

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROCHEMISTRY*

**THE ABSOLUTE ELECTRODE
POTENTIAL: AN EXPLANATORY NOTE**

(Recommendations 1986)

Prepared for publication by

SERGIO TRASATTI

Università de Milano, Italy

*Membership of the Commission for 1981–85 during which the recommendations were prepared was as follows:

Chairman: 1981–83 K. E. Heusler (FRG); 1983–85 S. Trasatti (Italy); *Vice-Chairman:* 1981–83 S. Trasatti (Italy); *Secretary:* 1981–83 J. C. Justice (France); 1983–85 K. Niki (Japan); *Titular and Associate Members:* J. N. Agar (UK; Associate 1981–85); A. J. Bard (USA; Titular 1981–83); A. Bewick (UK; Associate 1983–85); E. Budevski (Bulgaria; Associate 1981–85); L. R. Faulkner (USA; Titular 1983–85); G. Gritzner (Austria; Associate 1981–83, Titular 1983–85); K. E. Heusler (FRG; Associate 1983–85); H. Holtan (Norway; Associate 1981–83); J. C. Justice (France; Associate 1983–85); M. Keddam (France; Associate 1981–83); J. Koryta (Czechoslovakia; Associate 1983–85); D. Landolt (Switzerland; Titular 1983–85); V. M. M. Lobo (Portugal; Associate 1983–85); R. Memming (FRG; Associate 1981–83, Titular 1983–85); B. Miller (USA; Associate 1981–85); K. Niki (Japan; Titular 1981–83); R. Parsons (France; Associate 1981–85); O. A. Petrii (USSR; Associate 1983–85); J. A. Plambeck (Canada; Associate 1981–85); Y. Sato (Japan; Associate 1981–83); A. Yamada (Japan; Associate 1983–85); *National Representatives:* A. J. Arvía (Argentina; 1981–85); T. Rabockay (Brazil; 1983–85); B. E. Conway (Canada; 1981–85); G. Horányi (Hungary; 1981–85); S. K. Rangarajan (India; 1981–85); E. Gileadi (Israel; 1983–85); J. W. Tomlinson (New Zealand; 1981–85); S. Minč (Poland; 1981–83); Z. Zembura (Poland; 1983–85); R. L. Paul (S. Africa; 1983–85); E. Mattsson (Sweden; 1981–85); A. K. Covington (UK; 1981–85); D. Dražić (Yugoslavia; 1981–85).

Republication of this report is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference together with IUPAC copyright symbol (© 1986 IUPAC), is printed. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

The absolute electrode potential: an explanatory note (Recommendations 1986)

Abstract - The document begins with the illustration of the most widespread misunderstandings in the literature about the physical meaning of absolute electrode potential. The correct expression for this quantity is then derived by a thermodynamic analysis of the components of the emf of an electrochemical cell. It is shown that *in principle* three reference levels can be chosen to measure an absolute value of the electrode potential. Only one of these possesses all the requisites for a meaningful comparison on a common energy scale between electrochemical and physical parameters. Such a comparison is the main problem for which the adoption of a correct scale for absolute electrode potentials is a prerequisites. The document ends with the recommendation of a critically evaluated value for the absolute potential of the standard hydrogen electrode in water and in a few other protic solvents.

The "electrode potential" is often misinterpreted as the electric potential difference between a point in the bulk of the solid conductor and a point in the bulk of the electrolyte solution ($\Delta_{S\phi}^M$) (Note a). In reality, the transfer of charged particles across the electrode/electrolyte solution interface is controlled by the difference in the energy levels of the species in the two phases (at constant T and p), which includes not only electrical (electric potential difference) but also chemical (Gibbs energy difference) contributions since the two phases are compositionally dissimilar (refs. 1,2).

The value of the $\Delta_{S\phi}^M$ of a "single" electrode, *e.g.* one consisting of an electronic conductor in contact with an ionic conductor, is not amenable of direct experimental determination. This is because the two metallic probes from the measuring instruments, both made of the same material, *e.g.* a metal M_1 , have to be put in contact with the bulk of these two phases to pick up the signal there. This creates two additional interfaces: a M_1 /solution interface, and a M_1 /electrode metal interface.

The experimental set-up can be sketched as follows:



where M is the metal of the electrode under measure, S is the electrolyte solution, M_1 is the metal of the "connections" to the measuring instrument and the prime on M_1' indicates that this terminal differs from the other one (M_1) by the electrical state only. It is expedient to replace the M_1/S interface with a more specific, reproducible and stable system known as the reference electrode. It ensues that an electrode potential can only be measured against a reference system. The measured quantity is thus a *relative* electrode potential.

For the specific example of cell (1), the measured quantity E , the electrode potential of M relative to M_1 (Note b), is conventionally split into two contributions, each pertaining to one of the electrodes:

$$E = E^M - E^{M_1} \quad (2)$$

E^M and E^{M_1} can be expressed in their own on a potential scale referred to another reference electrode. In this respect, the hydrogen electrode is conventionally taken as the universal

Note a: This quantity, known as the Galvani potential difference between M and S , has been defined in ref. 3.

Note b: In accord with the IUPAC convention on the sign of electrode potentials, all electrode potentials in this document are to be intended as "reduction potentials", *i.e.* the electrode reaction is written in the direction of the reduction (refs. 3,4).

(for solutions in protic solvents) reference electrode for which, under standard conditions, $E^\circ(\text{H}^+/\text{H}_2) = 0$ at every temperature (Note c). Since E^M as measured is a *relative* value, it appeals to many to know what the *absolute* value may be: *viz.*, the value of E^M measured with respect to a universal reference system not including any additional metal/solution interface.

Actually, for the vast majority of practical electrochemical problems, there is no need to bring in absolute potentials. The one outstanding example where this concept is useful is the matching of semiconductor energy levels and solution energy levels. However, from a fundamental point of view, this problem comes necessarily about in every case one wants to connect the "relative" electrode potential to the "absolute" physical quantities of the given system.

