Comments to "Electroanalytical Obscurity: An Alternative View" by Robert de Levie

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1 Introduction

First of all, “Polemik” is one of the things that have been almost extinct in recent scientific publications. In that sense, the article, “Electroanalytical obscurity: an alternative view,” by Prof. de Levie [1] which is written in response to my reflection, or essay or note, entitled “Obscurity in Electroanalytical Chemistry” [2, 3], is highly welcome. Unfortunately, however, his comments in [1] miss the main points I raised in my reflection [2, 3].

1.1 Timeline

Before going into the details of my view on his alternative view, it would be felicitous to review the timeline of the relevant papers. My reflection originally published in Japanese in September 2014 [2] is not my response to Prof. de Levie’s article in 2014 [4], but to his lecture in the Prague ISE meeting in 2012, and also on his paper published earlier [5]. When I was writing [2] in August 2014, I was not aware of Prof. de Levie’s article [4] that had been published in July 20, 2014, and had been available online even earlier since April 18, 2014. During my stay at the J. Heyrovsky Institute in Prague in October 2014, Prof. Z. Samec kindly made me aware of the presence of [4]. After looking through the article, I felt that what I wrote in [2] was still meaningful for readers of Rev. Polarogr. to get an insight into the very essential points concerning the single ion activity, pH, and the nature of electrochemical systems, and rendered my reflection [2] into English during my stay at the J. Heyrovsky Institute in October 2014. The English version was published next year [3]. The expression in the third line of Introduction in [1], “[2] on my review [3]” (“[2]” and “[3]” in the quotation in the present communication are [3] and [4], respectively), is hence inappropriate: my reflection [2, 3] is not aimed to make all-out criticism of the view of Prof. de Levie detailed in [4]. I rather tried to reveal obscurity frequently seen in contemporary textbooks of electroanalytical chemistry, as well as relevant chapters of analytical chemistry textbooks, in introducing “Nernst equation”.

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1.2 Style for Polemik

Unfortunately, from the beginning, the style of argument by Prof. de Levie is away from a scientific norm; it rather reminds me of some politicians in the post-truth era in that they first fabricate a picture of the opponent, and take advantage of it for criticism. The first paragraph starts with "Below I will take a different view, viz. that a major goal of science in general, and of science education in particular, is to eliminate obscurity rather than to accept it" [1]. This sentence depicts my view as if I tried to plump up, or at least retain, the obscurity in science and science education. Of course, this is far from the truth, as it is readily comprehended if one reads my reflection without prejudiced eye. Firstly, the obscurity I described in [3], is existent objectively in any galvanic cell, i.e., independent of our mindset (vide infra).

In the second place, the obscurity is persistent in the description or understanding of this obscurity associated with the liquid junction in some textbooks and chapters of analytical chemistry as well as physical chemistry about the very nature of galvanic cell. The title of my reflection "Electroanalytical obscurity" implies both of these. What I presented in [3] is, opposite to what the loaded sentence above by Prof. de Levie [1] connotes, to clearly address the obscurity of galvanic cell because of the presence of the liquid junction. Furthermore, in [3] I showed by use of an ionic liquid salt bridge that it is possible to minimize the obscurity with the uncertainty on the order of submillivolt. In the second paragraph on the same page, Prof. de Levie wrote "we should try to clarify rather than excuse." The former attitude in this sentence is certainly agreeable, but who did try to make an excuse for the thermodynamic immeasurability of single ion activity? The latter half of this sentence suggests as if IUPAC and I did so. The immeasurability is a solid fact, for which nobody is responsible. His rhetoric again seems to be treacherous. As such, from the beginning the Prof. de Levie’s "alternative view" is apparently deemed not very successful for a fruitful Polemik.

