On a Recent Purported Determination of Individual Ion Activity Coefficients

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In a recent article "On the activity of ions and the junction potential: Revised values for all data," G. Wilczek-Vera, E. Rodil, and J. H. Vera proposed the amended version of a controversial method to derive ion activity coefficients from electromotive force data. Here we show that their method is incorrect. Using precise data available for HCl, we show that their approach does not identify an unequivocal single set of ion activity coefficients, but as many sets as those that are introduced as the input in the evaluation of the liquid junction potentials. That is, an infinite number of self-consistent sets. Indeed, the "ion activity coefficients" found echo the starting assumptions, with no relationship to the actual, but unknown real values.
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Introduction

Vera and colleagues[1] published a long series of papers on the determination of individual ion activity coefficients.[2-12] Of course, ion activity coefficients (γ_i) would be more useful than mean activity coefficients ($\gamma_\pm$). Yet, Taylor and Guggenheim showed in 1927–1930 that the γ_i are not only impossible to determine, but even impossible to define unequivocally.[13-15] Their conclusions were that:

(1) A vicious circle, recognized in 1926 by Harned,[16] affects the responses of the potentiometric cells with liquid junctions, explained by the fact that "in order to obtain the liquid junction potential we must know the ion activity coefficients but in order to evaluate the ion activity coefficients we must know the liquid junction potential," and "any postulates which lead to the evaluation of the individual ion activities are equivalent to an evaluation of the liquid junction potential."[16] Guggenheim points out that "under the most favourable circumstances the uncertainty due to the liquid junction potential is more than equivalent to the difference between the individual chemical potentials of two different ions of the same charge when present at the same concentration in the same solution."[14]

(2) Furthermore, "no thermodynamic information can be gained from a cell with transference which could not better be gained from a cell without transference"; the emf of any cell, with or without transference, is "a function of molecular free energies solely and is not a function of ionic free energies. It therefore can yield no information whatsoever concerning ionic energies" (Taylor).[13] Electrode potentials and liquid junction potentials, taken separately, have no physical meaning, and the ionic free energy is not a thermodynamically defined quantity.[13]

(3) The previous considerations "may be considered as a corollary to a more general principle" that may be expressed as follows (Guggenheim)[14]: "The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities; it is therefore a conception which has no physical significance."[14] This fact implies that "the decomposition of the electrochemical potential $\tilde{\mu}_i$ into the sum of a chemical term μ_i and electrical term $z_i\varepsilon\psi$ is quite arbitrary and without physical significance. In other words the chemical potential or the activity of a single ion, and the electric potential difference between two points in different media are conceptions without any physical significance."[15]

Much later, in their textbook, Robinson and Stokes[17] remark that the operation implied in the definition of the chemical

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potential of an ion, that is, to add to the solution a quantity of one kind of ion only, cannot be physically performed.

> "Even if this could be done, it would result in an enormous increase in energy of the solution due to the self-energy of the electric charge involved, an effect which we do not wish to be concerned with, since it depends on the shape of the portion of solution considered. This self-energy change could of course be exactly cancelled by the subsequent addition of the equivalent amount of the oppositely charged ion, when the resultant total free energy change would be that due to the addition of a quantity of the electrically neutral electrolyte (. . .). We may thus agree to discuss the free energy change due to the addition of one species of ion only, neglecting the self energy effect, provided that we end with formulae involving only electrically equivalent amounts of cations and anions."[17]

We reach once again the conclusion that, unlike the chemical potential of the electrically neutral electrolyte, the chemical potential of an ion in solution (and therefore, the corresponding γ_i) cannot be defined univocally.

Although all these arguments taken as a whole are incontrovertible, Vera and his school maintain that the experiments they perform using potentiometric cells with transport, ion-selective electrodes and a calibration method based on an approximate evaluation of the liquid junction potentials, overcome the conceptual problems of the question. Rebuttals based on theoretical considerations may not be persuasive in showing that the method is incorrect.

Therefore, we will avoid debating the theoretical aspects of the question. Instead, we will show that, even assuming that an experimental determination of individual γ_i is feasible, the method that Vera and his school adopt is unequal to this task. That is, we will prove that Vera's method does not yield any information about ion activity coefficients, but returns only an artifact of the arbitrary values used (implicitly or explicitly) as the input in the calculation of the liquid junction potentials, with no relationship to the real values of γ_i. (Note that an incorrect sign in the liquid junction potentials of Vera's previous papers was corrected by Wilczek-Vera, Rodil, and Vera in their 2004 paper[1]; however, this error is irrelevant because the method is intrinsically inconsistent.)

Our demonstration starts by examining a very simple system in which exact thermodynamic equations are consistently applied. If Vera's method is correct in the more complex systems that he examined, it should also be correct for this simple system. Conversely, if it fails even in the simplest case, it fails a fortiori in all cases.