On a customary basis, since the electrode potential is envisaged as the electric potential drop between M and S, the cell potential difference for system (1) is usually written as the electric potential difference between the two metallic terminals:

$$E = \phi^{M_1'} - \phi^{M_1} \quad (3)$$

Since three interfaces are involved in cell (1), eqn.(3) can be rewritten as:

$$E = (\phi^{M_1'} - \phi^M) + (\phi^M - \phi^S) + (\phi^S - \phi^{M_1}) \quad (4)$$

Comparison of eqn.(4) with eqn.(2) shows that the identification of the *absolute* electrode potential with $(\phi^M - \phi^S)$ is not to be recommended because it is conceptually misleading.

Since M' and M are in electronic equilibrium, then (ref. 3):

$$(\phi^{M_1'} - \phi^M) = (\mu_e^{M_1}/F - \mu_e^M/F) \quad (5)$$

where the right hand side of eqn.(5) expresses the difference in chemical potential of electrons in the two electrode metals. Substitution of eqn.(5) into eqn.(4) gives:

$$E = (\Delta_S^M \phi - \mu_e^M/F) - (\Delta_S^{M_1} \phi - \mu_e^{M_1}/F) \quad (6)$$

The two expressions in brackets do not contain quantities pertaining to the other interfaces. They can thus be defined as *single electrode potentials* (Note d).

Since eqn.(6) has been obtained with the two electrodes assembled into a cell, it is possible that terms common to both electrodes do not appear explicitly in eqn.(6) because they cancel out ultimately. The relationship between the truly absolute electrode potential and the single electrode potential in eqn.(6) can thus be written in the form (Note e) (ref. 5):

$$E^M(\text{abs}) = E^M(r) + K \quad (7)$$

where K is a constant depending on the "absolute" reference system, and

$$E^M(r) = (\Delta_S^M \phi - \mu_e^M/F) \quad (8)$$

may be termed (ref. 6) the *reduced* absolute potential because $E(\text{abs})$ reduces to $E(r)$ as the expressions for the two electrodes forming a cell are put together and common terms are dropped. Equation (8) readily shows that $E(r)$ is not a directly measurable quantity because neither μ_e nor $\Delta_S^M \phi$ are measurable.

The value of K depends on the reference system chosen. The choice is however not entirely free because it is anyway limited to a few alternatives. Since E can be experimentally defined in terms of the work to take an electron from the bulk of M to the bulk of M_1 , the potential of each single electrode can be defined in terms of the work to transfer an electron from the bulk of the metal to the chosen reference level. This work can be accomplished

Note c: All calculations in this paper refer to the specific condition $T = 298.15$ K.

Note d: In terms of eqns.(2) and (6) it turns out that the experimental *relative* potential of a given electrode with respect to another does not measure the *relative* value of the $\Delta_S^M \phi$. Therefore, two electrodes at the *same* experimentally measured *potential* E do not possess the same value of $\Delta_S^M \phi$, while the electrons at the Fermi level in the two metals are at the *same energy*. Two metals in contact (in electronic equilibrium) must have in fact the *same* electrode potential.

Note e: The reference electrode with respect to which an electrode potential is measured is customarily specified by a short-hand notation in brackets: *e.g.*, $E(\text{SHE})$ where (SHE) stands for "standard hydrogen electrode" or $E(\text{SCE})$ where (SCE) stands for "saturated calomel electrode". In conformity with this usage, it is here recommended to specify the reference state of a single electrode potential in the same fashion: *e.g.*, $E(\text{abs})$ or $E(r)$.

in not more than three different ways (ref. 7): (1) Electrons are brought from M to infinity and back to M_1 . It can be shown that $K = \phi^S$ in this case. ϕ^S is the electric potential in the bulk of the solution. The reference state is an electron in the ground state in a vacuum at infinity; (2) Electrons are brought from M to M_1 going through the solution. Calculations show that $K = \mu_e^S/F$. The (thermodynamic) reference state is a solvated electron in the liquid phase (Note f); (3) Electrons are brought from M to M_1 through the solution but with a gap between the two electrodes containing an inert gas. This situation corresponds to a separation of the two electrodes and does not imply that the electrode under measure should be assembled in a cell. This is illustrated in Fig. 1. This assemblage resembles that used to measure contact potential differences (ref. 9). The constant is now $K = \chi^S$ where χ^S is the dipole potential at the free surface of the pure solvent (Note g). The reference state is here a point in a vacuum close to the surface of the solution (the point where contact potentials are measured) (Note h).

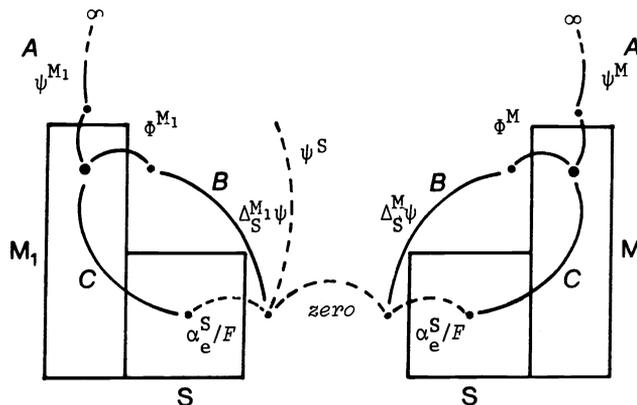


Fig. 1. Sketch to put in evidence the components of the electrode potential. Work along path B is expressed by eqn.(10) in the text. Work from $M(M_1)$ to infinity (path A) and work from $M(M_1)$ to S (path C) define the two other conceptually possible single electrode potentials.

