

Nernst equation given for e_2 is incorrect, as it violates electroneutrality (unless, of course, some other important parameters are included in the mysterious E_{ref} term) and as a consequence, eqs (4), (5) and (6) of their work have no physical significance. The Nernst equation can be applied only to chemical equations (representing an equilibrium transformation) and charge balance is an essential prerequisite. The requirement that any real solution be electrically neutral prevents any truly thermodynamic assignment of properties to individual ions although in dilute aqueous solutions thermodynamic properties such as partial molar free energy (related to activity), entropy, enthalpy compressibility, etc., can have additive contributions from individual ionic species.

Notwithstanding above quantitative arguments on the basis of Nernst equation, one can qualitatively accept the conclusions if all the following assumptions are true: 1. AgCl is an ionic conductor at room temperature; 2. Both silver and chloride ions move with equal transport number through the lattice in opposite direction; and 3. Silver chloride lattice has a remarkable ability to act as a buffer to nullify any concentration gradients across it irrespective of the nature of cations and anions.

Some of the other errors (perhaps minor?) in their text are also noteworthy. In the introductory paragraph, the first paradigm is not completely correct as impossibility of single ion activity measurement is valid for any type of electrolyte (irrespective of strong or weak) and ljp can be avoided by a proper selection of the reference electrode. If at least one potential determining ion is common with both the phases, equality of chemical potentials (or electrochemical potentials for charged species) for equilibrium allows one to measure potential accurately, i.e. without ljp's, provided both test compartment and reference electrode compartment have same concentration. Thus, the second paradigm given is also partly incorrect, although the objective of salt bridges is correctly given.

Another incorrect statement is that single ion activity would be a prerequisite for building electrochemical series without invoking arbitrary zero potential for the standard hydrogen electrode. We do have an absolute potential scale in comparison with energy

of electron in vacuum as zero (similar to the zero energy level of solid state physicists) and the whole electrochemical potential series is available⁵.

Similarly, we feel that the statements of Guggenheim have been misinterpreted regarding the role of activity coefficient of single ions 'completely unnecessary for an adequate treatment of thermodynamics of the cell with liquid junction', since much later he still had used the same terms in formulating the basic concept of electrochemical potential.

In summary, the experimental data of the authors do not prove that single ion activity coefficients are accessible to direct experimental measurement as there is no accurate elimination of phase boundary potentials as claimed by them. The solid ion transmitter bridge used in the experiment replaces a conventional salt bridge and it is difficult to invoke ionic transport at room temperature for explaining any experimental observation.

1. For complete references to all these important contributions, see Bonceat, N., *Electrochim. Acta*, 1977, 22, 1047.
2. For example, Sloth, P. and Sorenson, T. S., *J. Phys. Chem.*, 1990, 94, 2116.
3. Corrish, J., *J. Chem. Soc. Faraday*, 1989, 85, 437.
4. Aboagye, K. and Friarf, R. J., *Phys. Rev.*, 1975, B12, 3473.
5. IUPAC Recommendations, *Pure and Appl. Chem.*, 1986, 58, 956.

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K. VIJAYAMOHANAN

*Physical & Materials, Chemistry Division,
National Chemical Laboratory,
Pune 411 008, India*

Response

We have carefully read the comments of Vijayamohan and we are afraid that he is unable to transcend conventional ideas which have been deeply entrenched in the last several decades.

In the pursuit of science when a new result is reported, we should concern ourselves with the experimental data rather than what the previous authors have hypothesized. He claims that he has made careful analysis of the experimental conditions and has come to the

conclusion that phase boundary potentials exist. There is no basis for making this assertion as there is no liquid junction at all. This point is also covered on para 1 page 532 of our paper in reference. Further, Ag/AgCl electrode is invariably used for determining thermodynamic activities of electrolyte in aqueous solutions, where the anion is chloride and is always considered to be free from liquid junction potential. He has also asserted that incorrect expression is used to derive eq. (4). This will be worthy of attention if the reason why the expression is considered incorrect has been mentioned. If it is just the omission of liquid junction potential (ljp), the question will not arise as ljp is pointed out to be zero. Further we would like to clarify the basis of derivation of the equations mentioned in his comments.

For the cell $Zn/ZnCl_2(m)/AgCl/Ag$

$$e_1 = E_{Right} - E_{Left}$$

$$E_{Right} = E^0_{Ag/AgCl} - (RT/2F) \ln a^2_{Cl^-} \quad (4)$$

$$E_{Left} = E^0_{Zn/Zn^{2+}} + (RT/2F) \ln a_{Zn^{2+}} \quad (6)$$

$$e_1 = E^0_{Ag/AgCl} - (RT/2F) \ln a^2_{Cl^-} - \{E^0_{Zn/Zn^{2+}} + (RT/2F) \ln a_{Zn^{2+}}\}$$

$$e_1 = E^0_{Ag/AgCl} - E^0_{Zn/Zn^{2+}} - (RT/2F) \ln a_{Zn^{2+}} a^2_{Cl^-} \quad (3)$$

For the cell $Ag/AgCl, KCl (satd.) / bridge/ZnCl_2 (m), AgCl/Ag$

$$e_2 = E_{Right} - E_{Left}$$

$$E_{Right} = E^0_{Ag/AgCl} + (RT/F) \ln (1/a_{Cl^-})$$

$E_{Left} = +0.199 \text{ V (Ag/AgCl reference electrode potential)} = E_{Ref}$

$$e_2 = E^0_{Ag/AgCl} + (RT/F) \times \ln (1/a_{Cl^-}) - E_{Ref}$$

Salt bridges have very high ionic conductivity while AgCl bridge has conductivity of the order of 10^{-8} mho/cm. Any comparison of solid ion transmitter bridge with the conventional salt bridge will lead to wrong conclusion. He has further suggested that cations and anions move in solid matrix with equal transport number. It is generally known that in solid electrolyte the conducting ion could attain a maximum transport number value of 1. In the paper we have not suggested conductivity for any ion in solid phase. We have

suggested a Grothuss mechanism which is to be differentiated from normal conduction of any ion through a microporous membrane. Here again we have to draw attention to the fact that the solid ion bridge is absolutely free from microporosity and formation of a continuous pore structure in solid AgCl prepared by slow cooling of molten AgCl is ruled out to permit Knudson diffusion. We have again indicated in the paper that the bridge does not allow any pressure drop when high pressure gas is applied even for long duration, which also rules out microporosity. We find that even in a solution of HCl, the bridge is able to sense single ion activity, despite very high mobility of the proton.

In precision potentiometric measurements, even when high input impedance voltmeter is used, negligible current has to be reckoned with. Such orders of current will be carried by chloride ion induced movement of charge by Grothuss mechanism. This is proved by fusing AgCl at two ends of a silver wire and bending the wire as a bridge to connect the ionic solutions. Such a system reproduces the expected value of 45.6 mV, between calomel and Ag/AgCl reference electrode, dipped in satd. KCl. Clearly it is the chloride ion which mediates the completion of the measuring circuit. These results are being communicated shortly. From the reaction schematic shown in Figure 1b of our paper under reference, it will be readily

apparent that the electroneutrality will be maintained in both the half cells irrespective of any theory about solid AgCl bridge. We have also pointed out, if instead of AgCl bridge, a sheet of solid AgCl is bent to interconnect the test and the reference solution, the results are the same.

The other statements in our considered view do not justify the effort of our refutation.

S. PARTHASARATHY
K. RAMYA

SPIC Science Foundation,
110, Mount Road, Guindy,
Madras 600 032, India

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