# Reply to Comments by F. Malatesta on *J. Chem. Eng. Data* 2009, *54*, 345−350

**Grazyna Wilczek-Vera**[†] **and Juan H. Vera***[,‡]

Department of Chemistry and Department of Chemical Engineering, McGill University, Montreal, QC, Canada, H3A 2A7

In his comments, F. Malatesta confirms what we have stated in previous publications.[1,2] The "infinite sets of possible ion activity coefficients able to satisfy" the equation of a voltaic cell "reduce to one single set" if it is solved jointly with the equation for the junction potential. While this is a very positive step, Malatesta fails to notice that the values of this single set coincide closely with those obtained using only the equation for an ion-selective electrode (ISE) with an estimated value of the junction potential.[2] Moreover, Malatesta ignores the fact that data obtained by other researchers[3,4] using Nernstian ISEs also agree with these values. In the case of our measurements, the "coincidence" demonstrates that proper calibration of the electrode's response largely cancels any bias introduced by an error in the value of the junction potential. In fact, the slopes of ISEs used by us are closely Nernstian. In the case of the values reported by Zhuo et al.,[4] the coincidence is more striking as these authors collected and reduced the data using methods different from ours. They used a double junction instead of a single junction reference electrode and assumed a null junction potential. Instead of calibrating the ISE in the diluted region, they used an expression for the ionic activity and fitted its parameters using the data in the concentrated region. In addition to the above coincidences, we have also shown that changing the nature and concentration of the reference solution forming the junction with the sample solution does not affect significantly the ionic activities obtained.[5,6] In this path, we have followed Leonardo Da Vinci's advice:[7] "First I shall do some experiments before I proceed further, because my intention is to cite experience first and then with reasoning show why such experience is bound to operate in such a way. And this is the true rule by which those who speculate about the effects of nature must proceed."

Contrary to what Malatesta states, the equation to calculate the junction potential is far from arbitrary. Its derivation, based on the potential for ion diffusion, has been discussed elsewhere.[1] A junction potential between reference and a sample solution exists independently of the presence of an ISE in the system; i.e., the equation to calculate the junction potential is independent of the equation for the half-cell ISE. Thus, it is not surprising that the simultaneous solution of these two equations will "collapse" in a single set of ionic activities. G.N. Lewis and M. Randall,[8] referring to the possibility of measuring ionic activities, stated that: "This indeed might be accomplished if we had any general method of calculating the potential at a liquid junction." We have just proved that this statement is true.

Malatesta closes his note warning scientists not to rely on our measurements of ionic activities for validation purposes. He indicates that our results can only be used in the case of two salts with a common ion for comparison of the activities of the two counterions. Regrettably, this comparison can be done without using our measurements at all. It suffices to know the mean ionic activity coefficients of the two salts in solution. On the other hand, he states that our measurements in single electrolyte aqueous solutions cannot be used to decide whether the cationic activity coefficients are higher or lower than the anionic ones. This statement contradicts experimental observations. The fact is that, using the same Cl-ISE, the $Cl^-$ activity coefficients are higher than the mean ionic activity coefficients of KCl in KCl solutions and lower than the mean ionic activity coefficients of NaCl in NaCl solutions.[1,5] As we have shown that a bias introduced by the junction potential largely cancels due to the electrode calibration,[1,5,6] the conclusion regarding the relative magnitudes of the ionic activity coefficients seems unavoidable.

In closing, we acknowledge that there is much work to be done before the matter of ionic activities is settled. We know that the main source of uncertainty comes from the junction potential and that this term cancels out when measuring mean ionic activity coefficients. In an attempt to find weak points in our approach, we have tested different methods of calculation[1,2,9−11] and different experimental conditions, changing even the physical nature of the liquid junction.[5,6] The more tests we do, the more convinced we are that the measurement of ionic activities is possible and perfectible. We welcome the discussion of this topic in the hope that it will produce more light than heat.

## Literature Cited

(1) Wilczek-Vera, G.; Rodil, E.; Vera, J. H. On the activity of ions and the junction potential: Revised values for all data. *AIChE J.* **2004**, *50* (2), 445–462.
(2) Wilczek-Vera, G.; Vera, J. H. On the measurement of individual ion activities. *Fluid Phase Equilib.* **2005**, *236* (1−2), 96–110.
(3) Schneider, A. C.; Pasel, M. L.; Luckas, M.; Schmidt, K. G.; Herbell, J.-D. Bestimmung von Ionenaktivitätskoeffizienten in wässrigen Lösungen mit Hilfe ionenselektiver Elektroden. *Chem.-Ing.-Tech.* **2003**, *75*, 244–249.
(4) Zhuo, K.; Dong, W.; Wang, W.; Wang, J. Activity coefficients of individual ions in aqueous solutions of sodium halides at 298.15 K. *Fluid Phase Equilib.* **2008**, *274*, 80–84.
(5) Wilczek-Vera, G.; Rodil, E.; Vera, J. H. Towards accurate values of individual ion activities - Additional data for NaCl, NaBr and KCl, and new data for $NH_4Cl$. *Fluid Phase Equilib.* **2006**, *241* (1−2), 59–69.
(6) Arce, A.; Wilczek-Vera, G.; Vera, J. H. Activities of aqueous Na+ and Cl- ions from homoionic measurements with null junction potentials at different concentrations. *Chem. Eng. Sci.* **2007**, *62* (14), 3849–3857.
(7) Capra, F. *The Science of Leonardo*; Dubleday: NY, 2007.
(8) Lewis, G. N.; Randall, M. *Thermodynamics and the Free Energy of Chemical Substances*; McGraw-Hill Book Company, Inc.: NY and London, 1923.
(9) Wilczek-Vera, G.; Rodil, E.; Vera, J. A. A complete discussion of the rationale supporting the experimental determination of individual ionic activities. *Fluid Phase Equilib.* **2006**, *244* (1), 33—45.
(10) Khoshkbarchi, M. K.; Vera, J. H. Measurement and correlation of ion activity in aqueous single electrolyte solutions. *AIChE J.* **1996**, *42* (1), 249–258.
(11) Rabie, H. R.; Wilczek-Vera, G.; Vera, J. H. Activities of individual ions from infinite dilution to saturated solutions. *J. Solution Chem.* **1999**, *28*, 885–913.

Received for review July 17, 2009. Accepted July 20, 2009.

JE900607K

---

* Corresponding author. E-mail address: juan.vera@mcgill.ca.
[†] Department of Chemistry.
[‡] Department of Chemical Engineering.

10.1021/je900607k CCC: $40.75