

# Meaning and Measurability of Single-Ion Activities, the Thermodynamic Foundations of pH, and the Gibbs Free Energy for the Transfer of Ions between Dissimilar Materials

Alan L. Rockwood\*<sup>[a, b]</sup>

Considering the relationship between concentration and vapor pressure (or the relationship between concentration and fugacity) single-ion activity coefficients are definable in purely thermodynamic terms. The measurement process involves measuring a contact potential between a solution and an external electrode. Contact potentials are measurable by using thermodynamically reversible processes. Extrapolation of an equation to zero concentration and ionic strength enables determination of single-ion activity coefficients. Single-ion activities can

be defined and measured without using any extra-thermodynamic assumptions, concepts, or measurements. This method could serve as a gold standard for the validation of extra-thermodynamic methods for determining single-ion activities. Furthermore, it places the concept of pH on a thermodynamically solid foundation. Contact potential measurements can also be used to determine the Gibbs free energy for the transfer of ions between dissimilar materials.

## 1. Introduction

A proper thermodynamic definition of single-ion activities is a very old and vexing unsolved problem in physical chemistry, as is the thermodynamic measurement of these same quantities. Single-ion activities are widely considered to be either unmeasurable or physically meaningless,<sup>[1–3]</sup> but chemists, biologists, other scientists, and engineers simply cannot give up the idea of single-ion activities. For example, it would be hard to imagine a concept more widely used by chemists and biologists than that of pH, a concept that conceptually depends on the negative of the logarithm of hydrogen-ion activity, but the IUPAC Gold Book says: “pH cannot be measured independently because calculation of the activity involves the activity coefficient of single ion. Thus it can be regarded only as a notional definition.”<sup>[4]</sup> Similarly, NBS Special Publication 260-53 says this about the thermodynamic foundations of pH: “The use of pH in the expression  $pH = -\log a_{\text{H}}$  is purely a formalism because  $a_{\text{H}}$ , a single (hydrogen) ion activity, is indeterminate.”<sup>[5]</sup> Consequently, the pH scale is based on standardized measurement

schemes that are not based on a true thermodynamic method.<sup>[5,6]</sup>

Similarly, ion-selective electrodes are described as producing a potential that is “linearly dependent on the logarithm of the activity of a given ion in solution.”<sup>[7]</sup> This concept is subject to the same criticism as that of pH, namely, that single-ion activities have been considered to be physically meaningless, and yet ion-selective electrodes are widely used, and the results are conventionally interpreted in terms of single-ion activities.

The concept of single-ion activity is also intimately connected to processes involving unbalanced transport of ions between different materials. Some of these are of crucial importance to life itself. For example, it has long been known that both mitochondria and chloroplasts function through the formation of electrochemical potential gradients.<sup>[8]</sup> These gradients depend on unbalanced transfer of ions between cellular compartments separated by membranes. Nerve function and muscle contraction also depend on unbalanced charge transfer between cellular compartments separated by membranes.<sup>[8]</sup> These processes are among the more important processes in biology. They are understood at a qualitative level, perhaps even at a semiquantitative level, but a full understanding of the energetics of these processes requires single-ion activities or equivalent information.

Clearly, a rigorously defensible thermodynamic definition of single-ion activity is long overdue, as is a thermodynamically well-defined reference method for measuring single-ion activities that can serve as a gold standard to validate other methods of determining single-ion activities.

Historically, the meaning and measurability of single-ion activities have been entangled with questions about electrostatic

[a] A. L. Rockwood  
ARUP Laboratories  
500 Chipeta Way  
Salt Lake City, Utah 84108 (USA)  
E-mail: alan.rockwood@aruplab.com

[b] A. L. Rockwood  
Department of Pathology  
University of Utah School of Medicine  
Salt Lake City, Utah 84132 (USA)

© 2015 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

potential gradients across boundaries between materials. For example, Guggenheim's definition of single-ion activity requires separating the surface potential from the total free energy of an ion in a condensed phase.<sup>[1]</sup> Gibbs<sup>[9]</sup> and Guggenheim<sup>[1]</sup> criticized the physical meaning of surface potentials. Consequently, as Guggenheim himself noted, this calls into question the validity of Guggenheim's definition of single-ion activities.

Nevertheless, there has long been a continued and widespread interest in this problem.<sup>[10–22]</sup> This paper takes a fresh approach to the problem, one that does not separate the problematical surface potential from the other contributions to the free energy. This approach rests entirely on classical equilibrium thermodynamics, which results in a single-ion activity that is thermodynamically well defined and physically meaningful. It is also experimentally accessible by using purely thermodynamic measurements. Activities defined this way are generally applicable to thermodynamics of all processes involving ions, including those in which ions cross boundaries between materials. It is thus at an intersection of a large portion of chemistry, biology, physics, geology, and engineering.

