is far higher than that affecting the relative electrode potentials, no advantage comes from using the absolute scale in general practice.

ELECTROMOTIVE FORCE OF A HALF-REACTION

A galvanic cell is a device that generates electrical energy from a chemical reaction taking place at the electrodes. The reaction can be considered as being broken down into two processes occurring at each electrode or half-cell called *half-reactions*. For the cell represented in the diagram (16), to define the electrode potential the half-reactions are



The reaction corresponding to overall process is



Separating electrons from all other components the equilibrium condition of (26) may be expressed as

$$\sum v_i \tilde{\mu}_i = \sum v_e \tilde{\mu}_e + \sum v_j \tilde{\mu}_j = 0 \quad (27)$$

where v_i are the stoichiometric coefficients of the components involved in the reaction.

When all charged chemical components involved in a reaction occurring in the same phase, the following relation can be written

$$\sum v_j \tilde{\mu}_j = \sum v_j \mu_j \quad (28)$$

or taking all charged species in a given phase, α ,

$$\sum v_j \tilde{\mu}_j(\alpha) = \sum v_j \mu_j(\alpha) + F\phi(\alpha) \sum v_j z_j$$

The electroneutrality of the phase requires $\sum v_j z_j = 0$, thence (28) holds.

From (27) and (28) it can be shown that

$$\sum v_e \tilde{\mu}_e = v_e E F = \sum v_j \mu_j \quad (29)$$

This equation shows that for an open-circuit cell the electrical work is equal but of opposite sign to the Gibbs energy of the cell chemical reaction.

Applying (29) to equation (26) and expressing the chemical potentials as a function of the ion activity in solution, the electromotive force is

$$E(M^{z+}/M) = \frac{\mu_{M^{z+}}^{\circ}(\text{soln}) - \mu_M^{\circ}(M) - \mu_{H_2}^{\circ} - \mu_{H^+}^{\circ}}{ZF} + \frac{RT}{ZF} \ln a_{M^{z+}}(\text{soln}) \quad (30)$$

Taking SHE as reference, $\mu_{H_2}^{\circ}$ and $\mu_{H^+}^{\circ}$ are zero.

$E(M^{z+}/M)$ has been called the *electromotive force of the reduction / half / reaction* or *reduction / half / reaction potential* or more briefly the *reduction potential**. The direction in which the half-reaction has been considered, is indicated in brackets.

Including μ° in the standard half-reaction of reduction $E^{\circ}(M^{z+}/M)$, equation (30) can be written as

$$E_{M^{z+}/M} = E_{M^{2+}/M}^{\circ} + \frac{RT}{ZF} \ln a_{M^{z+}}(\text{soln}) \quad (31)$$

As electrode potential and reduction half - reaction electromotive force are

* The IUPAC Stockholm recommendation is *electromotive force of a half-cell* instead *electromotive force of half-reaction*^{20,21}.

given by the same value there is a tendency to identify them, or to take them as synonymous. The Stockholm convention admits that electromotive force of a half-cell of reduction might also be called electrode potential. Particularly, in teaching, the two quantities should keep different denominations, and it should be emphasised that they are two different concepts.

The right and left hand sides of the cell reaction can be reversed. This corresponds to a change in sign of the reaction Gibbs energy relative to what has been considered in deriving $E_{M^{z+}/M}$. The half - reaction for the couple M/M^{z+} is now written as an oxidation process and the expression obtained for the electromotive force is

$$E_{M/M^{z+}} = E_{M/M^{2+}}^{\circ} + \frac{RT}{ZF} \ln a_{M^{2+}}(\text{soln}) \quad (32)$$

$$\text{with } E_{M/M^{2+}}^{\circ} = \frac{\mu_M^{\circ}(M) - \mu_{M^{2+}}^{\circ}(\text{soln})}{ZF}$$

ELECTRODE POTENTIAL VERSUS ELECTROMOTIVE FORCE OF HALF-REACTION

Such a large diversity exists of terms and sign conventions that the interpretation of the electrode interface becomes rather more confusing than necessary. Electrode potential ε as defined by (15) is the most simple and direct property which can characterize an interface relative to SHE. From the value of ε for a certain electrochemical cell, electromotive force, polarity of electrode terminals, flow direction of electrons in the external circuit and of ions inside the solution, etc, are simply defined. The same may be achieved from oxidation or reduction electromotive force once they are related to the reactions that take place at the interfaces. However only electrode potential can be defined for a cell in equilibrium, *i.e.* zero current, because oxidation and reduction imply that the cell is working. The electrode at which oxidation occurs is called the *anode* and that at which reduction takes place is called the *cathode*. When charge and discharge are considered the use of electromotive force of half-reactions becomes more confusing. In fact, when a cell is under discharge and a minute rate regime passes to a minute charge regime by applying an external voltage, the electrode

potentials of both electrodes still remain but the oxidation and reduction electromotive force signs change following the variation of Gibbs energy.