2 Points of the Polemik

2.1 Nonthermodaynamic nature of galvanic cell

The essential point I raised in [2, 3] is the view that any electrochemical system that is made by splitting a redox reaction between the two redox couples, which undergo two simultaneous but individual electrode reactions at two electrodes, is intrinsically nonthermodynamic. Because the two solutions of different compositions, each of which contains one of the redox couples, should be made contact for ionic conduction for assembling an electrochemical cell, the presence of a liquid junction between the two electrolyte solutions of different compositions within the electrochemical cell is inevitable. The mixing of the two solutions at this contact is a time-dependent, irreversible process, which necessarily gives rise to the liquid junction potential, a nonthermodynamic quantity, whose magnitude may be negligibly small in comparison with the uncertainty in measuring the cell voltage, though.

The cell voltage , $E$, between the two electrodes is therefore inherently of nonthermodynamic
nature. $E$ is related to the Gibbs energy of the corresponding redox reaction, $\Delta G_r$, assuming the one electron transfer, through

$$E \approx -\Delta G_r / F$$

where $F$ is the Faraday constant.

2.2 The obscurity in so-called “Harned cell”

The so-called “Harned cell”, which has been playing the central role in defining pH in IU-PAC2002 recommendations [7] and, earlier, in standardizing NBS pH buffers, and more generally, in electrochemically studying thermodynamic properties of electrolyte solutions, has been known for absence of liquid junction.

However, MacInnes pointed out in his famous book, “The Principles of Electrochemistry” published in 1939 [8] the following.

It is important to note that the difference between cells with and without liquid junctions is one of the degree and not of kind. Thus the familiar cell:

$$(\text{Pt}); \text{H}_2, \text{HCl}, \text{AgCl(s)}; \text{Ag}$$

really contains two (or more) solutions, and should, strictly, be represented as follows:

$$(\text{Pt}); \text{H}_2, \text{HCl}($$\text{satd}.with\text{H}_2$$); \text{HCl}($$\text{satd}.with\text{AgCl}$$), \text{AgCl(s)}; \text{Ag}$$

I wonder why Prof. de Levie, versed to literatures of historical significance in the field of electrochemistry and physical chemistry, did not mention this MacInnes’s remark.

As a matter of fact, the cell voltage, ca. 0.2 V, or 20 kJ mol$^{-1}$ as $\Delta G_r$, is enough to drive the cell reaction,

$$\text{AgCl} + \frac{1}{2}\text{H}_2 \rightleftharpoons \text{Ag} + \text{Cl}^- + \text{H}^+$$

to the right. Experimentally, the junction part between the two sides of the above cell, usually a V-shaped glass tube, is occasionally seen darkened because of the precipitates of Ag formed by this reaction. This exemplifies the case why Gibbs mentioned, “cases of true equilibrium (even for open circuit) are quite exceptional.” [1, 9]

Although I have no means to check if Gibbs examined the cases of the above and/or other similar cells, it seems reasonable to suppose that he knew some galvanic cells with no apparent liquid junction, like Planté cell and Weston cell, at the time when both had been proposed and the former was employed for electric vehicles.

Prof. de Levie did not disclose his view on this very fact, and spent most of the space for emphasizing the thermodynamic properties obtainable with a galvanic cell, tacitly assuming that

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2The combination of Ag|AgCl and H$^+$/H$_2$ electrodes was employed earlier by Noyes and Ellis in 1917 ( [6]) for determination of ionic activities.

3National Bureau of Standards, USA. It was renamed as National Institute of Standards and Technology in 1988.
the cell voltage is a thermodynamic quantity. It is ironical to see that Prof. de Levie has the same view as IUPAC2002, which he has radically criticized, on the thermodynamic nature of the so-called Harned cell.

2.3 Externally usable electrical energy

The second line below II in page 78, Prof. de Levie wonders “From where came the need to generate externally usable electrical energy?” My answer to this naive question is that any potentiometric measurement relies on this “externally usable energy” because of the cell voltage $E$ is linked to the Gibbs energy of the cell reaction through eq (1) or, eq (2), approximately.

Needless to say, $\Delta G_r$ is the externally usable energy, however its amount may actually be minute, as is the case of pH measurements with a glass electrode. The case of Ag formation within the cell illustrated above is a good example when the usable energy kept in the so-called Harned cell was internally dissipated in the form of a chemical reaction. Generally, a minute amount of $\Delta G_r$, or the flow of charge at that cell voltage, suffices for potentiometry provided that a high impedance potentiometer, as illustrated in the first paragraph in page 77 of [1], is employed.