The experimental method proposed in this work can serve as a reference method to which other experimental measurement methods and theoretical calculations can be compared, and it places pH on a rigorous and defensible thermodynamic foundation. Furthermore, the experimental technique of contact potential measurements discussed herein can be used to determine the Gibbs free energy for the transfer of ions between dissimilar materials.

## 2. Theoretical Development

As done by Lewis and Randall and others,<sup>[23,24]</sup> let us posit that every substance has a finite vapor pressure and further posit that in the limit of zero concentration every solute follows Henry's law [Eq. (1)]:

$$f = k_{\text{H}}C \quad (1)$$

in which  $f$  is the fugacity,  $k_{\text{H}}$  is Henry's law constant, and  $C$  is the concentration. For ions, the fugacity is so small that one could use pressure ( $P$ ) in place of fugacity, but fugacity is used herein for thermodynamic rigor.

At higher concentrations, the fugacity will not necessarily obey Equation (1), but one can use a related equation [Eq. (2)]:

$$f = \gamma k_{\text{H}}C \quad (2)$$

in which  $\gamma$  is a concentration-dependent correction factor chosen to force Equation (2) to be true. Applied to ions of a single species, parameter  $\gamma$  characterizes the nonideality of the solution. It therefore, defines a single-ion activity coefficient. Vapor pressure and fugacity depend on all components of the free energy that binds an ion to a solution, so the surface potential contributions (if they can even be said to exist as separately identifiable and well defined thermodynamic

quantities) are implicitly included in the fugacity and, hence, in  $\gamma$ .

Internal consistency between Equations (1) and (2) requires that [Eq. (3)]:

$$\lim_{C \rightarrow 0} \gamma = 1 \quad (3)$$

The vapor pressure local to the region of space just outside of the solution but near the surface of the solution will depend only on the properties of the solution itself. Therefore, by applying Equation (2) in terms of the fugacity of the gas near the surface of the material of interest, the activity depends only on the inherent properties of the material itself, independent of any potential gradients that may exist in space outside of the solutions under study. Activities defined in this way will be called "inherent" activities.

Consider the transfer of ions between materials 1 and 2 having compositions  $C_1$  and  $C_2$  with fugacities  $f_1$  and  $f_2$ , and let the total pressure applied to the solutions be unit pressure, for example, 1 bar (1 bar = 0.1 MPa). For convenience, consider materials 1 and 2 to be solutions, although many of the relationships developed in this paper apply to materials of any type. The Gibbs free energy ( $\Delta G$ ) of transfer of ions from material 1 to a gas of the same fugacity located just outside of material 1 is given by Equation (4):

$$\Delta G = 0 \quad (4)$$

The Gibbs free energy to compress the gas from  $f_1$  to  $f_2$  is given by Equation (5):

$$\Delta G = RT \ln \left( \frac{f_2}{f_1} \right) \quad (5)$$

in which  $R$  is the gas constant and  $T$  is the absolute temperature.

The Gibbs free energy for the transfer of the gas from a point near the surface of solution 1 to a point near the surface of solution 2 is given by Equation (6):

$$\Delta G = q\psi_{2,1} = q(\psi_2 - \psi_1) \quad (6)$$

in which  $\psi_1$  is the electrostatic potential in the region of space just outside of material 1,  $\psi_2$  is the electrostatic potential in the region of space just outside of material 2, and  $q$  is the molar charge of the ions being transferred, sign included. The quantity  $\psi_{2,1}$  may refer to an equilibrated or nonequilibrated system.

The Gibbs free energy for the transfer of ions from the gas phase into material 2 from a point near the surface of material 2, in which both phases are of fugacity  $f_2$ , is given by Equation (7):

$$\Delta G = 0 \quad (7)$$

Summing the Gibbs free energies of these steps, the total Gibbs free energy for the transfer of ions between the two ma-

terials is given by Equation (8):

$$\Delta G = RT \ln \left( \frac{f_2}{f_1} \right) + q\psi_{2,1} \quad (8)$$

If the two materials are at equilibrium with respect to the species being transferred, the Gibbs free energy for the process is zero [Eq. (9)]:

$$\Delta G = 0 \quad (9)$$

so Equation (8) becomes Equation (10):

$$0 = RT \ln \left( \frac{f_2}{f_1} \right) + q\psi_{2,1} \quad (10)$$

Equation (10) is general and refers to materials of any type.