All the three single electrode potentials defined above correspond to physically feasible electronic work and are thus *in principle* amenable of experimental determination. There are however substantial differences in the practical applicability. Case (1) does not reproduce the usual conditions of electronic energy experimental determination (the quantities generally resulting from experiments are difference in electronic energy between a point inside a phase and a point just outside it, and that between two points inside the same phase). The inadequacy of this reference state for the measurement of absolute electronic energies is better illustrated with specific examples in Appendix A at the end of this document. Case (2) does not correspond to a universal reference state since it depends in fact on the nature of the liquid phase. In fact, $E = 0$ for a given metal in two different solvents in such potential scale does not mean that the energy of the electrons at the Fermi level of the metal is the same in the two cases. In addition, the experimental determination of the electron work function of a liquid polar phase presents more problems than that of a metal (ref. 11). Only case (3) does correspond to a truly universal absolute reference state (ref. 12). The

Note f: If solvated electrons are treated as anions, their chemical potential is defined in the same way as for any other charged species (ref. 3). In particular, the standard state is the hypothetical ideal solution of molality 1 mol kg^{-1} at standard pressure. Energetically, this corresponds to the situation of a single particle interacting with an infinite phase. It has been recommended by IUPAC (ref. 8) that the standard state pressure should be changed from 1.01325 bar (1 atm) to 1 bar . Since the change shifts the standard electrode potential scale by only about $2.6 \times 10^{-4} \text{ V}$, it makes no essential influence on any of the content of the present document.

Note g: The surface potential of a given electrolyte solution depends on its actual composition. Definitions of quantities are however based on the phases in their standard states. For electrolyte solutions, this is experimentally achieved by extrapolation to infinite dilution, *i.e.* to the pure solvent.

Note h: The physical meaning of a point close to a phase as a reference level in Volta potential measurements has been illustrated in ref. 10. Briefly, the point is at a distance from the surface such that the charged particle located there is not sensitive to image interactions but is still entirely under the effect of the outer electric potential ψ due to the presence of free charges on the phase.

energy of electrons in a vacuum just outside the phase is in fact adopted by physicists to measure the electronic energy in the bulk (cf. the experimental determination of the electron work function of metals). This reference state is suitable to relate the potential scale of electrochemists with the energy scale of physicists. Since the standard hydrogen electrode is the conventional universal reference for electrochemists, it is of interest to find the value of the *absolute potential* of this electrode.

From eqns.(7), (8) and the discussion above, it follows:

$$E^M(\text{abs}) = \Delta_S^M \phi - \nu_e^M/F + \chi^S \quad (9)$$

In terms of measurable quantities (refs. 3,10,13), eqn.(9) can be rewritten as:

$$E^M(\text{abs}) = \Phi^M + \Delta_S^M \psi \quad (10)$$

where Φ^M is the electron work function of metal M (Note i) and $\Delta_S^M \psi$ is the metal/solution contact (Volta) potential difference.

Eqn.(10) defines the absolute electrode potential as the difference in electronic energy between a point inside the metal (Fermi level) and a point outside the solution. This definition makes only use of physical quantities.

If attention is focussed on the electrochemical equilibrium established at the metal/solution interface, *viz.*, in our specific example, $M^{z+} + ze \rightleftharpoons M$, it is possible to express $E^M(\text{abs})$ also in terms of thermodynamic quantities relevant to the electrode reaction. In particular, by applying a suitable Born-Haber cycle, it can be shown that (ref. 7) (cf. Appendix B):

$$E(M^{z+}/M)(\text{abs}) = (\Delta_{\text{at}} G^\circ + \Delta_{\text{ion}} G^\circ + \alpha_{M^{z+}}^S)/zF \quad (11)$$

where the right hand side includes the atomization and the ionization Gibbs energy of M, and the real solvation Gibbs energy of M^{z+} in the solvent S (real potential of species M^{z+} in phase S as defined in ref. 3).

It is worth stressing that eqn.(10) and not eqn.(11) is the basis for the experimental determination of the absolute electrode potential. The value of $\alpha_{M^{z+}}^S$ is in fact derived from the experimentally determined value of $\Delta_S^M \psi$ along with the values of $\Delta G_{\text{ad}}^\circ$ and $\Delta G_{\text{ion}}^\circ$ (for the exact expression, cf. Note k concerning the specific case of the hydrogen electrode). However, if the same set of data is used to calculate $\alpha_{M^{z+}}^S$ and $E(\text{abs})$ from eqn.(11), the resulting value must have the same accuracy as that obtained by eqn.(10). The complex nature of eqn.(11) may however originate some inaccuracy in the calculation of the absolute electrode potential if the above requirements are not met.

RECOMMENDED VALUES OF $E^\circ(\text{H}^+/\text{H}_2)$ (abs) AT 298.15 K

In the particular case of the hydrogen electrode under standard conditions, eqn.(11) becomes:

$$E^\circ(\text{H}^+/\text{H}_2)(\text{abs}) = (\Delta_{\text{at}} G^\circ + \Delta_{\text{ion}} G^\circ + \alpha_{\text{H}^+}^{\circ,S})/F \quad (12)$$

In terms of eqn.(10), the work function is that of the metal constituting the electrode. Since this quantity depends on the nature of the metal and on the actual state of its surface, it is expedient to make use of more reliable experimental data by means of a metal conversion. Physical quantities are best known for the ideally polarizable Hg electrode. For the potential of zero charge of this metal it is possible to write:

$$E_{\sigma=0}^{\text{Hg}}(\text{SHE}) = E_{\sigma=0}^{\text{Hg}}(\text{abs}) - E^\circ(\text{H}^+/\text{H}_2)(\text{abs}) \quad (13)$$

$$E_{\sigma=0}^{\text{Hg}}(\text{abs}) = \Phi^{\text{Hg}} + \Delta_S^{\text{Hg}} \psi_{\sigma=0}^\circ \quad (14)$$

From eqns.(13) and (14) it results:

$$E^\circ(\text{H}^+/\text{H}_2)(\text{abs}) = \Phi^{\text{Hg}} + \Delta_S^{\text{Hg}} \psi_{\sigma=0}^\circ - E_{\sigma=0}^{\text{Hg}}(\text{SHE}) \quad (15)$$

The potential of zero charge of Hg is that in the absence of any specific adsorption of ions as measured in dilute fluoride solutions or as obtained by extrapolation to zero concentration of specifically adsorbed ions. The last two terms in eqn.(15) can be obtained by measuring the standard potential difference of the particular cell:



which is given by:

$$E_{16}^{\circ} = \Delta\psi^{\circ}(\text{Hg}, \text{H}_2) = E^{\circ}(\text{H}^+/\text{H}_2)(\text{abs}) - \phi^{\text{Hg}} \quad (17)$$

where subscript 16 identifies the cell. From eqn.(17) combined with eqn.(15), it results:

$$E_{16}^{\circ} = \Delta_S^{\text{Hg}}\psi_{\sigma=0}^{\circ} - E_{\sigma=0}^{\text{Hg}}(\text{SHE}) \quad (18)$$