2.4 One hand clapping and Nernst equation

2.4.1 Naming “Nernst equation”

In section 3, “Illustrating electrochemical obscurity” in [1], Prof. de Levie examined my way in Sections 3 and 4 in [3] of explaining the secret of so-called Nernst equation commonly seen in many text books of electroanalytical chemistry and related disciplines.

In doing so, he did not clearly state his understanding of what the Nernst equation is. However, from the sentence, “since the Nernst equation supposedly describes an electro-chemical equilibrium,” it is highly likely that he assumes the Nernst equation being of the type,

$$E = -\frac{1}{nF}\Delta G_r$$

(2)

where $n$ the number of electron transferred in the cell reaction and $\Delta G_r$ the Gibbs energy of the redox reaction between the two redox couples, Ox$_1$/Rd$_1$ and Ox$_2$/Rd$_2$,

$$\text{Ox}_1 + \text{Rd}_2 \rightleftharpoons \text{Rd}_1 + \text{Ox}_2$$

(3)

Indeed, in the subsequent page 81, Prof. de Levie wrote, "Hamer & Wu specifically list the Nernst equation for the sample cell", and presented for

Pt, H$_2$ (g)|HCl($m$)|AgCl(s), Ag(s)

his Nernst equation

$$E = E^\circ - \frac{RT}{F}\ln\left(m_{H^+}\gamma_{Cl^-}m_{Cl^-}\gamma_{H^+}\right)$$

(4)
It seems now certain that Prof. de Levie understands this type of expression as the Nernst equation. However, historically, equations of the type (4) that correlates the cell voltage to the mean activities of the electrolyte, HCl in the present case, cannot be directly ascribed to Nernst mainly for the two reasons. First, Nernst’s interest when he published his work in 1889 was not to correlate the cell voltage with $\Delta G_r$, and, necessarily, with the concentrations of the relevant redox species, because the basic (approximate) relationship had been established at that time for the former by Helmholtz and others [10, 11], and for the latter, by van ’t Hoff [12]. It would be more appropriate to call eq (4) the Helmholtz-van ’t Hoff equation.

Nernst’s originality in his famous article in 1889 is the proposal of the following expression for the electrode potential by modeling the dissolution of metal that constitutes the electrode into the adjacent solution as metal ions,

$$ E = 0.860T \ln \frac{P}{P'} \times 10^{-4} \text{Volt} \tag{5} $$

where, notably, $E$ stands for the potential drop across the metal|solution interface, not for the cell voltage, $T$ the absolute temperature, $p$ the osmotic pressure of the dissolved metal ion, and $P'$ the dissolution pressure of the metal ions in the metal in contact with the solution.

He proposed a constitutive approach to the cell voltage, as being given by the difference in $E$ values defined by eq (5) at the two electrodes in addition to the liquid junction potential. For appreciation of his creative contribution, focusing attention to the potential drop across the metal-solution interface, the term “Nernst equation” should be withheld for this and similar equations that represent the single electrode potential, which is not thermodynamically measurable, though.

In eq (4) the activities, instead of the concentrations, appear in the argument of the logarithm. This important change that reflects the advances in understanding of electrolyte solutions at the turn of the century from the 19th to the 20th was made by Lewis [13], as is well known and Prof. de Levie mentioned [1]. This is the second reason why the eq (4) and the likes that link the cell voltage to the activities of two redox couples participating in the whole cell reaction should not be simply called “Nernst equation”.

Before his volte-face in 1900 [14], he had repeatedly emphasized the significance of his constitutive approach for understanding the mechanism of galvanic cells [15, 16].