Let us now assume the materials are solutions. Substituting from Equation (2) into Equation (10) we obtain Equation (11):

$$\begin{aligned} 0 &= RT \ln \left( \frac{\gamma_2 k_H C_2}{\gamma_1 k_H C_1} \right) + q\psi_{2,1} \\ &= RT \ln \left( \frac{\gamma_2 C_2}{\gamma_1 C_1} \right) + q\psi_{2,1} \end{aligned} \quad (11)$$

which, simplified and rearranged, becomes Equation (12):

$$\ln(\gamma_1) = \ln(\gamma_2) + \ln \left( \frac{C_2}{C_1} \right) + \frac{q\psi_{2,1}}{RT} \quad (12)$$

In the rest of this paper it will be assumed that the system has equilibrated unless otherwise indicated. At equilibrium,  $\psi_{2,1}$  is the contact potential.

A priori we do not know  $\gamma_2$  for any finite concentration of solution 2. However, from Equation (3), we know its limiting value, so one can calculate  $\gamma_1$  from Equation (13):

$$\ln(\gamma_1) = \lim_{C_2 \rightarrow 0} \left( \ln(\gamma_2) + \ln \left( \frac{C_2}{C_1} \right) + \frac{q\psi_{2,1}}{RT} \right) \quad (13)$$

which, by applying Equation (3), simplifies to Equation (14):

$$\ln(\gamma_1) = \lim_{C_2 \rightarrow 0} \left( \ln \left( \frac{C_2}{C_1} \right) + \frac{q\psi_{2,1}}{RT} \right) \quad (14)$$

Broadly speaking, an experimental scheme would measure the contact potential,  $\psi_{2,1}$ , at a series of concentrations,  $C_2$ , and recover the value of  $\gamma_1$  by extrapolating Equation (14) to zero concentration.

In the thought experiment just described, ions are transferred through an equilibrated gas phase. However, the rate of evaporation of ions would be far too slow for this process to establish equilibrium on a laboratory timescale. Therefore, consider an alternative equilibration method. Assume the ion under study is a metal ion,  $M^{n+}$ , for which  $n = q/F$ ;  $F$  is Faraday's constant. If the reaction given in Equation (15) is reversible, one could separate solutions 1 and 2 with a plate or mem-

brane composed of metal M:



The process denoted in Equation (15) would take place at both solution/metal interfaces and would serve to establish equilibrium of  $M^{n+}$  between the two solutions. Because the Gibbs free energy is a state function, the final state of the system would be equivalent to the state in which equilibrium would be established by gas-phase transport of ions, which implies that one can use the equilibrium relations discussed previously to analyze the free energy of the process. The rate of achieving equilibrium could be fast by using the alternative method to establish equilibrium, and this would make the alternative method a practical experimental possibility.

Now consider suspending metal plates composed of metal M above each of the two solutions, and further assume that these two plates are electrically connected to the metal plate separating the solutions, as illustrated in Figure 1.

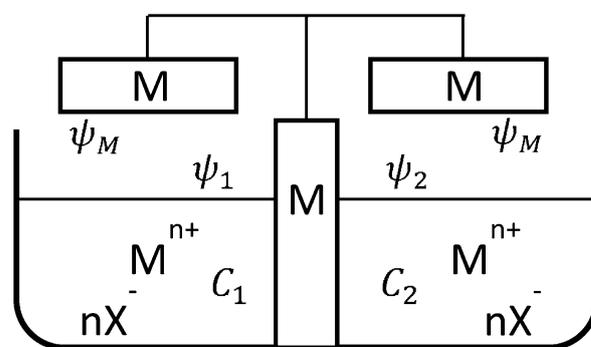


Figure 1. Schematic of the apparatus for the equilibration of  $M^{n+}$  between solutions 1 and 2.

Let  $\psi_M$  denote the electrostatic potential in space just outside of the metal plate suspended above solution 1. The metal plate suspended above solution 2 is composed of the same metal, so  $\psi_M$  is also the potential in space just outside of the second external electrode.

Breaking  $\psi_{2,1}$  into the sum of two parts [Eq. (16)]:

$$\psi_{2,1} = (\psi_M - \psi_1) + (\psi_2 - \psi_M) = \psi_{M,1} + \psi_{2,M} \quad (16)$$

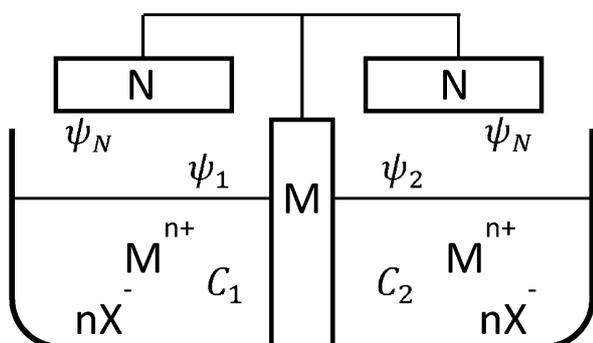
Equation (14) can be written as Equation (17):

$$\begin{aligned} \ln(\gamma_1) &= \lim_{C_2 \rightarrow 0} \left( \ln \left( \frac{C_2}{C_1} \right) + \frac{q((\psi_M - \psi_1) + (\psi_2 - \psi_M))}{RT} \right) \\ &= \lim_{C_2 \rightarrow 0} \left( \ln \left( \frac{C_2}{C_1} \right) + \frac{q(\psi_{M,1} + \psi_{2,M})}{RT} \right) \end{aligned} \quad (17)$$