Aqueous solutions

Table 1 summarizes the values of the quantities appearing in eqns.(12) and (15). The early results for $\alpha_{\text{H}^+}^{\circ}$ in water obtained by Randles (ref. 14) with the Hg jet electrode have been confirmed and improved by Farrell and McTigue (ref. 15) and are supported by calculations based on gas-phase hydration data (ref. 16). One may argue that the surface of the Hg jet is possibly not in the same conditions of cleanliness as in a vacuum. This is because it could be oxidised by the residual oxygen and its work function could be modified by the adsorption of the water vapour in the inert gas or of the inert gas itself. Extensive tests carried out by Randles as well as by Farrell and McTigue have shown that the cell potential difference of systems like (16) is not detectably affected by the composition of the gaseous atmosphere and the flow rate of the aqueous solution provided the flow rate of the Hg jet is higher than a critical value. This suggests that, under similar conditions, the newly formed surface on the Hg tip can be regarded as being in the same state as in contact with a vacuum. Therefore, the electron work function to be used in eqn.(15) is that of the *bare* Hg surface.

TABLE 1. Values of quantities needed to calculate the absolute potential of the standard hydrogen electrode in water (298.15 K)

$\frac{1}{2}\text{H}_2 \rightarrow \text{H}$	$\Delta_{\text{at}}G^{\circ} = 203.30 \text{ kJ mol}^{-1}$	ref. (17)
$\text{H} \rightarrow \text{H}^+ + \text{e}$	$\Delta_{\text{ion}}G^{\circ} = 1313.82 \text{ kJ mol}^{-1}$	(1,17)
$\text{H}^+(\text{vacuum}) \rightarrow \text{H}^+(\text{water})$	$\alpha_{\text{H}^+}^{\circ} = -(1088 \pm 2) \text{ kJ mol}^{-1}$	(15)
Potential of zero charge of Hg	$E_{\sigma=0}(\text{SHE}) = -(0.192 \pm 0.001) \text{ V}$	(18)
Electron work function of Hg	$\phi = (4.50 \pm 0.02) \text{ eV}$	(19)
E° of cell (16)	$E_{16}^{\circ} = -(0.0559 \pm 0.0002) \text{ V}$	(15)
Contact potential difference ^a	$\Delta_{\text{H}_2\text{O}}^{\text{Hg}}\psi = -(0.248 \pm 0.001) \text{ V}$	

^aFrom eqn.(18)

It is to be noted that the determination of the *standard* value for the Volta potential difference at electrode/solution interfaces necessarily involves some extrapolation to zero concentration of the salt in solution based on model assumptions. If the plausibility of Guggenheim's convention for the activity coefficients of single ionic species (Note j) is accepted, there remains the question of the reliability of the linear extrapolation. More specifically, in Farrell and McTigue's work, some overestimation of the extrapolated value might be involved in their Fig. 4 because of some apparent concavity downward of the plots. However, it can easily be shown that the resulting uncertainty is not more than 1 to 2 mV, well below the intrinsic inaccuracy in the knowledge of the work function value for Hg ($\pm 0.02 \text{ eV}$).

On the basis of the values in Table 1 the recommended absolute potential of the standard hydrogen electrode, as results from both eqns.(12) and (15) with the same accuracy, is: (Note k)

$$E^{\circ}(\text{H}^+/\text{H}_2)_{\text{H}_2\text{O}}^{\circ}(\text{abs}) = (4.44 \pm 0.02) \text{ V} \quad \text{at } 298.15 \text{ K} \quad (19)$$

Note j: The activity coefficients of the single ionic species of a z-z electrolyte are assumed to be equal to γ_{\pm} in the region of validity of the Debye-Hückel theory.

Note k: It must be stressed that calculations based on eqns.(12) and (15) are only apparently independent since the quantities involved derive from the same set of experimental data. For instance, $\alpha_{\text{H}^+}^{\circ}$ is obtained from (ref. 15): $-\Delta_{\text{at}}G^{\circ} - \Delta_{\text{ion}}G^{\circ} + E_{16}^{\circ}F + \phi^{\text{Hg}}F$. It should be noted that, owing to the role of the decimal figures, eqn.(15) gives 4.448 V, *i.e.* 4.45 V. However, in view of the discussion concerning eqns.(10) and (11), the value calculated by means of eqn.(12) is to be preferred because it ensues directly from the experimental data.

By means of equations similar to eqn.(13), it is possible to convert all *relative* values of electrode potential to the *absolute* scale. The direct experimental determination of $E(\text{abs})$ is thus needed for only one particular electrode for each solvent. A sketch for the interconversion between electronic energy and electrode potential for electrodes in aqueous solutions is given in Fig. 2. It is to be noted that the uncertainty in the knowledge of $E^\circ(\text{H}^+/\text{H}_2)(\text{abs})$ (± 20 mV) by far exceeds the accuracy of most measurements of electrode potentials. Therefore, any convenience in the use of the absolute potential scale is confined to the specific cases when calculations of electronic energy levels are needed. It is not recommended to replace the usual convention $E^\circ(\text{H}^+/\text{H}_2) = 0$, *e.g.* to compile tables of standard electrode potentials.

It is seen from eqn.(19) and Table 1 that the uncertainty in the value of the absolute electrode potential of the standard hydrogen electrode is entirely determined by the experimental accuracy in the measurement of the electron work function of Hg. Any doubt regarding the possibility that the potential of zero charge of Hg could always contain some contributions due to residual adsorption is thus irrelevant because (a) the experimental uncertainty can hardly be as high as ± 20 mV, and (b) the independent knowledge of this quantity is actually unnecessary as eqns.(12), (15), (18) and Note k show.