### 2.4.2 Reference electrode and one hand clapping

However, in his address at the 7th general assembly of the German Society of Electrochemsitry in Zürich, August 10, 1900, Nernst said, “Uebrigens dürfte, weil eben die absoluten Potentiale bei keiner elektrochemischen Untersuchung einen direkten Einfluss ausüben, die erwähnte Frage für den Elektrochemiker zunächst wenigstens keine besondere Bedeutung besitzen [14].” (google translate: “Moreover, since the absolute potentials do not exert any direct influence in any electrochemical investigation, the question mentioned for the electrochemist has at least no special

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4 His description above may seem to be indicating that Hamer and Wu also called eq (4) the Nernst equation. But, they did not, though they did use eq (4) for the basis of determining the mean activity from the cell voltage.

5 An appropriate naming would be “Helmholtz-van ’t Hoff-Lewis” equation.
significance at all”). Nernst then recommended the use of a normal hydrogen electrode, that is, a platinum electrode dipped in an aqueous 1 mol L\(^{-1}\) hydrogen ion solution saturated with hydrogen gas as the reference electrode to compare the potentials of other redox couples.

Two points about his new proposal are worth mentioning. First, the use of a reference electrode was not new at that time, because already the normal electrode, that is, a calomel electrode in contact with an aqueous 1 mol L\(^{-1}\) KCl solution had been widely used [17]. The use of a hydrogen electrode had also been common [18]. The originality in the Nernst’s new proposal is thus feeble in comparison with his previous idea, eq (5).

Second, the use of reference electrode necessarily delineates the presence of the liquid junction potential between the test solution and the solution phase of the reference electrode, which is by the way usually called “inner solution”.\(^6\) In other words, the reference electrode is expected to keep the electrode potential constant whatever the composition of the test solution side is. Particularly noteworthy here is that his, and also Ostwald’s preceding, proposals of using a reference electrode premises a separate handling of the reference solution side and the working electrode side, both experimentally and conceptually. Once the idea of assigning different roles to reference and working electrode, which is common in electroanalytical chemistry, is accepted, one can readily enjoy “one hand clapping” [1] with a working electrode.

### 2.5 Nernst equation for one hand clapping

By use of a reference electrode, in which in most of the cases, the salt bridge usually made of a concentrated potassium chloride solution is employed, explicitly or implicitly, we can focus our attention to the electrochemistry at the working electrode, of course setting aside the problem of the liquid junction potential.

To focus our attention on the potential of the working electrode, we need to split the whole cell reaction eq (3) into two half-cell reactions, one at the reference electrode and the second to the working electrode, that is,\(^7\)

\[
\text{Ox}_1 + n\text{e}^- \rightleftharpoons \text{Rd}_1
\]

and

\[
\text{Ox}_2 + n\text{e}^- \rightleftharpoons \text{Rd}_2
\]

In expressing such half cell reactions, it is customary to explicitly write the electron for the charge balance on both sides of each of the half cell reaction.\(^8\) The statement by Prof. de Levie in the final sentence in section 3.1 (page 9) in [1], “The argument [2] that ‘At least one of Ox and Rd is an ionic species, and hence its activity is a single ion activity’, is clearly wrong,” is thus clearly inappropriate.

\(^6\)In that respect, the normal electrode proposed by Ostwald is far better than the normal hydrogen electrode in terms of the diminution of the liquid junction potential.

\(^7\)Here, I use \(\rightleftharpoons\) instead of “\(\rightleftharpoons\)” [3], while Prof. de Levie prefers “\(\rightleftharpoons\)” [1], but such a distinction does not add anything more rigorous or marvelous to the present arguments.

\(^8\)Note that in these expressions the location of the electron is immaterial, as long as they are assumed to be in the same environment, though Prof. de Levie states “The electron e\(^-\) resides in the metal rather than in the solution phase” in section 3.1 [1].
For each half-cell reaction when \( n = 1 \), we may write:

\[
E = E^\circ + \frac{RT}{F} \ln \frac{a_{Ox}}{a_{Red}}
\]

which is the same as equation (2) in [3], and Prof. de Levie examined on page 8 [1]. \( E \) can be defined in two ways: one as the potential drop across the working electrode|solution interface, and the other as the cell voltage referred to the reference electrode employed to construct a galvanic cell with the working electrode. Since the former is immeasurable, the latter is a practicable interpretation of eq (8) as a viable way to correlate the phenomena at the working electrode to the measurable cell voltage.