The value of  $\psi_M$  affects the quantities  $\psi_{M,1}$  and  $\psi_{2,M}$  individually, but it cancels out from the quantity  $(\psi_{M,1} + \psi_{2,M})$ , so it does not affect the determination of the single-ion activity coefficient. Consequently, one can determine the contact poten-

tial between solution 1 and solution 2 by measuring  $\psi_{M,1}$  and  $\psi_{2,M}$ .

A further substitution is possible by replacing the metal suspended over the solutions with a conductor of a different material, N (Figure 2).



**Figure 2.** Schematic of the apparatus for the equilibration of  $M^{n+}$  between solutions 1 and 2 with an alternative conductor, N, for the external electrode.

Equation (18):

$$\psi_{2,1} = (\psi_N - \psi_1) + (\psi_2 - \psi_N) = \psi_{N,1} + \psi_{2,N} \quad (18)$$

substitutes  $\psi_{2,1} = (\psi_M - \psi_1) + (\psi_2 - \psi_M) = \psi_{M,1} + \psi_{2,M}$  in the equations just presented and the expression for the single-ion activity coefficient becomes Equation (19):

$$\ln(\gamma_1) = \lim_{C_2 \rightarrow 0} \left( \ln \left( \frac{C_2}{C_1} \right) + \frac{q(\psi_{N,1} + \psi_{2,N})}{RT} \right) \quad (19)$$

The substitution of N for M is transparent to the investigator because the value of  $\psi_N$  cancels, which leaves a net result of  $\psi_{2,1}$ . As a corollary, if there is a shift in contact potential due to adsorption of gases on the electrode N, the shift cancels if the difference is taken in Equation (19), provided that atmospheric conditions exposed to electrode N are held constant.

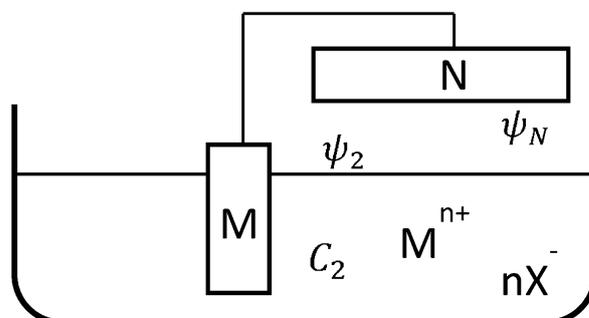
The previous discussion pointed out that  $\gamma_1$  can be determined by measuring  $\psi_{2,1}$  at a series of  $C_2$  concentrations. For one of these measurements one could use the same concentration for both solutions in the apparatus, that is,  $C_2 = C_1$ . For this special case, there is mirror image symmetry between the left-hand side and the right-hand side of the apparatus, so by symmetry [Eq. (20)]:

$$\psi_{N,1} = -\psi_{2,N} \quad (20)$$

and it does not matter if we measure  $\psi_{2,N}$  in the left-hand side of the apparatus or in the right-hand side. Furthermore, for this special case the left-hand side is redundant and can be eliminated altogether. A simple way to do this would be simply to drain the solution from the left side of the apparatus.

This now raises the following question. What if we were to perform two experiments, one for a series of measurements of

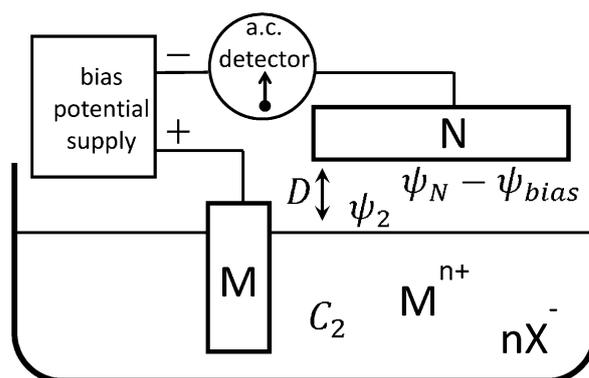
$\psi_{2,N}$  at different concentrations,  $C_2$ , with solution 1 present and the other for a similar series of measurements for  $\psi_{2,N}$  with solution 1 absent. For one of the measurements in each series we would specify that  $C_2 = C_1$ . Would  $\psi_{2,N}$  be the same for each choice of  $C_2$ , regardless of whether solution 1 was present or absent? If so, then one can eliminate the left-hand side and use a simplified device illustrated in Figure 3. For the rest of



**Figure 3.** Schematic of the simplified apparatus containing a single solution and an alternative conductor, N, for the external electrode.

the paper it will be assumed that this is valid. However, the proposal that the two experiments would give the same result is amenable to experimental validation, and as discussed elsewhere in this paper, there is a backup option in case the proposed equivalence fails validation.