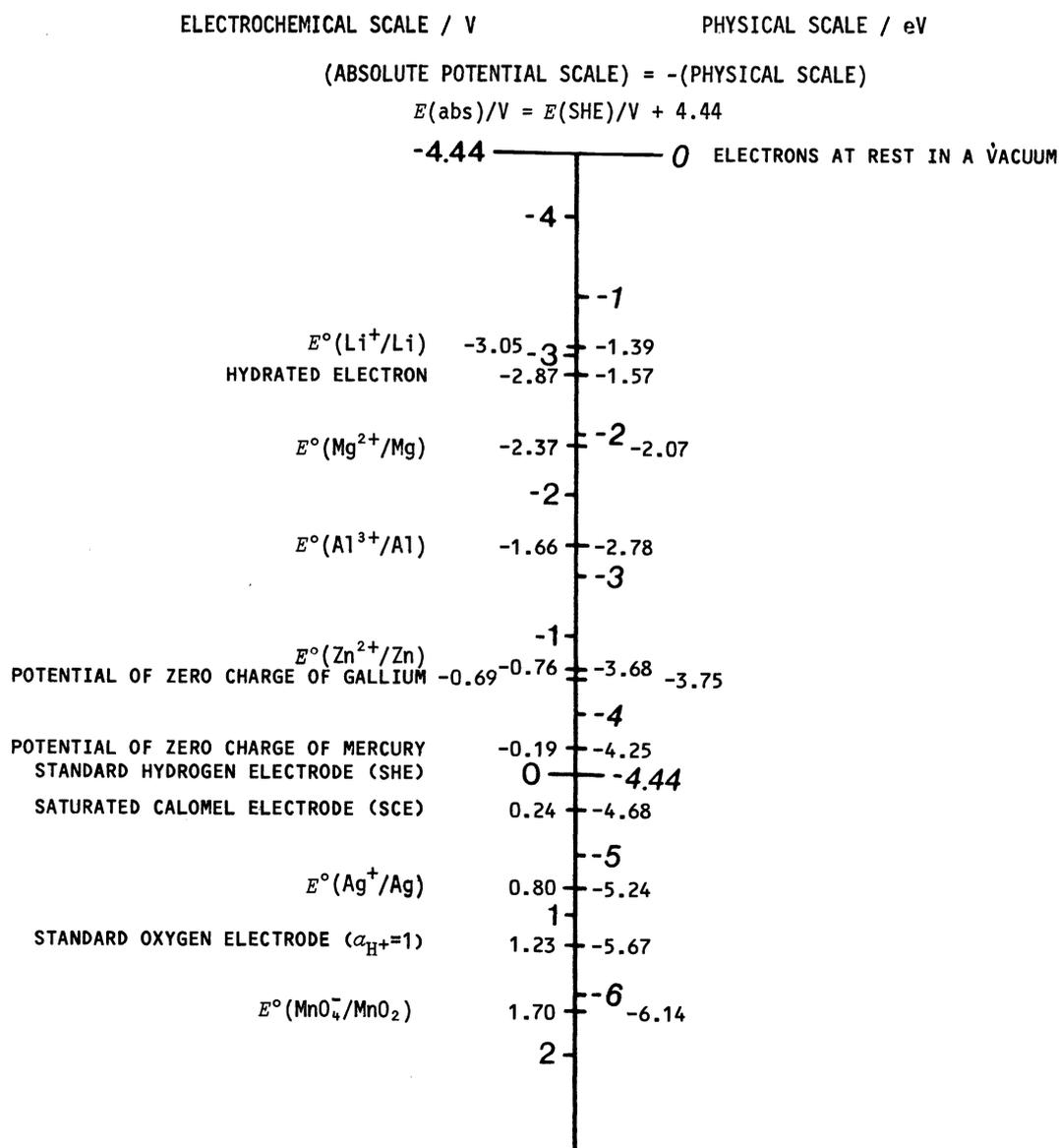


Fig. 2. Conversion of relative electrode potentials into electronic energies for aqueous systems.

Two values differing from that recommended here are very often referred to in the literature and need be scrutinized. Gomer and Tryson (ref. 20) have measured the electrode/solution contact potential difference in an electrochemical cell with a static liquid surface. They used a shallow pyrex dish with a rubber stopper with apparently no means of refreshing the surface of the solution. Since no specific purification procedures have been adopted for the solution and no particular precautions have been used to protect its surface from impurities, their experimental set-up does not ensure the necessary conditions of cleanliness of the solution phase. Therefore, their value of 4.78 V (Note 1) for $E^\circ(\text{H}^+/\text{H}_2)(\text{abs})$ is not to be recommended.

This conclusion is corroborated by other indirect experimental evidence. If an electrode is slowly drawn out of the solution, it is possible to measure its work function while in contact with the liquid phase thus in principle determining its absolute electrode potential. With such a set-up, a value of 4.7 V has been found (ref. 21) for the absolute potential of the standard hydrogen electrode. However, more recent results have shown (ref. 22) that the surface emerging from the solution is contaminated.

Lohmann (ref. 23) has calculated a value of $E^\circ(\text{abs}) = 4.48$ V for the standard hydrogen electrode. His calculations, based on the application of eqn.(11) to Ag with final conversion to the standard hydrogen electrode using $E^\circ(\text{SHE}) = 0.800$ V for the Ag/Ag⁺ electrode, are conceptually correct. His value is however less accurate for two reasons: (1) He used the ΔH° and not the ΔG° of Ag ionization; (2) His value of $\alpha_{\text{Ag}^+}^\circ$ differs by about 2 kJ mol⁻¹ from that obtained by substrating the recommended value of $\alpha_{\text{H}^+}^\circ$ (ref. 15) from the relative value of the Gibbs energy of hydration of Ag⁺ (ref. 24). More specifically, if the conventional Gibbs energy of hydration, $\Delta G_{\text{hydr}}^\circ(\text{Ag}^+) = (\alpha_{\text{Ag}^+}^\circ - \alpha_{\text{H}^+}^\circ)$, is regarded as usually very accurate because based on equilibrium thermodynamic measurements, it is then possible to check the accuracy of $\alpha_{\text{Ag}^+}^\circ$ using the value of $\alpha_{\text{H}^+}^\circ$ recommended here as a reference. Since Randles' original data are slightly different from those of McLighe not owing to experimental deviations but because he used $\Delta H_{\text{ion}}^\circ$ instead of $\Delta G_{\text{ion}}^\circ$ for hydrogen and a slightly different value for ϕ^{Hg} (4.53 eV), also the $\alpha_{\text{Ag}^+}^\circ$ used by Lohmann turns out to be affected by the same inadequancies because based on Randles' work.

