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## Comments on 'Single-ion activities by a solid ion transmitter bridge and a reference electrode without liquid junction'

The problem of activity coefficients of single ionic species remains one of the most controversial and elusive topics of classical physical chemistry. Although Guggenheim, Gibbs and Taylor shared the opinion that individual ion activities have no physical reality and are inaccessible on the basis of thermodynamic measurements, Pitzer and Brewer, Kirkwood and Openheim etc. had positive opinion, and the experimental measurements were always found to contain some deviation from strict premises of equilibrium thermodynamics such as deviation from electroneutrality, nonisothermal conditions etc<sup>1</sup>. In a recent communication (*Curr. Sci.*, 1995, 69, 529) Parthasarathy and Ramya have claimed that it is possible to measure thermodynamic values of single ion activity using a solid ion conductor by eliminating liquid junction potentials. On the contrary, a careful analysis of the experimental conditions indicates that phase boundary potentials or liquid junction potentials are not eliminated completely and more importantly, incorrect expressions are used to derive eq. (4) given in their work so as to arrive at inaccurate conclusions.

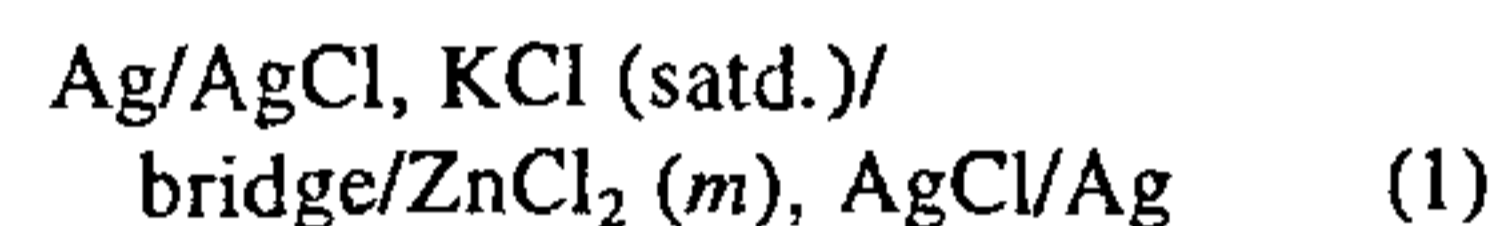
In this communication, we present evidence to disprove their conclu-

sions and to reinforce the argument that single ion activities are still experimentally inaccessible, although models based on statistical mechanics can be used to compute them theoretically<sup>2</sup>.

The 'solid ion transmitter bridge' does not eliminate the liquid junction potential (ljp) because it is only acting as another salt bridge - an inorganic membrane, which cancels two phase boundary potentials and thus minimizing ljp. Probably cations and anions are moving through this solid matrix in opposite directions with equal transport numbers (possible due to Knudson diffusion in microporous membranes) and it is almost impossible to invoke any special role for ionic conduction involving the lattice. Silver ion transport in crystalline silver chloride requires at least few eV at room temperature and any other phenomena such as solvation energy or space charge effects cannot compensate this<sup>3</sup>. Indeed, the formation energies for the predominant cation Frenkel defects require temperature of at least 250-300°C and chloride ion transport through the lattice is almost impossible<sup>4</sup>.

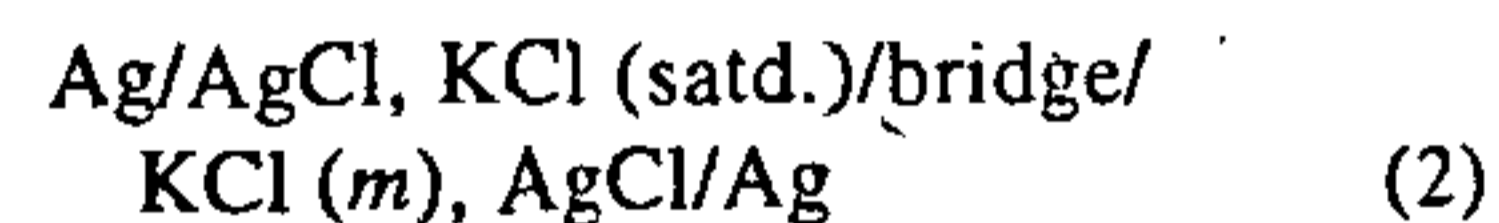
A more serious difficulty is encountered when one analyses the cell representations and emf calculations given on

page 532 of their article. The ljp of the cell,



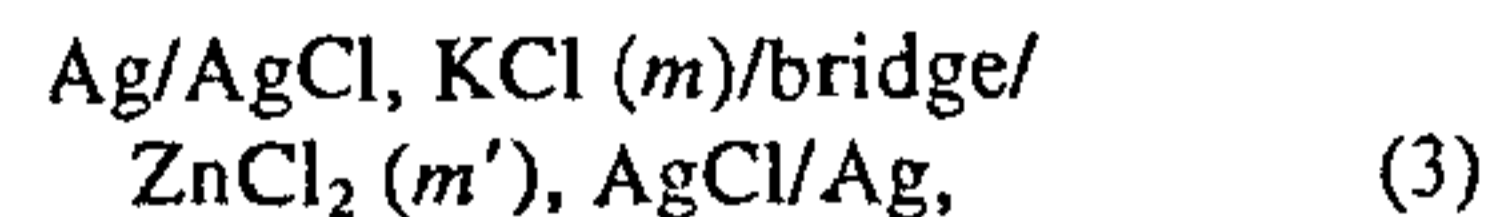
is not zero as two specific contributions of ljp's can be identified.

(i) Difference in the chloride ion concentration alone can cause a contribution, which can be visualized easily by comparing the concentration cell,



and

(ii) Difference in the nature of the cations, contributing a ljp, which is more difficult to account, although the Henderson equation can be used, at least in principle to calculate this. This can be represented as



where  $m$  and  $m'$  can be selected to give identical chloride ion activity or concentration. This type of hetero-ion ljp cannot be eliminated, although approximate correction can be included in the experimental emf values. Both these are present in the cell represented by (i) and hence, ljp is not zero as claimed in their text. More importantly, the form of

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, 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 available<sup>5</sup>.

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.

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## 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