It has been known for over a century that contact potentials can be measured by using a Kelvin vibrating capacitor method, also known as a Kelvin probe.<sup>[25]</sup> It uses the principle that the contact potential is independent of the gap between the two materials. If the materials are arranged as two opposing planes then the charge differential between the two materials is proportional to the contact potential and inversely proportional to the distance between the materials. Thus, if one modulates the gap distance between the planes then an alter-



**Figure 4.** Schematic of the simplified apparatus including bias potential source and ac current detector. The distance between the surfaces,  $D$ , is modulated. The quantity  $\psi_{bias}$  is defined as  $(V_+ - V_-)$ , in which  $V_+$  is the potential appearing at the terminal on the bias potential supply labeled + and  $V_-$  is the potential appearing at the terminal on the bias potential supply labeled -. The labels + and - on the bias power supply are arbitrary and do not necessarily imply the polarity used in any particular experiment. Regarding  $V_+$  and  $V_-$ , only the difference  $(V_+ - V_-)$  is significant.

nating current will appear in the wire connecting the two materials, and current is proportional to the contact potential.

Applying this principle to Figure 4, which is an elaboration of Figure 3, one would vary the distance,  $D$ , between the external electrode and the surface of the solution while measuring the current in the wire connecting electrodes N and M. It is customary in contact potential measurements to include a compensating voltage ( $\psi_{\text{bias}}$ ) to cancel the contact potential. Under the null condition, no ac current flows in the wire connecting the electrodes, and the value of  $\psi_{2,N}$  is given by the bias voltage under the null condition. This completes a minimal description to enable the measurement of single-ion activity coefficients. The Kelvin method has already been used to measure contact potentials in electrochemical systems, albeit without application to the problem of single-ion activity coefficients.<sup>[26–28]</sup>

### 3. Improving the Extrapolation to Zero Concentration and Ionic Strength

Consider substituting Equation (21) in place of  $\gamma_2$  in Equation (13):

$$\gamma_2 = \gamma_{2,R} \gamma_{2,S} \quad (21)$$

in which  $\gamma_{2,S}$  is an estimate for  $\gamma_2$ , and  $\gamma_{2,R}$  is a residual factor of  $\gamma_2$  not accounted for by  $\gamma_{2,S}$ . Equation (13) now becomes Equation (22):

$$\ln(\gamma_1) = \lim_{C_2 \rightarrow 0} \left( \ln(\gamma_{2,R}) + \ln(\gamma_{2,S}) + \ln\left(\frac{C_2}{C_1}\right) + \frac{q(\psi_{N,1} + \psi_{2,N})}{RT} \right) \quad (22)$$

Without significant loss of generality constrain  $\gamma_{2,S}$  as follows [Eq. (23)]:

$$\lim_{C_2 \rightarrow 0} \gamma_{2,S} = 1 \quad (23)$$

which, combined with Equation (3), forces [Eq. (24)]:

$$\lim_{C_2 \rightarrow 0} \gamma_{2,R} = 1 \quad (24)$$

in which case Equation (22) becomes Equation (25):

$$\ln(\gamma_1) = \lim_{C_2 \rightarrow 0} \left( \ln(\gamma_{2,S}) + \ln\left(\frac{C_2}{C_1}\right) + \frac{q(\psi_{N,1} + \psi_{2,N})}{RT} \right) \quad (25)$$

To illustrate with a simple example, let  $\gamma_{2,S}$  be given by the Debye–Hückel limiting law [Eq. (26)]:

$$\ln(\gamma_{2,S}) = -An^2 I^{1/2} \quad (26)$$

in which  $A$  depends on temperature and a number of physical constants, and  $I$  is the ionic strength, which in turn depends on  $C_2$ . Equation (25) then becomes Equation (27):

$$\ln(\gamma_1) = \lim_{C_2 \rightarrow 0} \left( -An^2 I^{1/2} + \ln\left(\frac{C_2}{C_1}\right) + \frac{q(\psi_{N,1} + \psi_{2,N})}{RT} \right) \quad (27)$$

The condition  $I \rightarrow 0$  included in this expression reminds us that the solution might be a mixed electrolyte and that the ionic strength and, hence, the concentrations of all ions must be made to approach zero in the limiting process. (We should also include  $I \rightarrow 0$  in most of the other limiting expressions in the paper, but for convenience we just assume  $I \rightarrow 0$  is implicitly present.) Other functions for  $\gamma_{2,S}$  would yield different though analogous equations for the extrapolation function, but the same result must be obtained in the limiting case. Other extrapolation strategies are possible, but consideration of these is beyond the scope of the present paper.