The simulated system and its potentiometric behavior

Let us examine the electromotive force (emf, E) of the following cells:

Cell 1 (E_1 = *emf*)

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{HCl}\ (m^*)\ \vdots\ \mathrm{HCl}\ (m)\,|\,\mathrm{H_2}(p = 101.325\ \mathrm{kPa}),\ \mathrm{Pt}\,|\,\mathrm{Ag}$$

Cell 2 (E_2 = *emf*)

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{HCl}\ (m^*)\ \vdots\ \mathrm{HCl}\ (m)\,|\,\mathrm{ISE}\ (\mathrm{Cl^-})\,|\,\mathrm{Ag}$$

where m (variable) and m^* (constant) are molal concentrations. The value of m^* is 3 mol kg^{-1}. A chloride-ion–selective membrane electrode, ISE ($\mathrm{Cl^-}$), rather than an AgCl/Ag electrode, is preferred in cell 2 to eliminate problems arising from the nonnegligible solubility of AgCl. We assume that the potential of the ISE is perfectly linear with $\ln(m\gamma_-)$, with γ_- representing the activity coefficient of $\mathrm{Cl^-}$, with the Nernst exact slope $-RT/F$, and that the "standard potential " of the ISE, $E^\circ_{(\mathrm{ISE})}$, is equal to the standard potential of the silver–silver chloride electrode, $E^\circ_{(\mathrm{AgCl/Ag})}$ (222.414 mV,[18] translated from international volt into volt units). In fact, if the internal electrode of the ISE is an AgCl/Ag electrode and the membrane of the ISE is permeable only to $\mathrm{Cl^-}$, the relationship $E^\circ_{(\mathrm{ISE})} = E^\circ_{(\mathrm{AgCl/Ag})}$ is obeyed, both practically and theoretically.[19]

Both cell 1 and cell 2 can be analyzed by an exact thermodynamic development. The general equation describing isothermal cells[13,20] yields

$$E_1 = -E^\circ_{(\mathrm{AgCl/Ag})} + \mathrm{RTF}^{-1}\ln(m^*\gamma^*_-) - \left[\mathrm{RTF}^{-1}\int_\alpha^\omega \sum_i t_i z_i^{-1} d\ln(m_i\gamma_i)\right] + \mathrm{RTF}^{-1}\ln(m\gamma_+) = E_{0(1)} + E_J + \mathrm{RTF}^{-1}\ln(m\gamma_+) \quad (1)$$

$$E_2 = -E^\circ_{(\mathrm{AgCl/Ag})} + \mathrm{RTF}^{-1}\ln(m^*\gamma^*_-) - \left[\mathrm{RTF}^{-1}\int_\alpha^\omega \sum_i t_i z_i^{-1} d\ln(m_i\gamma_i)\right] + E^\circ_{(\mathrm{ISE})} - \mathrm{RTF}^{-1}\ln(m\gamma_-) = E_{0(2)} + E_J - \mathrm{RTF}^{-1}\ln(m\gamma_-) \quad (2)$$

where the integrals range between the left solution α, HCl at $m^* = 3$ mol kg^{-1}, and the right solution ω, HCl at m mol kg^{-1}. $E_{0(1)}$ with the minus sign is the potential of an AgCl/Ag electrode in 3 mol kg^{-1} HCl saturated by AgCl, $E_{0(2)}$ is $[E_{0(1)} + E^\circ_{(\mathrm{ISE})}]$, that is, $\mathrm{RTF}^{-1}\ln(m^*\gamma^*_-)$, and the quantity

$$E_J = -\mathrm{RTF}^{-1}\int_\alpha^\omega \sum_i t_i(m_1, m_2, \ldots, m_i, \cdots) z_i^{-1} d\ln(m_i\gamma_i) \quad (3)$$

(where the sum extends to all ions present, 1, 2, . . . , i,· · ·; in the present case, only $\mathrm{H^+}$ and $\mathrm{Cl^-}$) is the exact general expression of the diffusion potential (the "liquid junction" potential). Because of the particular conditions selected (only two ions involved, thus $m_+ = m_- = m$; $t_- = 1 - t_+$; $z_+ = -z_- = 1$), the activity coefficients and transport numbers are functions of the unique variable m, and Eq. 3 reduces to the following equation

$$E_J = -\mathrm{RTF}^{-1}\left\{\int_\alpha^\omega t_+(m) d\ln(m\gamma_+) - \int_\alpha^\omega [1 - t_+(m)] d\ln(m\gamma_-)\right\} \quad (4)$$