Eq (8) may be called the Nernst equation, or, taking account of the contribution of Lewis, the Nernst-Lewis equation, because eq (8) looks as if it is concerned only with the working electrode, as was the case of the Nernst’s original idea in 1889, allowing the one hand clapping.

2.6 Nernst equation and single ion activity measurements

It is straightforward to get an estimate of the single ion activity based on eq (8), as I illustrated in [3], provided that the liquid junction potential remains the same or negligibly small for a series of test solutions of different compositions so that the value of \( E^\circ \) stays constant.

In section 3.2 A corrected argument, Prof. de Levie considered the argument above a “defective example” [1] Yes, I cannot agree more. Indeed, the aim of my reflection is not to explain didactically the concepts of electrochemistry. Rather, I started with the “defective example,” commonly seen in many textbooks and chapters on electroanalytical chemistry, and tried to reveal what is tacitly assumed. It may not be an efficient and authoritative way for a standard textbook, but hopefully be useful for some, given the situation that eq (8) is introduced “unapologetically” [1] in quite a few textbooks.9.

9For example, Harris Quantitative Chemical Analysis (8th ed., W. H. Freeman and Company, New York, (2010), p. 288 and ff. “13-4 Nernst Equation”

For the half-cell reaction

\[
aA + ne^- \rightleftharpoons bB
\]

the Nernst equation giving the half-cell potential, \( E \), is

\[
Nernst\ equation\quad E = E^0 - \frac{RT}{nF} \ln \frac{A^B}{A^A}
\]

where \( E^0 = \) standard reduction potential (\( A_A = A_A = 1 \))

\( R = \) gas constant (8.314 J/(K \cdot mol)) = 8.314(V \cdot C)/(K \cdot mol)),

\( T = \) temperature (K),

\( n = \) number of electrons in the half-reaction,

\( F = \) Faraday constant (9.649 × 10^4 C/mol)

\( A_i = \) activity of species \( i \).

Thus, the physical meaning of \( E^0 \) remains unexplained.
The answer to the question by Prof. de Levie in section 3.1, “Is the Nernst equation not thermodynamically rigorous” is threefold “no”, because, firstly, Nernst’s original equation is nonthermodynamic, secondly, the "so-called" Nernst equation that Prof. de Levie assumes is nonthermodynamic (see eq (1)), and, thirdly, eq (8) implies the nonthermodynamic assumption that \( E^\circ \) stays constant over the change in the electrolyte compositions, as described above. I hope my answer does not make “matters only more confusing” [1].

2.7 Falsifiability of single ion activities

Prof. de Levie considers that the single ion activity is beyond the demarcation line that separates science from nonscience because of the thermodynamically immeasurability that is not equipped with falsifiability [5].

In section 2 in [3], “falsifiability of single ion activity”, I questioned his view by citing Figure 1 that shows the dependence of the mean activity coefficients of HCl, HBr, and HI up to the molality of 5 mol kg\(^{-1}\). The three curves exhibited different dependencies on the ionic strength beyond ca. 0.05 mol kg\(^{-1}\). In my view, this different dependencies can only be interpreted by taking account of the difference in the anionic species, which fact naturally leads us to suppose the difference in the single ion activities of the anions in HX solutions.\(^\text{10}\) In section 4.1 in [1], Prof. de Levie wrote “understanding the meaning of the resulting numerical values must come from models or other extra-thermodynamic insights.” What? In interpretation of experimental results, do we allow people to rely on anything that is beyond the Prof. de Levie’s demarcation line, like the Emperors’s clothes or a magic wand or other imaginary staff? Prof. de Levie wrote on the same page, “And since all those other sources show an explicit dependence of \( \gamma^\pm_{\text{HX}} \) on \( \gamma_{X^-} \).” So, the concept of single ion activity coefficient was employed here to reasonably explain the results shown in Fig.1!