It is to be stressed that the values of $E^\circ(\text{H}^+/\text{H}_2)(\text{abs})$ at temperatures other than 298.15 K cannot be derived from eqn.(19) and the temperature coefficient of the standard hydrogen electrode as measured with non-isothermal cells. Apart from the non-thermodynamic significance of the latter experimental quantity, the arguments given in this paper clearly show that such quantity does not coincide with the temperature coefficient of $E^\circ(\text{H}^+/\text{H}_2)(\text{abs})$. The latter can be obtained by measuring, for instance, the standard potential difference of cell (16) at various temperatures. Equation (17) then shows that, for that particular cell, the determination of $E^\circ(\text{H}^+/\text{H}_2)(\text{abs})$ at different temperatures calls for the knowledge of the temperature coefficient of the electron work function of Hg. Experimental data are presently insufficient to recommend any specific value for $dE^\circ(\text{H}^+/\text{H}_2)(\text{abs})/dT$.

Non-aqueous solvents

Table 2 summarizes all the relevant quantities. The absolute electrode potential of the standard hydrogen electrode in a non-aqueous solvent S has been calculated by means of eqn.(12). Values have been summarized in Table 3.

TABLE 2. Values of quantities needed to calculate the absolute potential of the standard hydrogen electrode in non-aqueous solvents (298.15 K)

Solvent	$-\alpha_{\text{H}^+}^\circ(\pm 6)/\text{kJ mol}^{-1}$
Acetone	1118 (ref. 26)
Acetonitrile	1077 (ref. 27)*; 1070 (ref. 26)
Ethanol	1111 (ref. 25), 1110 (ref. 26)
Formamide	1103 (ref. 25), 1102 (ref. 28)
Methanol	1113 (ref. 25), 1112 (ref. 26)

In all cases but (), the quantity measured experimentally was $\alpha_{\text{Cl}^-}^\circ$.
In (*), it was $\alpha_{\text{Ag}^+}^\circ$.

Note 1: It is to be noted that the value of 4.73 V given in the original paper corresponds in fact to the value for the quantity $E^\circ(\text{H}^+/\text{H}_2)(\text{r})$ as defined by eqn.(8) above.

TABLE 3. Calculated values (volt) of the absolute potential of the standard hydrogen electrode in non-aqueous solvents (298.15 K)

Solvent	ref. (25)	ref. (26)	ref. (27)	ref. (28)	recommended
Acetone	-	4.13±0.06	-	-	4.13±0.06
Acetonitrile	-	4.63±0.06	4.56±0.06	-	4.60±0.10
Ethanol	4.20±0.06	4.22±0.06	-	-	4.21±0.07
Formamide	4.28±0.06	-	-	4.30±0.06	4.29±0.07
Methanol	4.18±0.06	4.20±0.06	-	-	4.19±0.07

It is worth stressing that the difference between the values of the absolute potential of the standard hydrogen electrode in two different solvents does not measure the *Gibbs energy of transfer* of the proton from one to the other solvent. The relationship between the two quantities is the following:

$$E^\circ(\text{H}^+/\text{H}_2)^{S_1}(\text{abs}) - E^\circ(\text{H}^+/\text{H}_2)^{S_2}(\text{abs}) = \alpha_{\text{H}^+}^{\circ, S_1} - \alpha_{\text{H}^+}^{\circ, S_2} \quad (20)$$

$$\Delta_{S_2}^{S_1} \alpha_{\text{H}^+}^{\circ} = \Delta_{S_2}^{S_1} \mu_{\text{H}^+}^{\circ} + F \Delta_{S_2}^{S_1} \chi \quad (21)$$

where $\Delta_{S_2}^{S_1} \mu_{\text{H}^+}^{\circ}$ is the *Gibbs energy of transfer* of the proton and $\Delta_{S_2}^{S_1} \chi$ is the difference of the surface potentials of the two solvents. The splitting implied in eqn.(21) cannot be operated experimentally. It necessarily involves extrathermodynamic assumptions.

For the same reasons, the knowledge of $E^\circ(\text{SHE})(\text{abs})$ in different solvents does not imply necessarily that a unified pH scale can be achieved. Such scale is in fact based on $\Delta_{S_2}^{S_1} \mu_{\text{H}^+}^{\circ}$ and not on $\Delta_{S_2}^{S_1} \alpha_{\text{H}^+}^{\circ}$.