Table 1. Available Data for HCl, Cell 1, and Cell 2

m (mol kg^{-1})	$\gamma_{\pm}$*	t_+**	$t_+^{(\alpha,\omega)}$	E_1 (mV)†	E_2 (mV)††	$\gamma^{G\,\ddagger}$
3	1.318	0.8449	0.8449	−151.788	0.000	0.475
2.5	1.150	0.8438	0.8443	−154.338	13.832	0.487
2	1.011	0.8429	0.8439	−157.169	29.086	0.503
1.5	0.898	0.8420	0.8434	−160.450	46.659	0.524
1	0.811	0.8407	0.8428	−164.582	68.579	0.556
0.5	0.759	0.8379	0.8414	−170.889	101.341	0.615
0.2	0.766	0.8338	0.8394	−178.617	140.173	0.696
0.1	0.795	0.8309	0.8379	−184.326	168.180	0.754
0.05	0.830	0.8284	0.8367	−190.030	195.883	0.807
0.02	0.875	0.8259	0.8354	−197.626	232.659	0.865
0.01	0.905	0.8246	0.8347	−203.424	260.791	0.899
1×10^{-3}	0.965	0.8221	0.8335	−222.953	356.239	0.965
1×10^{-4}	0.989	0.8213	0.8331	−242.674	453.617	0.988
1×10^{-5}	0.996	0.8210	0.8330	−262.445	551.762	0.996
1×10^{-6}	0.999	0.8209	0.8329	−282.236	650.162	0.999

*Smoothed activity coefficients of HCl, the Pitzer equation.[21]

**Robinson and Stokes,[17] and empirical equation $t_+ = 0.8209 + 0.0392m^{1/2} - 0.0260m + 0.0656m^{3/2}$.

†Equation 6.

††Equation 7.

‡Equation 14.

Robinson and Stokes[17] report numeric $t_+(m)$ values of HCl, found to vary between 0.8209 (infinite dilution) and 0.845 ($m = 3$ mol kg^{-1}) with a monotone trend (empirically, $t_+ = 0.8209 + 0.0392m^{1/2} - 0.0260m + 0.0656m^{3/2}$). Thus, the value of the definite integrals in Eq. 4 is intermediate between the extreme values corresponding to the two approximations of a constant $t_+ = 0.821$ and a constant $t_+ = 0.845$ (as to say, the relevant E_J estimations differ by no more than 2.7%). Substituting the average value 0.833 for $t_+(m)$, the error introduced in E_J has to be around 1.5% or less. Even better, one can select a different "average transport number, " $t_+^{(\alpha,\omega)} = [t_+(\alpha) + t_+(\omega)]/2$, for any solution ω examined. Using $t_+^{(\alpha,\omega)}$ for $t_+(m)$ into Eq. 4 and integrating Eq. 4, we obtain the following expression

$$E_J = -\mathrm{RTF}^{-1}\{t_+^{(\alpha,\omega)}\ln[(m\gamma_+)/(m^*\gamma_+^*)] - [1 - t_+^{(\alpha,\omega)}]\ln[(m\gamma_-)/(m^*\gamma_-^*)]\} \quad (5)$$

and Eqs. 1 and 2 reduce to, respectively,

$$E_1 = -E^{\circ}_{(\mathrm{AgCl/Ag})} + 2\mathrm{RTF}^{-1}\{t_+^{(\alpha,\omega)}\ln(m^*\gamma_{\pm}^*) + [1 - t_+^{(\alpha,\omega)}]\ln(m\gamma_{\pm})\} \quad (6)$$

$$E_2 = 2t_+^{(\alpha,\omega)}\mathrm{RTF}^{-1}\ln[(m^*\gamma_{\pm}^*)/(m\gamma_{\pm})] \quad (7)$$

Note that E_1 and E_2 are both *independent* of the individual ion activity coefficients. Therefore, it does not seem plausible that information not contained in E_1 and E_2 can then be extracted from E_1 and E_2, irrespective of the method one uses to attempt this!

All data involved in Eqs. 6 and 7 are available for HCl. Thus, we are able to calculate a reliable set of "synthetic " values of E_1 and E_2 strictly consistent with the $t_+^{(\alpha,\omega)}$ and $\gamma_{\pm}$ values also used in the subsequent treatments aimed at recovering γ_+ and γ_-, and thus more appropriate to our purposes than new real experiments. Because we are dealing with synthetic data, we have no problems in providing precise values, even at such extreme dilution levels as 10^{-6} mol kg^{-1}, where real experiments are hardly feasible. These values are reported in Table 1. The Pitzer empirical equation, with a range of validity $0 \leq m$ (mol kg^{-1}) ≤ 6 for HCl,[21] is used as the source of the $\gamma_{\pm}$ values. Table 1 also contains $t_+^{(\alpha,\omega)}$ values derived from the data reported in Robinson and Stokes.[17]

Note that we are not able to evaluate the corresponding E_J (which cannot be measured experimentally) before making suitable preliminary hypotheses about the γ_+^*, γ_-^*, γ_+, and γ_- values required by Eq. 5.