### 4. Error Budget

According to one vendor, Kelvin probe measurements can be accurate to  $\pm 2$  mV,<sup>[29]</sup> and according to another vendor, accuracy can be  $\pm 0.1$  mV.<sup>[30]</sup> If we arbitrarily take an intermediate value of  $\pm 0.5$  mV as representative of the uncertainty in contact potential measurements, we can estimate the uncertainty in the determination of  $\gamma$  to be  $\pm 2\%$  at room temperature by considering only the dependence of the extrapolation equations [e.g. Equation (17) or (22)] on the contact potential. If we more optimistically accept  $\pm 0.1$  mV as a reasonable estimate of the uncertainty in the contact potential measurement then the uncertainty in the determination of  $\gamma$  arising from uncertainty in the contact potential measurement becomes  $\pm 0.4\%$ . Also, consider the fact that if there is a constant offset in the contact potential measurements it cancels out in the calculation of  $\psi_{N,1} + \psi_{2,N}$ . Other sources of uncertainty include the uncertainty of concentrations (probably well under 1%), the absolute temperature (well under 1%), and the specific choice of extrapolating function (unknown uncertainty, but possibly well under 1% if the functional form of  $\gamma_{2,R}$  is sufficiently well-behaved).

### 5. Relationship of Single-Ion Activities to Standard States

If the electrostatic potential in space just outside of the surfaces of two solutions in Figure 2 is the same (i.e.  $\psi_1 = \psi_2 = \psi$ , which implies that  $\psi_{2,1} = 0$ ), then substituting into Equation (8), the Gibbs free energy for transferring ions between two materials is given by Equation (28):

$$\Delta G = RT \ln\left(\frac{f_2}{f_1}\right) \quad (28)$$

The Gibbs free energy is also given by Equation (29):

$$\Delta G = \left(\frac{\partial G_2}{\partial x}\right)_\psi - \left(\frac{\partial G_1}{\partial x}\right)_\psi = \bar{G}_{2,\psi} - \bar{G}_{1,\psi} \quad (29)$$

in which  $x$  is the number of moles of ions being transferred, the subscript  $\psi$  specifies the (same) potential just outside of the two materials,  $\bar{G}_{1,\psi}$  is the partial molar Gibbs free energy of this species in solution 1, and  $\bar{G}_{2,\psi}$  is defined analogously for this species in solution 2.

Equating  $\Delta G$  from the last two equations and rearranging, we obtain Equation (30):

$$\bar{G}_{2,\psi} = \bar{G}_{1,\psi} + RT \ln\left(\frac{f_2}{f_1}\right) \quad (30)$$

This applies to any composition,  $C_2$ , so one can remove the numerical subscript, 2, from  $\bar{G}_{2,\psi_2}$  and  $f_2$ . If solution 1 is an extrapolation from infinite dilution to unit composition by using an ideal solution extrapolating function, then the resulting solution defines a standard state, and Equation (30) becomes Equation (31):

$$\bar{G}_\psi = G_\psi^0 + RT \ln\left(\frac{f}{f^0}\right) \quad (31)$$

The quantity  $f/f^0$  defines an activity, so Equation (31) becomes Equation (32):

$$\bar{G}_\psi = G_\psi^0 + RT \ln(a) \quad (32)$$

If  $\psi = 0$ , then we obtain Equation (33):

$$\bar{G}_{\psi=0} = G_{\psi=0}^0 + RT \ln(a) \quad (33)$$

If  $\psi_1 \neq \psi_2$ , then Equation (34) is obtained:

$$\bar{G}_{\psi_2} = G_{\psi_2}^0 + RT \ln(a) + q\psi_{2,1} \quad (34)$$

or if  $\psi_1 \neq \psi_2$  and  $\psi_1 = 0$ , then Equation (35) applies:

$$\bar{G}_{\psi_2} = G_{\psi_1=0}^0 + RT \ln(a) + q\psi_2 \quad (35)$$

In both Equations (34) and (35) the activity is of the solution for which the potential just outside of the solution is specified as  $\psi_2$ .

From Equations (1), (2), (31), (32), and so on, and by keeping in mind the definition of the standard state as an extrapolation to unit concentration for an ideal solution, one easily concludes that [Eq. (36)]:

$$\frac{\gamma C}{C^0} = \alpha \quad (36)$$

which is identical to the relationship between concentration, activity coefficient, and activity for neutral species. Thus, neutral species and charged species can be treated identically, provided one is careful in dealing with  $\psi$ .