REFERENCES

1. S. Trasatti, *J. Electroanal. Chem.* 52, 313 (1974).
2. S. Trasatti in J. O'M. Bockris, B.E. Conway and E. Yeager (Eds.), *Comprehensive Treatise of Electrochemistry*, Vol. 1, Plenum Press, New York, 1980, p. 45.
3. R. Parsons, *Pure Appl. Chem.* 37, 501 (1974).
4. Manual of Symbols and Terminology for Physico-chemical Quantities and Units, *Pure Appl. Chem.* 51, 1 (1979).
5. A.N. Frumkin and B.B. Damaskin, *J. Electroanal. Chem.* 66, 150 (1975).
6. A. De Battisti and S. Trasatti, *J. Chim. Phys.* 74, 60 (1977).
7. S. Trasatti, *J. Electroanal. Chem.* 139, 1 (1982).
8. Appendix IV to Manual of Symbols and Terminology for Physico-chemical Quantities and Units, *Pure Appl. Chem.* 54, 1239 (1982).
9. V.A. Rabinovich, T.E. Alekseeva and L.A. Voronina, *Elektrokhimiya* 9, 1434 (1973).
10. R. Parsons in J. O'M. Bockris (Ed.), *Modern Aspects of Electrochemistry*, Vol. 1, Butterworths, London, 1954, p. 103.
11. R.R. Dogonadze, L.I. Krishtalik and Yu.V. Pleskov, *Elektrokhimiya* 10, 507 (1974).
12. A.N. Frumkin and B.B. Damaskin, *Dokl. Akad. Nauk SSSR* 221, 395 (1975).
13. S. Trasatti and R. Parsons, *Pure Appl. Chem.* 55, 1251 (1983).
14. J.E.B. Randles, *Trans. Faraday Soc.* 52, 1573 (1956).
15. J.R. Farrell and P. McTigue, *J. Electroanal. Chem.* 139, 37 (1982).
16. C.E. Klots, *J. Phys. Chem.* 85, 3585 (1981).
17. *JANAF Thermodynamical Tables*, 2nd Edition, 1971; *JANAF Thermodynamical Tables*, 1975 supplement.
18. D.C. Grahame, E.M. Coffin, J.I. Cummings and M.A. Poth, *J. Am. Chem. Soc.* 74, 1207 (1952).
19. S. Trasatti, *J. Chem. Soc. Faraday I* 70, 1752 (1974); *Chim. Ind. Milan* 53, 559 (1971); V.S. Fomenko, *Emission Properties of Materials*, Naukova Dumka, Kiev, 1981; J. Hölzl and F.K. Schulte, *Springer Tract. Mod. Phys.* 85, 1 (1979).
20. R. Gomer and G. Tryson, *J. Chem. Phys.* 66, 4413 (1977).
21. W.N. Hansen and D.M. Kolb, *J. Electroanal. Chem.* 100, 493 (1979).
22. O. Hofmann, K. Doblhofer and H. Gerischer, *J. Electroanal. Chem.* 161, 337 (1984).
23. F. Lohmann, *Z. Naturforsch.* 22a, 843 (1967).
24. L. Benjamin and V. Gold, *Trans. Faraday Soc.* 50, 797 (1954).
25. B. Case and R. Parsons, *Trans. Faraday Soc.* 63, 1224 (1967).
26. I. Zagörska and Z. Koczorowski, *Rocz. Chem.* 44, 1559 (1970).
27. B. Case, N.S. Hush, R. Parsons and M. Peover, *J. Electroanal. Chem.* 10, 360 (1965).
28. R. Parsons and B.T. Rubin, *J. Chem. Soc. Faraday I* 70, 1636 (1974).
29. A. De Battisti and S. Trasatti, *J. Electroanal. Chem.* 79, 251 (1977).
30. A.J. Swallow, *Ann. Rep. Progr. Chem. C* 77, 145 (1980).

APPENDIX A

A point in a vacuum at an infinite distance from a phase, besides being a very impractical reference, is conceptually suitable to measure the outer electric potential ψ (which really vanishes at infinity) but not the *electrochemical* (chemical + electrical) energy of single charged species. The inadequacy of this reference for energies is best shown by making a specific example.

Let us suppose to have two electronically conducting solid phases, α and β . Upon contact, electrons flow from the phase (say α) with the lower work function (Φ^α) to that with the higher work function, Φ^β , until

$$\tilde{\mu}_e^\alpha = \tilde{\mu}_e^\beta \quad (1a)$$

If the charge (electrons) transferred from α to β is compositionally negligible and does not affect the electron distribution existing at the surface of the uncharged phases, the experimentally measured Volta (contact) potential difference, recalling (ref. 3) that $\tilde{\mu}_e^\alpha = -(\Phi^\alpha + \psi^\alpha)F$, is given by

$$(\psi^\alpha - \psi^\beta) = (\Phi^\beta - \Phi^\alpha) \quad (2a)$$

While $\Delta_\beta^\alpha \psi$ is a well defined quantity, it can be shown that values of ψ^α and ψ^β depend on the relative amount of the two phases. For the electroneutrality, there must always be

$$q^\alpha = -q^\beta \quad (3a)$$

For the sake of simplification, let us assume that α and β are spheres of radius r . The outer potential is then given by (ref. 10)

$$\psi = \frac{q}{r} \quad (4a)$$

Let us suppose first that α and β have equal sizes. Thus:

$$\psi^\alpha = \frac{q^\alpha}{r^\alpha} \quad \text{and} \quad \psi^\beta = \frac{q^\beta}{r^\alpha} \quad (5a)$$

For eqn.(3a) it follows that:

$$\psi^\alpha = -\psi^\beta \quad (6a)$$

Fig. 3 shows that the common electrochemical potential of electrons in the two phases lies exactly in the middle between the two levels of the original work functions.

Let us suppose now that $r^\alpha = 2r^\beta$. Electroneutrality must again be fulfilled, but the total charge transferred from α to β will be different. In fact

$$\psi'^\alpha = \frac{q'^\alpha}{r^\alpha} \quad \text{and} \quad \psi'^\beta = \frac{2q'^\alpha}{r^\alpha} \quad (7a)$$

Since $\Delta_\beta^\alpha \psi$ must always be the same, if we assume that r^α is the same in the two cases, it follows that eqn.(2a) can be fulfilled only with

$$q'^\alpha \neq q^\alpha \quad \text{and} \quad q'^\alpha = -q'^\beta \quad (8a)$$

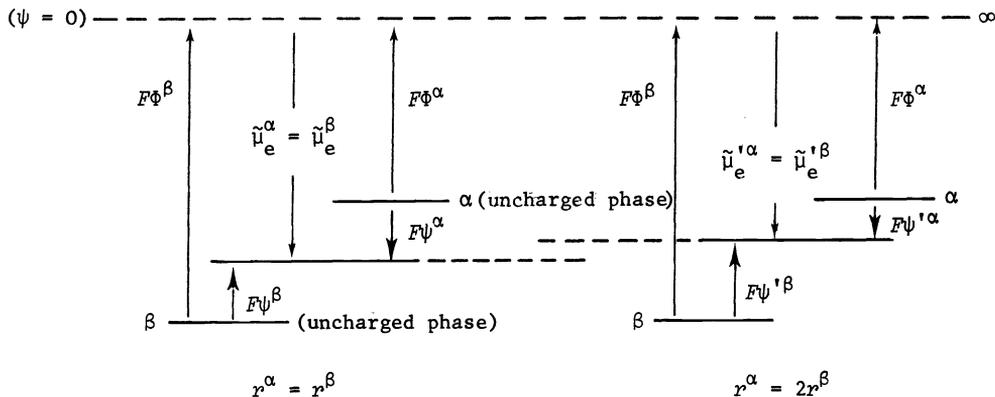


Fig. 3. Energy diagram to show that the "absolute" value of $\tilde{\mu}_e$ for two phases (spheres of radius r) in electronic equilibrium depends on their relative amount.