Back-calculation of γ_+ and γ_- by the Vera Method

We will now submit the data in Table 1 to the Vera procedure to identify the purported "experimental " activity coefficients, $\gamma_{+(\mathrm{exp})}$ and $\gamma_{-(\mathrm{exp})}$. The method starts by an approximate evaluation of the liquid junction potentials E_J (step 1) and of the potentials $E_{0(1)}$ and $E_{0(2)}$ (step 2). Once E_J, $E_{0(1)}$, and $E_{0(2)}$ are identified, their values are introduced in Eqs. 1 and 2, yielding

$$\ln \gamma_{+(\mathrm{exp})} = [E_1 - E_{0(1)} - E_J]/(\mathrm{RTF}^{-1}) - \ln m \quad (8)$$

$$\ln \gamma_{-(\mathrm{exp})} = -[E_2 - E_{0(2)} - E_J]/(\mathrm{RTF}^{-1}) - \ln m \quad (9)$$

Rather than E_1, E_2, and E_J separately, Wilczek-Vera, Rodil, and Vera prefer to deal with the quantities $\phi_1 = E_1 - E_J$ and $\phi_2 = E_2 - E_J$, and indicate as S_1 and S_2 rather than RTF^{-1} and −RTF^{-1} as the slopes. In their notation, Eqs. 8 and 9 become

$$\ln \gamma_{+(\mathrm{exp})} = [\phi_1 - E_{0(1)}]/S_1 - \ln m \quad (10)$$

$$\ln \gamma_{-(\mathrm{exp})} = [\phi_2 - E_{0(2)}]/S_2 - \ln m \quad (11)$$

Wilczek-Vera, Rodil, and Vera also consider the possibility that S_1 and S_2 do not coincide with the Nernst slopes; therefore, they determine "practical" S_1 and S_2 from the trend of ϕ_1 and

ϕ_2 in the dilute region. They believe that a slope different from the theoretical one can arise because of the inaccurate values of E_J, and can allow in part for the corresponding error in ϕ_1 and ϕ_2, thus creating a self-correction effect. They also believe that, because of such self-correction effects, $\gamma_{+(\text{exp})}$ and $\gamma_{-(\text{exp})}$ calculated from Eqs. 10 and 11 with the appropriate "practical" S_1 and S_2 values (unlike those calculated using Eqs. 8 and 9 and Nernst slopes) are scarcely influenced by the incorrect input values of γ_+ and γ_-, which are introduced in the E_J Eq. 5.

However, this is not the case. Indeed, we will see that the two procedures, using either Eqs. 8 and 9 or Eqs. 10 and 11, become identical provided E_1 and E_2 are sufficiently precise and attain sufficiently high dilution levels. "Practical" S_1 and S_2 differing from the Nernst value can be found if E_1 and E_2 are imprecise in the dilute regions, or if the ion-selective electrodes are intrinsically characterized by a non-Nernst slope. Incidentally, Wilczek-Vera, Rodil, and Vera also allow this possibility, although we cannot approve of their choice. Should the electrode potential obey a relationship of the kind $E_{\text{ISE}} = \text{const.} + S_i \ln(m_i \zeta_i) = \text{const.} + S_i^{\circ} \ln(m_i \zeta_i)^{\eta}$, with $\eta = S_i/S_i^{\circ}$ and S_i° equal to the Nernst slope, no theoretical bases exist for ζ_i to be really γ_i and not—as is much more probable—some function of the composition and the ISE that is not better identified. Thus, the idea that a similar ISE can be used to determine γ_i does not work.

Step 1: evaluation of E_J

The general cases that Wilczek-Vera, Rodil, and Vera deal with do not admit an exact thermodynamic resolution because more than two different ion species are involved. Thus in their paper an approximate and convoluted treatment is necessary, requiring some starting hypothesis about the concentrations, transference numbers, and activity coefficients of the different ions in the transition regions. Leaving aside the question of their correctness, these simplifications and approximations are no longer necessary in the present case in which only two ionic species, H^+ and Cl^-, are involved and thus the liquid junction potential is independent of the concentrations in the transition regions (Eq. 5). Thus, no approximations or arbitrary assumptions are required in the present calculations of E_J, except for the input values of the ion activities that need to be introduced in Eq. 5.