## 6. Gibbs Free Energies of Processes Involving Ions

It seems reasonable that a useful definition of single-ion activities should be directly applicable to the thermodynamics of all ion processes, including those in which ions cross boundaries between dissimilar materials. Definitions of single-ion activity that depend on removing the surface potentials are incapable of this because they do not include all contributions to the Gibbs free energy, but the approach presented in this paper does not suffer from this deficiency because surface potentials are implicitly included in the fugacity or vapor pressure of ions.

Reviewing concepts presented earlier, the process of transferring ions between two materials can be broken down into Equations (37)–(40):

$$A_{\text{phase}1,f_1,\psi_1}^n \rightarrow A_{\text{gas},f_1,\psi_1}^n \quad (37)$$

$$A_{\text{gas},f_1,\psi_1}^n \rightarrow A_{\text{gas},f_2,\psi_1}^n \quad (38)$$

$$A_{\text{gas},f_2,\psi_1}^n \rightarrow A_{\text{gas},f_2,\psi_2}^n \quad (39)$$

$$A_{\text{gas},f_2,\psi_2}^n \rightarrow A_{\text{phase}2,f_2,\psi_2}^n \quad (40)$$

in which  $n$  is the ionic charge. The overall process is given by Equation (41):

$$A_{\text{phase}1,f_1,\psi_1}^n \rightarrow A_{\text{phase}2,f_2,\psi_2}^n \quad (41)$$

The Gibbs free energy of the process is given by Equation (42):

$$\begin{aligned} \Delta G &= RT \ln\left(\frac{f_2}{f_1}\right) + q\psi_{2,1} \\ &= RT \ln\left(\frac{f_2}{f_1}\right) + nF\psi_{2,1} \end{aligned} \quad (42)$$

where  $\psi_{2,1}$  refers to either an equilibrated state or an unequilibrated state. The steps leading up to Equation (42) do not require the solutions to have the same solvent, or even that the two phases or materials are solutions. Therefore, Equation (42) is a completely general equation for the Gibbs free energy for the transfer of ions between any two materials, although it does require the materials to be sufficiently conductive for the contact potential expression to apply. This would include all conductors and virtually all semiconductors, electrolyte solutions, and ionic liquids.

If there is an electrostatic potential drop going across a boundary between a condensed phase and the gas phase it is automatically reflected in the fugacities,  $f_1$  and  $f_2$ , so the treatment of single-ion activities in this paper does not depend on removing the surface potential, but rather the surface potential is included. Furthermore, it is not necessary to know the value of the surface potential, or even to assume its existence as a separately identifiable and definable physical property.

We now rewrite Equation (2) by using additional subscripts to take into account that we may be dealing with solutions having different solvents, which therefore have different Henry's law constants as well as different concentrations and different activity coefficients [Eqs. (43) and (44)]:

$$f_1 = \gamma_1 k_{H1} C_1 \quad (43)$$

$$f_2 = \gamma_2 k_{H2} C_2 \quad (44)$$

Substituting into Equation (42) we arrive at Equation (45):

$$\begin{aligned} \Delta G &= RT \ln \left( \frac{\gamma_2 k_{H2} C_2}{\gamma_1 k_{H1} C_1} \right) + q\psi_{2,1} \\ &= RT \ln \left( \frac{\gamma_2 k_{H2} C_2}{\gamma_1 k_{H1} C_1} \right) + nF\psi_{2,1} \end{aligned} \quad (45)$$

If the ion is equilibrated between materials 1 and 2, the Gibbs free energy of ion transfer is zero, so [Eq. (46)]:

$$\begin{aligned} 0 &= RT \ln \left( \frac{\gamma_2 k_{H2} C_2}{\gamma_1 k_{H1} C_1} \right) + q\psi_{2,1} \\ &= RT \ln \left( \frac{\gamma_2 k_{H2} C_2}{\gamma_1 k_{H1} C_1} \right) + nF\psi_{2,1} \end{aligned} \quad (46)$$

Rearranging Equation (46) gives Equation (47):

$$\frac{f_2}{f_1} = \frac{\gamma_2 k_{H2}}{\gamma_1 k_{H1}} = \frac{C_2}{C_1} e^{-\left(\frac{nF\psi_{2,1}}{RT}\right)} \quad (47)$$

All of the quantities on the far right-hand side are measurable, which shows that it is possible to determine the ratio of fugacities between ions in two different solvents, and if Equation (47) is rearranged Equation (48) is obtained:

$$\frac{k_{H2}}{k_{H1}} = \frac{\gamma_1 C_1}{\gamma_2 C_2} e^{-\left(\frac{nF\psi_{2,1}}{RT}\right)} \quad (48)$$

and considering that  $\gamma_1$  and  $\gamma_2$  are also measurable, then one can also determine the ratio of Henry's law constants for ions in two different solvents. Thus, although it may be impractical to determine absolute fugacities for ions in any given solvent, one can nevertheless learn quite a bit about fugacities of ions by determining their ratios in different solvents.