Therefore,

$$\psi'^{\alpha} \neq \psi^{\alpha} \quad \text{and} \quad \psi'^{\alpha} \neq \psi'^{\beta} \quad (9a)$$

Thus, the amount of charge on the phases and the values of the outer electric potentials are both functions of the relative amount of the phases. In particular, in the latter example

$$\psi'^{\alpha} = -\frac{1}{2} \psi'^{\beta} \quad (10a)$$

Thus, the Fermi level of the larger phase (α) moves less than the Fermi level of the smaller phase (β). The result, as Fig. 3 shows, is that the common electrochemical potential of electrons in the two phases has now a different "absolute" value from the former case, although *thermodynamically* the system is still in the same condition. The position of the common electrochemical potential of the electrons in the two phases can thus have any value between ϕ^{α} and ϕ^{β} (starting from uncharged phases) depending on the ratio r^{α}/r^{β} . It will coincide with the work function of one of the two phases only in the specific case that the size of that phase becomes infinite.

APPENDIX B

If a point in a vacuum close to the surface of the solution is chosen as the reference level for electrons, that implies that the electrode reaction is written in following way:

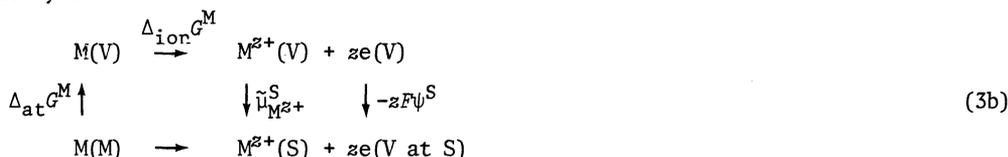


where M stands for metal phase, S for solution and V for vacuum. Since the true electrode equilibrium is



eqn.(1b) does not represent an electrochemical equilibrium in that e(M) is not in equilibrium with e(V at S). The electrochemical Gibbs energy change in (1b) is thus $\Delta\tilde{G} \neq 0$.

$\Delta\tilde{G}$ can be split into its components if eqn.(1b) is written in the form of the following Born-Haber cycle:



ψ^S is the electric potential in a point in a vacuum close to the surface of the solution (outer or Volta potential of the solution (refs. 3,10)). It follows that:

$$\Delta\tilde{G} = zFE(M^{z+}/M) (\text{abs}) = z(\tilde{\mu}_e^V \text{ at } S - \tilde{\mu}_e^M) \quad (4b)$$

since the measurement of this electrode potential entails taking an electron from the Fermi level of the metal to a point in a vacuum close to the surface of the solution. Since:

$$\tilde{\mu}_e^V \text{ at } S = -F\psi^S \quad (5b)$$

and (refs. 3,12)

$$\tilde{\mu}_e^M = \mu_e^M - F\phi^M \quad (6b)$$

$$\phi = \chi + \psi \quad (7b)$$

$$\mu_e^M/F - \chi^M = -\phi^M \quad (8b)$$

where ϕ^M is the electron work function of metal M, it results:

$$\begin{aligned} \Delta\tilde{G} &= zFE(M^{z+}/M) (\text{abs}) = -zF\psi^S - z\tilde{\mu}_e^M = (\phi^M + \Delta_S^M\psi)zF = \Delta_{at}G^M + \Delta_{ion}G^M + \tilde{\mu}_{M^{z+}}^S - zF\psi^S = \\ &= \Delta_{at}G^M + \Delta_{ion}G^M + \alpha_{M^{z+}}^S \end{aligned} \quad (9b)$$

where (ref. 3)

$$\alpha_{M^{z+}}^S = \mu_{M^{z+}}^S + zF\chi^S \quad (10b)$$

Equation (9b) shows the equality between eqns.(10) and (11) in the text.

SYMBOLS AND DEFINITIONS

E^M	Electrode potential of metal M.
$E^M(\text{SHE})$	Electrode potential of metal M relative to the standard hydrogen electrode.
$E^M(\text{SCE})$	Electrode potential of metal M relative to the saturated calomel electrode.
$E^M(\text{abs})$	Absolute electrode potential of metal M.
$E^M(\text{r})$	"Reduced" absolute electrode potential, <i>i.e.</i> the constant term in $E^M(\text{abs})$ has been dropped.
$E^\circ(\text{H}^+/\text{H}_2)^S(\text{abs})$	Absolute potential of the standard hydrogen electrode in solvent S.
$E_{\sigma=0}^M(\text{SHE})$	Potential of zero charge of metal M relative to the given reference electrode.
$\Delta_{\text{at}}G^\circ(\text{B})$	Standard Gibbs energy of atomization of B.
$\Delta_{\text{ion}}G^\circ(\text{B})$	Standard Gibbs energy of ionization of B.
α_B^S	Real solvation Gibbs energy of B in solution S.
$\Delta_{S_2}^{S_1}\alpha_B^\circ$	Standard <i>real</i> Gibbs energy of transfer of B from solvent S_1 to solvent S_2 .
μ_e^M	Chemical potential of electrons in metal M.
$\Delta_{S_2}^{S_1}\mu_B^\circ$	Standard Gibbs energy of transfer of B from solvent S_1 to solvent S_2 .
$\Delta_S^M\phi$	Difference in electric potential between a point in the bulk of metal M and a point in the bulk of solution S (Galvani potential difference).
χ^S	Dipole potential at the free surface of solution S.
$\Delta_S^M\psi$	Difference in electric potential between a point in the gas phase close to the surface of metal M and a point in the gas phase close to the surface of solution S in contact with M (Volta or contact potential difference).
ϕ^M	Electron work function of metal M, <i>i.e.</i> minimum work to extract an electron from the Fermi level of the uncharged metal M in contact with a vacuum.