The simplest one of the equations used by Wilczek-Vera, Rodil, and Vera does not consider the effect of the ion activity coefficients inside E_J, that is, such values of E_J are those that Eq. 5 provides by setting all the γ_i at 1 as in an "ideal" solution. That is a first arbitrary possibility; we designate the corresponding E_J as E_J^{id}. The values are, therefore, $E_J^{id} = \text{RTF}^{-1}[2t_+^{(\alpha,\omega)} - 1]\ln(m^*/m)$; $\phi_1^{id}$and ϕ_2^{id} are the corresponding ϕ_1 and ϕ_2; $\gamma_+^{id}$and γ_-^{id}, the corresponding activity coefficients. However, to set values of γ_i all at 1 is not consistent with the $\gamma_\pm$ values. A still arbitrary, but self-consistent, alternative possibility is to assume that $z_+^{-2}\ln \gamma_+ = z_-^{-2}\ln \gamma_- = z_\pm^{-2}\ln \gamma_\pm$ as the ion interaction theory predicts in dilute solutions. Because HCl is a 1:1 electrolyte, this assumption means to introduce $\gamma_+ = \gamma_- = \gamma_\pm$ and $\gamma_+^* = \gamma_-^* = \gamma_\pm^*$ in Eq. 5. Thus, the values of E_J are automatically assumed to hold $\text{RTF}^{-1}[2t_+^{(\alpha,\omega)} - 1]\ln[(m^*\gamma_\pm^*)/(m\gamma_\pm)]$. We will indicate as E'_J, ϕ'_i, and γ'_i the relevant E_J, ϕ_i, and γ_i.

Two further arbitrary possibilities are now considered, consisting in γ_+ equal to the mean activity coefficients of $AgNO_3$ (why not?) and $\gamma_- = \gamma_\pm^2(\text{HCl})/\gamma_+$ (E''_J, ϕ''_i, and γ''_i the corresponding E_J, ϕ_i, and γ_i); or oppositely, γ_- equal to the mean activity coefficients of $AgNO_3$ and $\gamma_+ = \gamma_\pm^2(\text{HCl})/\gamma_-$ (E'''_J, ϕ'''_i, and γ'''_i). The mean activity coefficients of $AgNO_3$ are those that the Pitzer empirical equation provides (range of validity, from 0 to 6 mol kg^{-1} for $AgNO_3$).[21] Thus four different "input " selections, three of which are consistent with the $\gamma_\pm$ values, are sufficient for our purposes.

The Wilczek-Vera, Rodil, and Vera method requires that $E_{0(1)}$ and $E_{0(2)}$ be determined by extrapolation, from the ϕ_1 and ϕ_2 available in dilute solutions; values of $E_{0(1)}$ and $E_{0(2)}$ are then introduced in Eqs. 10 and 11 to provide $\gamma_{+(\text{exp})}$ and $\gamma_{-(\text{exp})}$ at all concentrations. The procedure is theoretically correct, except for the arbitrary choice of the γ_i input values introduced in Eq. 5 to obtain E_J and calculate ϕ_1 and ϕ_2. Wilczek-Vera, Rodil, and Vera believe that their method is sufficiently self-correcting so that the imprecise γ_i values of the input set do not cause significant errors. Thus, supposing that the Wilczek-Vera, Rodil, and Vera procedure really determines the individual ion activity coefficients, and not a mere result of the input assumptions, we would expect that any theoretically admissible set of γ_+ and γ_- introduced in E_J as an input, would lead to an identical and unique output set of $\gamma_{+(\text{exp})}$ and $\gamma_{-(\text{exp})}$. To confirm this crucial point, we will compare the results of the four input selections E_J^{id}, E'_J, E''_J, and E'''_J.

Step 2: evaluation of $E_{0(1)}$ and $E_{0(2)}$

Following Wilczek-Vera, Rodil, and Vera, we have

$$\phi_1 = E_{0(1)} + S_1 \ln(m\gamma_+) \tag{12}$$

$$\phi_2 = E_{0(2)} + S_2 \ln(m\gamma_-) \tag{13}$$

in which, as a starting hypothesis, S_1 and S_2 are assumed not necessarily to be coincident with the Nernst slopes. In very dilute solutions γ_+ and γ_- are indistinguishable from γ^G calculated by means of the Güntelberg approximation of Debye–Hückel theory,[1] which is for 1:1 electrolytes

$$\ln \gamma^G = -1.1749 m^{1/2}/(1 + m^{1/2}) \tag{14}$$

(We use 1.1749, and not 1.1762,[1] to be consistent with other physical constants embedded in our software, with which the synthetic $\gamma_\pm$ have been created. In our calculations, the value of RTF^{-1} is assumed to be 25.693 mV.) Plotting ϕ_i vs. $\ln(m\gamma^G)$, one finds in the dilute region a linear trend of the experimental S_i and $E_{0(\text{i})}$ by extrapolation. In real experiments, such an extrapolation is risky because moderate errors in the dilute regions may cause appreciable errors in S_i and $E_{0(i)}$. However, in the present case, we have the advantage that there is no experimental error. If extreme dilutions are selected, and the ϕ_1 and ϕ_2 values used in the extrapolation are those for the range 10^{-6}–10^{-5} mol kg^{-1}, then one finds that the "experimental" values of S_1 and S_2 are always the same using either the E_J^{id}, E'_J, E''_J, or E'''_J approximations, and coincide with the Nernst slopes; the "experimentally extrapolated" $E_{0(1)}$ and $E_{0(2)}$, in turn, coincide with those calculated more directly by means of the following theoretical relations