Following this it is seen that no advantage comes from employing the concepts of oxidation and reduction electromotive force to this case. In just the reverse is true, and therefore, these terms should fall into disuse, such that electrode potential should be the only concept recommended²²⁻²⁵.

OLD ROOTS OF SIGN CONVENTIONS

Sign conventions regarding electrode potential and electromotive force of a half reaction date back to the early days of the thermodynamic study of electrochemical processes. Because of different conventions, this soon became a misleading area.

Gibbs was the first author to introduce the electrode potential. In his monumental work "The Equilibrium of Heterogeneous Substances" written between 1875 and 1878 Gibbs defined "electrical potential" as the difference of electrical potential in "pieces of the same kind of metal connected with" the actual electrode and with the reference electrode²³.

About a decade later Nernst adopted a different concept of electrode potential and a different sign convention as established in his famous equation²⁴. He defined the "potential difference metal/electrolyte" and gives a positive sign when the metal is negatively charged and the solution positively charged. This author was the first to propose the Normal Hydrogen Electrode, NHE, as a reference for electrode potential. Whereas Gibbs does not explicitly consider the interface, Nernst defined the potential drop at the interface which is measured against NHE. On the other hand the sign of metal/electrolyte potential given by Nernst is opposite to that proposed by Gibbs for the electrode potential. By introducing the terms electrode/electrolyte that consider that of the half - reaction and using a sign convention opposite to this one used by Gibbs, Nernst initiated a polemic about terminology and sign of electrode potential which has crossed the whole history of electrochemistry.

Abbegg, Auerbach and Luther adopted Gibbs concept in the tabulation of electrode potential for the Deutsche Bunsen Gesellschaft²⁵.

Lewis and Randall in the well-known book *Thermodynamics and the Energy of Chemical Substances* followed Nernst and clarified the concepts used

by him²⁶. The "single potential", defined for "a junction represented by electrode, electrolyte measures the tendency for negative electricity to pass from right to left, that is from the electrolyte to the electrode". As the junction was represented by expressions *electrolyte, electrode*, its single potential is opposite in sign relative to that for the couple *electrode, electrolyte*. The authors introduced in the book a table of single electrode potentials of elements represented as M, M^{z+} i.e. oxidation potentials.

Two conventions were followed by electrochemists: one, whose birth was due to Gibbs is known as the "European Convention" as it was mainly used by European chemists; the other coming from Nernst and consolidated by Lewis and Randall, was denominated the "American Convention" because it was favoured by the majority of the American Physical Chemists.

Latimer was another influent author in favour of Nernst point of view²⁷. Adopting the term of "half-reaction potential", and considering that a positive value for this quantity means that the reduced form is a better reducing agent than H_2 , he presented a table of standard oxidation-reduction potentials for a large number of systems written with electrons on the right-hand side of the equation. The brief title of his book (inserted in the cover) is "Oxidation Potentials".

In 1953 at a meeting held in Stockholm the Commission on Physicochemical Symbols and Terminology and the Commission on Electrochemistry of IUPAC joined together to deal with conventions regarding electrode potential²¹. In the conclusions of the meeting, known as the Stockholm Conventions, half-cell electromotive forces and electrode potential were distinguished and clarified. The convention started by Nernst, later adopted and worked out by Lewis, Randall and Latimer, and that introduced by Gibbs and followed mainly by European chemists were both ratified in Stockholm conventions.

The electrode potential concept has become increasingly adopted and today is by far the most used one.

CONCLUSIONS

The potential drop at an electrode interface has been considered in terms of electrode potential and electromotive force of the corresponding half reaction. The former is more directly related to the electric charge of the electrode whereas the second is related to the cell reaction. While the electrode potential is an

unvariant quantity, independent of conventions, electromotive force of a half-reaction is a bivariant quantity, and depends on the cell reaction. The electrode potential electromotive force of half-cell for reduction and for oxidation have frequently been also used. The use of these three parameters is unnecessary and introduces confusion into the understanding of the subject. It is recommended that the concept of half-cell reactions be abandoned, and that only the of electrode potential should be used.

Although electrode potential is a relative quantity no restriction exists for its use in the interpretation of electrochemical processes. Absolute electrode potential is of use only for specific cases for which absolute values of parameters related for the interface are required due to larger uncertainty in its values. The absolute electrode potential can only be calculated from the definitions and properties of the respective interface, such that, the results obtained are less accurate than those obtained for relative potentials. The use of absolute potential is restricted for specific cases in electrochemistry at solid state physics.