Then, a natural and logical question from curiosity is what is the magnitude of \( \gamma_{X^-} \)? Is it 0.5, 1.0, or 10, or even 100? This is the point I raised previously in [3] to illustrate the falsifiability of single ion activities: it may be 0.5 or 1.0, but not 10, nor 100, in ordinary electrolyte solutions. Unfortunately, however, no response was found this time in [1] about this crucial point with regard to the falsifiability. Is that criterion still believed to be indispensable?

I plan to separately write a note on philosophical aspects of the measurability of single ion activities. Briefly, Prof. de Levie founded his view on the falsifiability claimed by Karl Popper in the 1950s [5]. About 60 years since then, it seems proven that Popper’s positivism in the context of the philosophy of science is unable to explain the development of science and technology. Naturally, it has been forgotten or maybe remembered among contemporary philosophers as an old-fashioned variant of positivism [21]. Interestingly, some economists have recently tried to revive him or his view for authorizing their neoliberalism policy lines,\(^\text{11}\) which is intriguing because of its revival in harmony in the 21st century.

\(^{10}\) According to the DH-SiS model of the activities of monoprotic mineral acids [19, 20], the activity of hydrogen ions also vary with the type of the counter anion, which is reasonably understood within the framework of his model.

\(^{11}\) Notably, Mr. Haruhiko Kuroda, the Governor of the Bank of Japan since 2013 to the present.
3 Odds and ends

3.1 Heyrovsky’s polarography and Gouy’s electrocapillarity studies

In page 78, Prof. de Levie rightly pointed out that, in electrocapillarity measurements by Gouy and polarography by Heyrovsky, the cell did not contain any liquid junction. Actually, Gouy’s work was concerned with the electrocapillarity at the interface between mercury and an aqueous electrolyte solution when the interface was considered to be polarized; no appreciable faradaic current passed across the interface within a certain range of the potential window.

At such a polarized electrode, as demonstrated by the thermodynamics of electrocapillarity [22, 23], we have an additional degree of freedom in controlling the potential of the working electrode externally, which is distinct from the case when the working electrode is nonpolarized because of the presence of a faradaic process. Obviously, in the former, the liquid junction may not be present thanks to uniformity of the solution composition and the absence of the faradaic process at the working electrode. Polarography originated from electrocapillarity studies of mercury electrode to make use of the controllability of the electrode potential with externally applied voltage.

In polarography, however, in contrast to Gouy’s and other electrocapillarity studies, the current flowing across the interface is recorded as a function of the voltage externally applied to the working, dropping-mercury electrode (DME) with respect to the reference electrode, which was in early days of polarography a mercury pool whose surface area was much larger than that of the DME, so that the small current at the DME did not appreciably affect the potential of the reference, mercury pool electrode. For an accurate determination of half-wave potentials, however, use of a more stable reference electrode, such as a saturated calomel electrode, was recommended [24].

Furthermore, in most of electroanalytical measurements, nowadays, a potentiostat that employs a three electrode system is commonly used to maintain the electrode potential of the working electrode at an input value referred to the reference electrode. In such modern arrangements, the reference electrode is in contact with a sample solution, and, again, the liquid junction should be taken into account.

It is noteworthy that the half-wave potential determined in voltammetry is affected by the activities of Rd and Ox in the solution; the formal potential varies when the activity of the relevant species is altered, as has been illustrated elegantly by Kolthoff long time ago [25].

This is another example that the experimental results measured with a one hand clapping system reflect the magnitude of single ion activities, not the concentrations, of the redox species. Conversely, the magnitude of single ion activity is nonthermodynamically measured as the shift of the half-wave potential with changing the type and concentration of supporting electrolytes. Again, this “nonthermodynamic measurability” of the single ion activities is due to the one hand clapping of the galvanic cell, which in case of voltammetry is temporally formed between the reversible reference electrode and the otherwise polarized working electrode which becomes non-polarized because of the faradaic process.
3.2 Bates’s view on single ion activities

Roger G. Bates, who was the most prominent proponent of the IUPAC2002 definition of pH, and is well known for his achievement in the field of pH measurements. In stressing the significance of the “swamping” method in the final part of Introduction, Prof. de Levie made mention of Bates [1], “Near the end of his scientific career, Bates et al. [13-15] finally reached a similar conclusion, and proposed its use for certain aqueous solutions of major scientific and general interest, such as for monitoring the pH of seawater, but by then he had already retired from his position at NBS, and the IUPAC protocol had already been implemented.”