Table 2. Liquid Junction Potential and Ion Activity Coefficients Consistent with Input Approximations $\gamma^{id}_{+} = \gamma^{id}_{-} = 1$ (E^{id}_J) and $\gamma'_{+} = \gamma'_{-} = \gamma_{\pm}$ (E'_J)

m (mol kg^{-1})	E^{id}_J *	$\gamma^{id}_{+(\mathrm{exp})}$	$\gamma^{id}_{-(\mathrm{exp})}$	E'_J **	$\gamma'_{+(\mathrm{exp})}$	$\gamma'_{-(\mathrm{exp})}$
3	0.000	1.085	1.600	0.000	1.318	1.318
2.5	3.226	1.041	1.270	5.641	1.150	1.150
2	7.165	0.999	1.022	11.852	1.011	1.011
1.5	12.232	0.963	0.837	18.999	0.898	0.898
1	19.351	0.932	0.706	27.893	0.811	0.811
0.5	31.434	0.912	0.631	41.120	0.759	0.759
0.2	47.223	0.913	0.643	56.672	0.767	0.767
0.1	59.054	0.923	0.685	67.821	0.795	0.795
0.05	70.831	0.935	0.737	78.820	0.830	0.830
0.02	86.360	0.952	0.805	93.411	0.875	0.875
0.01	98.106	0.962	0.850	104.577	0.904	0.904
1×10^{-3}	137.205	0.983	0.947	142.537	0.965	0.965
1×10^{-4}	176.447	0.992	0.985	181.366	0.989	0.989
1×10^{-5}	215.770	0.996	0.996	220.553	0.996	0.996
1×10^{-6}	255.119	0.999	0.999	259.857	0.999	0.999

*"Experimental" $E^{id}_{0(1)} = -182.131$ mV, $E^{id}_{0(2)} = 40.280$ mV, $S_1 = 25.710$ mV (theoretical, 25.693 mV), $S_2 = -25.676$ mV (theoretical, -25.693 mV).
**"Experimental" $E'_{0(1)} = -187.101$ mV, $E'_{0(2)} = 35.313$ mV, $S_1 = 25.693$ mV, $S_2 = -25.693$ mV.

$$E_{0(1)} = \phi_{1(\mathrm{dil})} - \mathrm{RTF}^{-1}\ln(m_{(\mathrm{dil})}\gamma_{+(\mathrm{dil})}) \qquad (15)$$

$$E_{0(2)} = \phi_{2(\mathrm{dil})} + \mathrm{RTF}^{-1}\ln(m_{(\mathrm{dil})}\gamma_{-(\mathrm{dil})}) \qquad (16)$$

where the subscript (dil) indicates any solution of HCl that is so dilute (such as 10^{-5} mol kg^{-1}) for $\gamma_{+(\mathrm{dil})} = \gamma_{-(\mathrm{dil})} = \gamma_{\pm(\mathrm{dil})} = \gamma^G$ that will certainly hold. That is, the hypothesized self-correcting features of the "practical " S_1 and S_2 and $E_{0(1)}$ and $E_{0(2)}$ do not exist because there are no differences in the results of the "practical " and "theoretical " procedure if E_1 and E_2 are precise and high dilutions are reached (as for this point, we note that the input approximation E^{id}_J, inconsistent with the values of $\gamma_{\pm}$, causes a dilution level of even 10^{-6} mol kg^{-1} to be still insufficient for the "practical " S_1 and S_2 coincide perfectly with the correct theoretical slopes; see Table 2).