Equations that have been deduced above for potential and electromotive forces at the metal/electrolyte solutions interface can be generalized for any oxidation-reduction processes. Representing such a process as



The following expressions are obtained

$$\varepsilon(\text{ox, red}) = \varepsilon^\circ(\text{ox, red}) + \frac{RT}{ZF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}} \quad (34a)$$

$$E(\text{ox/red}) = E^\circ(\text{ox/red}) + \frac{RT}{ZF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}} \quad (34b)$$

$$E(\text{ox/red}) = E^\circ(\text{red/ox}) + \frac{RT}{ZF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}} \quad (34c)$$

$$\varepsilon^\circ(\text{ox/red}) = E^\circ(\text{ox/red}) = -E^\circ(\text{red/ox}) = \frac{\mu_{\text{red}}^\circ - \mu_{\text{ox}}^\circ}{ZF} \quad (34d)$$

ACKNOWLEDGEMENT

The author expresses to Prof. J. Simões Redinha her thanks for his helpful contribution to the discussion on some topics presented in this work.

REFERENCES

1. R. Parsons in *Modern Aspects of Electrochemistry*, (ed. by J. O'M. Bockris and B.E. Conway, Vol. I, Butterworth Sc. Pub., London, 1954).
2. N.F. Mott, R. Parsons and R.J. Watts-Tobin, *Phil. Mag.*, **7**, 483 (1962).
3. M.J. Sparnaay, *The Electrical Double Layer*, Pergamon Press, Glasgow, 1972.
4. I. Fried, *The Chemistry of Electrode Processes*, Academic Press, London, 1973.
5. E.A. Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929).
6. R.F. Gould, *Solvated Electron*, Adv. Chem. Ser. n° 50, American Chem. Publ., Washington, 1965.
7. J.N. Levine, *Physical Chemistry*, McGraw-Hill Book Co., Singapore, 1988.
8. E. Kanesky, *Z. Fiz. Khim.*, **22**, 1397 (1948); **24**, 1511 (1950); **25**, 854 (1951); **26**, 633 (1952); **27**, 296 (1953).
9. J.O'M. Bockris and S.D. Argade, *J. Chem. Phys.*, **49**, 5133 (1968).
10. S. Trasatti, *J. Electroanal. Chem.*, **139**, 1 (1982).
11. S. Trasatti in *Advances in Electrochemistry and Electrochemical Engineering* (ed. by H. Gerischer and C. W. Tobias), Vol. 10, Wiley-Interscience, New York, 1976.
12. A.N. Frumkin and B.B. Damaskin, *J. Electroanal. Chem.*, **66**, 150 (1975).

13. S. Trasatti, *Electrochimica Acta*, **35**, 269 (1990).
14. H. Reiss, *J. Electrochem. Soc.*, **135**, 247C (1988).
15. H. Reiss and A. Heller, *J. Phys. Chem.*, **89**, 4207 (1985).
16. S. Trasatti, *J. Pure Appl. Chem.*, **58**, 955 (1986).
17. R. Gomer and G. Tryson, *J. Chem. Phys.*, **66**, 4413 (1977).
18. Yu. Ya. Guverich and Yu. Y. Pleskov, *Sov. Electrochem.*, **18**, 1315 (1982).
19. F. Lohmann, *Z. Naturforsch.*, **A22**, 843 (1967).
20. J.J. Lingane, *Electroanalytical Chemistry*, 2nd ed., Interscience Publ., New York, 1958.
21. J.A. Christiansen and M. Pourbaix, *Compt. Rendus of the 17th Conference of the International Union of Pure and Applied Chemistry*, Maison de la Chimie, Paris, **82** (1954).
22. T.S. Licht and A.J. de Béthune, *J. Chem. Ed.*, **34**, 433 (1957).
23. F.C. Anson, *J. Chem. Ed.*, **36**, 394 (1959).
24. A.J. de Béthune, *J. Electrochem. Soc.*, **102**, 288 C (1955).
25. S. Barnartt, *J. Electrochem. Soc.*, **102**, 16C (1955).
26. J. W. Gibbs, *Trans. Connecticut Acad.* **III**, 439 (1878).
27. W. Nernst, *Z. Physik. Chemie.*, **4**, 129 (1889).
28. R. Abbeg, F. Auerbach and R. Luther, *Abhandlungen der Deutschen Bunsengesellschaft n°5 Halle*, 1911.

29. G.N. Lewis and M. Randall, *Thermodynamics and Free Energy of Chemical Substances*, Mc Graw-Hill Book Co. Inc., London, 1923.
30. W.M. Latimer, *Oxidation Potentials. The Oxidation States of The Elements and Their Potentials in Aqueous Solutions*, 2 ed., Prentice Hall, New York, 1953.

(Received, 21 April 1994

Revised form, 26 October 1994)