From this sentence, most of the readers probably have the impression that Bates at the end of his scientific career realized the usefulness of the swamping method in pH determination, in place of his earlier definition of pH based on the the previous problematic definition of pH based on the single ion activity of hydrogen ions, but was too late to turn over the IUPAC recommendations.

Actually, this picture looks odd because it is totally different from what Bates wrote in the late 1970s and 1980s. When Bates was working on pH of seawater in the late 1970s, he came to Japan, gave a talk at Sofia University, Tokyo, and left a paper entitled, “Problem of single ion activity” [26]. In that paper, he said, “With some justification, one may take the view that the failure of thermodynamics to offer a guide to the activity has been overemphasized, and that it is not as serious a limitation as it has been considered to be in the past” [26].

Even much later in 1989, he wrote, “Although not accessible to direct measurement, the single electrode potential and the activities of individual ionic species nonetheless appear explicitly in many formulations of electrochemical metrology” and “The result is a conventional basis for scale of ionic activities which, despite its nonthermodynamic nature, satisfies the requirements of modern electroanalytical chemistry [27].” Thus, his stance remained unchanged throughout his scientific career; it is highly unlikely that it was too late for Bates in the 1970s, or later, to topple the IUPAC2002 recommendations, in that since he retired from then NBS he had more than twenty years before the IUPAC finally agreed on the recommendations in 2002. What a contrast!

“No mouth to the dead.” Care must be exercised in telling old stories particularly when people are busily engaged with front-line science, having little time to trace back mossy literatures, and “post-truth” attitudes are rampant.

3.3 Missing part in English version

I noticed that one paragraph in [2] was inadvertently missing in my English version [3]. Though that paragraph is irrelevant to any extent to the present Polemik, I translate that paragraph below just for completeness and apologize for my lack of attentiveness. After the first paragraph of Introduction section, to be inserted is

“Bob de Levie is an outstanding scientist well known for contributions with high originality to electrochemistry, such as the phase transition of adsorbed monolayers, ion transfer across bilayer lipid membranes, and the electrode reactions of porous electrodes. He is versed to classical papers in physical chemistry published more than 100 years ago in different languages, and after the retirement from Georgetown University, he has published many papers on fundamental points
in analytical chemistry and electrochemistry in J. Chem. Edu. and others. Moreover, he has published several nice books, such as “Aqueous acid-base equilibrium and titrations,” (Oxford Univ. Press (1999)) and “Advanced Excel for Scientific Data Analysis,” (2nd ed., Oxford Univ. Press, (2008), 3rd ed., Atlantic Academic (2012)). He is thus a respectful scholar in the fields of electrochemistry, physical chemistry, analytical chemistry, and chemical education. I did not expect such view was claimed by the very person. For nearly two hours, I tried to keep my ears open not to miss hearing what such a highly esteemed scientist said about reasons why he claimed so.”

4 Conclusion

Once we agree to assign separate roles to working and reference electrodes in a galvanic cell, we need to recognize that the working electrode responds to the single ion activity, no matter whether we intentionally employ a salt bridge or not. The primary quantity nonthermodynamically measured is the activity. This splitting, a common practice in electroanalytical chemistry, is just a direct outcome or articulation of the intrinsically nonthermodynamic nature of galvanic cells.

The “Nernst equation” or, more properly, “Nernst-Lewis equation”, should be the one that reflects this fact. I plan to write a note about this subject, which I briefly described above.

5 Acknowledgments

I would like to sincerely thank Prof. de Levie for an opportunity to present my comments, this time, and also for giving me motivation for further work, which is definitely the fruit out of this Polemik. My special thank also goes to Prof. Osakai, the editor, for allowing me to exceed two pages beyond his original plan, and also for his meticulously careful reading of my manuscript.

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