Results and Discussion

The same computations have been repeated for the four input hypotheses E^{id}_J, E'_J, E''_J, and E'''_J. The results in Tables 2 and 3 show immediately that—contrary to what Vera and coworkers maintain—$\gamma_{+(\mathrm{exp})}$ and $\gamma_{-(\mathrm{exp})}$ are not independent of the selected input. More precisely, $\gamma'_{+(\mathrm{exp})}$ and $\gamma'_{-(\mathrm{exp})}$, $\gamma''_{+(\mathrm{exp})}$ and $\gamma''_{-(\mathrm{exp})}$, and $\gamma'''_{+(\mathrm{exp})}$ and $\gamma'''_{-(\mathrm{exp})}$ obtained as the output, are found to be exactly the same as γ'_{+} and γ'_{-}, γ''_{+} and γ''_{-}, or γ'''_{+} and γ'''_{-} used as the input inside the corresponding E_J, and their values are thus completely arbitrary. The input values $\gamma^{id}_{+} = 1$ and $\gamma^{id}_{-} = 1$, which are incompatible with the values of $\gamma_{\pm}$, of course generate a different output, $\gamma^{\mathrm{id}}_{+(\mathrm{exp})}$and $\gamma^{\mathrm{id}}_{-(\mathrm{exp})}$, consistent with the values of $\gamma_{\pm}$. In practice, any self-consistent set of γ_{+} and γ_{-} used as the input is then found again as the output without any change. It is particularly impressive that the two series of $\gamma_{+(\mathrm{exp})}$ and $\gamma_{-(\mathrm{exp})}$, corresponding to the E''_J and E'''_J paths, are exactly exchanged with each other, thus also suggesting that the result presented by Vera and his school, of the activity coefficients being greater for the cation or the anion of the different electrolytes, can easily be reversed. Clearly, if one suspects that any series of activity coefficient values attributed to cations can contrarily pertain to the anions and vice versa, there is no way to further improve γ_{+} and γ_{-}, beyond the generic consideration that their values are pre-

Table 3. Liquid Junction Potential and Ion Activity Coefficients Consistent with Input Approximations $\gamma''_{+} = \gamma_{\pm}(\mathrm{AgNO_3})$, $\gamma''_{-} = \gamma^2_{\pm}/\gamma''_{+}$ (E''_J), and, Reverted, $\gamma'''_{+} = \gamma''_{-}$, γ'''_{-}, $= \gamma''_{+}$ (E'''_J)

m (mol kg^{-1})	$\gamma_{\pm}(\mathrm{AgNO_3})$*	E''_J **	$\gamma''_{+(\mathrm{exp})}$	$\gamma''_{-(\mathrm{exp})}$	E'''_J †	$\gamma'''_{+(\mathrm{exp})}$	$\gamma'''_{-(\mathrm{exp})}$
3	0.250	0.000	0.250	6.948	0.000	6.948	0.250
2.5	0.278	−0.625	0.278	4.750	11.907	4.750	0.278
2	0.314	−0.825	0.314	3.254	24.530	3.254	0.314
1.5	0.361	−0.277	0.361	2.236	38.275	2.236	0.361
1	0.426	1.741	0.426	1.546	54.044	1.546	0.426
0.5	0.531	7.578	0.531	1.084	74.663	1.084	0.531
0.2	0.652	18.109	0.652	0.901	95.235	0.901	0.652
0.1	0.729	27.349	0.729	0.868	108.292	0.868	0.729
0.05	0.793	37.298	0.793	0.870	120.343	0.870	0.793
0.02	0.858	51.200	0.858	0.893	135.620	0.893	0.858
0.01	0.895	62.121	0.895	0.914	147.033	0.914	0.895
1×10^{-3}	0.964	99.847	0.964	0.966	185.227	0.966	0.964
1×10^{-4}	0.988	138.651	0.988	0.989	224.081	0.989	0.988
1×10^{-5}	0.996	177.835	0.996	0.996	263.270	0.996	0.996
1×10^{-6}	0.999	217.139	0.999	0.999	302.575	0.999	0.999

*Calculated by means of Pitzer equation.[21]
**"Experimental" $E''_{0(1)} = -144.383$ mV, $E''_{0(2)} = 78.031$ mV, $S_1 = 25.693$ mV, $S_2 = -25.693$ mV.
†"Experimental" $E'''_{0(1)} = -229.817$ mV, $E'''_{0(2)} = -7.404$ mV, $S_1 = 25.693$ mV, $S_2 = -25.693$ mV.

sumably of the same order of magnitude of the mean activity coefficients.

A possible objection against our critical discussions that rely on cells 1 and 2 and HCl, consists in remarking that these cells are very particular, and thus the information on the single ion activity coefficients has disappeared because of the particular symmetry conditions. A single electrolyte is present in all sections of the cell, and this fact makes the liquid junction potential depend on the activity coefficient of the counter-ion in such a way that it combines with the activity coefficient of the target ion and eliminates the individual contributions, leaving only an overall dependency on $\gamma_{\pm}$. Let us assume now, although Taylor's arguments deny this possibility,[13] that the cells with a liquid junction between different electrolytes no longer fulfill the situation in which the combination of the electrode potential and E_J completely erases individual ion contributions. Yet, residual unpaired contributions of single ions do not mean a cell whose emf depends on the concentration of the target ion i times its activity coefficient. These only mean, at the best, a cell whose emf depends on the concentration of the target ion times a not well-identified quantity, ζ or $\gamma_{(?)}$, which is a sort of convoluted combination of the activity coefficients of several ions, and also involves irresolvable contributions arising from the real patterns of the ion concentrations in the transition regions. The $\gamma_{(?)}$ empirical factors, whose order of magnitude is comparable with that of known (or predicted) mean activity coefficients in similar solutions, do not coincide with either γ_i or $\gamma_{\pm}$. Suitable conventions and standardized procedures can be selected for $m_i\gamma_{(?)}$ to be used as a "conventional activity" of i. Such conventional activities can be very useful for practical purposes (we have a typical example in the operational pH values); however, the *conventional* nature of such individual ion activities should never be forgotten.

