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Comments & Replies

Comments on Measurement of Ion Activity Coefficients in Aqueous Solutions of Mixed Electrolytes with a Common Ion: $NaNO_3 + KNO_3$, $NaCl + KCl$, and $NaBr + NaCl$

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A recent paper in this journal provides experimental activity coefficients (γ) of individual ionic species.[1] A careful examination reveals, however, that these are conventional and not real values.

The general thermodynamic equation of Voltaic cells is

$$E = -E_{0\alpha} - RTF^{-1}\sum_i \left[\nu_{i\alpha}\ln a_{i\alpha} + \int_{\alpha}^{\omega}\tau_i \mathrm{d}\ln a_i + \nu_{i\omega}\ln a_{i\omega}\right] + E_{0\omega} \qquad (1)$$

in which F is the faraday; R and T have their usual significance; $E_{0\alpha}$ and $E_{0\omega}$ are the standard potentials of the terminal electrodes; $\nu_{i\alpha}$ and $\nu_{i\omega}$ are the moles of any i (ions or neutral species) formed at the respective electrodes when one faraday of electricity goes through the cell from left to right; τ_i are the mole of i transferred in the direction of positive current for one faraday; and a_i is the activity of i.[2] Equation 1 applies to cells with or without liquid junctions and membranes (there are no conceptual differences, the liquid junctions and membranes are cell sections where diffusion potentials of an identical nature take place), thus including also cells with non-Nernstian ISES. The suggested dependence of E on individual ion activities is an illusion since, rearranging eq 1 properly,[3] the terms referring to unmatched charged species disappear and what remain are only terms that belong to molecular species and electrically neutral ion groupings. (This general principle was first recognized by Taylor in late 1927,[4] and it remains perfectly valid like the Pythagoras theorem. Vera and his school, in their last reply to my arguments against their method,[5] could not cancel this verity).

Equation 1 is consistently solved by the infinite number of sets of individual ion activities which match with the correct mean activities. Vera and his school find one single set because of their conventional assumptions: (i) they consider $-RTF^{-1}\sum_i \int_{\alpha}^{\omega} \tau_i \mathrm{d}\ln a_i$ to be the same thing as the liquid junction potential, $E_{J(\alpha,\omega)}$, also in the case of non-Nernstian ISEs, neglecting the diffusion potentials of membranes, which are responsible for the non-Nernstian behavior; (ii) they match eq 1 with an arbitrary eq 2

$$-RTF^{-1}\sum_i \int_{\alpha}^{\omega}\tau_i \mathrm{d}\ln a_i = Y_{(\alpha,\omega)} \qquad (2)$$

where $Y_{(\alpha,\omega)}$ is an approximate function for $E_{J(\alpha,\omega)}$. As a consequence, the infinite sets of possible ion activity coefficients able to satisfy eq 1 reduce to one single set, the one which is able to meet both eq 1 and eq 2. Yet, it is exactly a set of *conventional* values—whose convention is eq 2—and not the set of the ion activity coefficients which remains unknown.

In conclusion, the values reported are not the real activity coefficients of the ions. An admissible use for such values is to make comparisons between γ_{K^+} and γ_{Na^+} in $NaNO_3 + KNO_3$ or $NaCl + KCl$ solutions or between Br^- and Cl^- in $NaBr + NaCl$ solutions, since the bias cancels off in $\gamma_{K^+}/\gamma_{Na^+} = (\gamma_{\pm KCl}/\gamma_{\pm NaCl})^2$ and $\gamma_{Br^-}/\gamma_{Cl^-} = (\gamma_{\pm NaBr}/\gamma_{\pm NaCl})^2$. On the contrary, comparisons between conventional values of Na^+ (or K^+) and NO_3^- (or Cl^- or Br^-) have no physical meaning and cannot decide whether γ_+ is really higher or lower than γ_-. Scientists concerned with electrolyte theories are warned not to rely on these values for validation purposes.

Literature Cited

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