To address the question of the peculiar cells used in our demonstration in another way, let us consider now a modified cell 1 (or cell 2) in which the left vessel (the reference electrode) and salt bridge have been substituted, leaving only the vessel of the target solution and the relevant electrode unchanged. Thus, the cells examined so far, which do not provide information about the ion activity coefficient of H^+ (or Cl^-), transform in one of the typical cells in which Vera and collaborators determine their reported ion activity coefficients. At this point, one can ask how the change of the reference electrode (that is, a mere shift of E_1 or E_2 by a constant value) and a more complex liquid junction (say, an E_J no longer liable to an exact representation, and thus unknown, even in the hypothetical occurrence of all ion activity coefficients already known at all different compositions encountered throughout the cell) should improve the situation so as to transform an emf that does not contain information on γ_+ or γ_- into a new emf that now contains the desired information, and permits such information to be extracted. The only answer is that this possibility does not exist.

Conclusions

It has long been known that individual ion activities can be defined only in conventional terms.[14] Therefore, it was not unexpected that the "absolute" ion activity coefficients reported by Vera and coworkers revealed, by a more accurate analysis, to consist in only *one arbitrary guess* among the infinite arbitrary ways in which the mean activity coefficients can be divided in two parts that obey the Debye–Hückel law in the limit of infinite dilution. As previously noted,[22] the method that Vera and coworkers propose cannot work because it would require correct ion activity coefficients to calculate the liquid junction potentials, and correct liquid junction potentials to determine the ion activity coefficients. The use of hypothetical approximate values, with the hope that these can break the circle, thus yielding—by iterative methods, if necessary—the correct γ_i, is an illusion; the values obtained are a mere result of the values entered. There is no way the liquid junction potentials and activity coefficients so obtained can be connected to the real values.

Wilczek-Vera, Rodil, and Vera believe that "while for the evaluation of the activities of individual ions it is required to know the junction potential, the inverse is not necessarily true" because "there is no reason to believe that future advances in electronics would not make possible the direct measurement of junction potentials," thus making ion activity coefficient determinations possible without any preliminary assignment of their values. Unfortunately, the experimental determination of E_J is in its turn *conceptually* impossible. This point is clearly explained in the Harned and Owen book,[23] which reports the Guggenheim considerations about the electric potential differences between points in nonidentical phases.[14,15] We can conceptually measure only the electrostatic potential difference between two points that lie in the air phase in the nearer neighborhoods of the solutions m^* and m; however, this difference is biased by the interfacial potentials m^*/air and m/air that, like E_J, depend on the unknown ion activities; thus, such an "external " difference of potential does not represent E_J. As for hypothetical "internal " measurements, one cannot use two electrodes, thus introducing additional potentials that depend on the unknown quantities to be determined. In a mere ideal electrostatic experiment one transfers a very small charge from a point to a different point, measures the work expended, and divides the work by the charge, thus obtaining the difference of the electrostatic potential. Such an experiment is conceptually feasible only between two points belonging to two exactly identical phases, not to different phases.[14,15]

Because immaterial charges do not exist, let us consider the transfer an H^+ ion (or a Cl^- ion) from the solution m^* to the solution m. The work expended is the sum of two effects, one of which arises from the different value of the chemical potential, $\mu_i^\circ + RT\ln(m_i\gamma_i)$, in the two solutions, the other arising from the different electric potential E_J. Once again, for the E_J contribution to be separated it is necessary to assign γ_i and γ_i^* preliminarily—which is exactly what we are not able to do, except by a convention. The same considerations also apply if one uses a species that is not really contained in the two solutions, such as a solvated or bare electron, in the ideal experiment; also the electron indeed has a different activity coefficient in the two solutions, given that the interactions with the ion clouds are different. Thus, we are once again not able to separate the electric work from total work measured; on the other hand, the ratio between total expended work and charge is different for H^+, Cl^-, and the electron. Even the possibility of an unambiguous *definition* of E_J is questionable. Therefore, the problem of the "true " value of E_J cannot be solved by future advances in electronics, and the individual ion activity coefficients are deemed to remain unattainable.

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