Given that one can measure the ratios of fugacities, then one can substitute those into Equation (42) to determine the Gibbs free energy for the transfer of ions between two solutions of differing compositions for any choice of  $\psi_{2,1}$ , whether the difference in composition is in the ion concentration or the solvent composition, or both. If  $\psi_{2,1} \neq 0$  then Equation (42) applies, unmodified, and if  $\psi_{2,1} = 0$  then the Gibbs free energy of transfer is given by Equation (49):

$$\Delta G = RT \ln \left( \frac{f_2}{f_1} \right) \quad (49)$$

These relationships open the door to studying the thermodynamics of a wide variety of processes that involve unbal-

anced transfer of ions between dissimilar materials. Several of these are from biology, including oxidative phosphorylation, photosynthesis, nerve signal conduction, and muscle contraction. Each of us depends on these processes to sustain life itself. All involve the unbalanced transfer of ions across membranes separating two aqueous solutions of differing compositions, and because the transfer is unbalanced, a rigorous thermodynamic analysis of these processes would require either single-ion activity coefficients or equivalent information. Single-ion activities defined as they are defined herein are also applicable to processes occurring within a single material and can be used similarly to activities of neutral species.

## 7. Thermodynamic Foundations of pH

Outside of temperature and mass, pH is, arguably, the most frequently performed chemical measurement. It is notionally defined as the negative of the logarithm of the hydrogen-ion concentration, and yet as discussed in the Introduction, standardization organizations have recognized that pH is not currently on a solid thermodynamic foundation. Nevertheless, if single-ion activities can be given a rigorous thermodynamic definition it would place the definition of pH on a solid thermodynamic foundation. Furthermore, if the measurement process can be devised that is thermodynamically rigorous then the actual measurement of pH can also be placed on a solid thermodynamic foundation.

Given that the single-ion activity of the hydrogen ion is nothing more than a special case of single-ion activity, all of the development given previously in the paper applies, and under the definitions presented in this paper the hydrogen-ion activity becomes a thermodynamically well-defined quantity. Furthermore, given the fact that the hydrogen electrode can be arranged as a special case of Figure 4, the hydrogen-ion activity and, hence, the pH become thermodynamically well-measurable quantities. This implies that other devices and methods of measuring pH, such as pH meters and acid/base indicator compounds, can be validated and calibrated against a thermodynamically rigorous reference method. This would make practical pH methods traceable to a thermodynamically well-defined standard method.

Furthermore, the discussion just presented on the free energy of transfer of ions between different materials makes it possible to rigorously define and measure pH in different solvents and to give the thermodynamic relationship between pH measurements in different solvents. This may relate to a recent proposal for a unified pH scale for all materials.<sup>[31]</sup> A detailed discussion of the relationship is a topic for further research, but in general terms, Himmel et al. proposed a gas-phase reference state for the proton of 1 bar ideal gas and treated the acidity of protons in other materials in terms of the thermodynamics of ion solvation.<sup>[31]</sup>

The idea of using a gas-phase reference state for protons is related to an approach to absolute half-cell potentials wherein a standard state of gas-phase electrons was defined in terms of an ideal electron gas at unit pressure.<sup>[32]</sup> Bartmess proposed another approach for defining the standard state of gas-phase

electrons and protons that is similar in some respects but different in specific details.<sup>[33]</sup> These ideas, together with the method presented herein for determining single-ion activity coefficients, earlier work on partial molar entropies of electrons in metals,<sup>[34,35]</sup> partial molar entropies of ions in solution,<sup>[35]</sup> thermodynamics of work function measurements,<sup>[36]</sup> and absolute half-cell entropies<sup>[37]</sup> lays the basis for a more complete theory of charged particle thermodynamics that would unify the thermodynamics of gas-phase ion processes with ion-solvation thermodynamics and thermodynamics of ions in condensed phases into a more generalized system of electrochemistry and acid–base chemistry.

As part of their proposal for a universal pH scale, Himmel et al. also discussed the Gibbs free energy of proton solvation, and they presented computed values for the standard Gibbs free energy of proton solvation in several solvents<sup>[31]</sup> (a method for determining Gibbs free energies of ion solvation by using absolute half-cell thermodynamics was proposed earlier, e.g. in Ref. [32]). As discussed in the present paper, contact potential measurements provide a way to determine the ratio of Henry's law constants for ions in different solvents and the difference in partial molar Gibbs free energies for ions in different solvents. This provides a path toward a partial test of the theoretical calculations in Ref. [31], wherein theoretical Gibbs free energies for transfer of ions between materials can be tested against the differences in the same quantities determined by contact potential measurements.

Additionally, the same reasoning applies to other types of ion-selective electrodes. This puts the entire field of ion-selective electrodes on a solid thermodynamic foundation and points to a reference method that could be used to validate such devices.

## 8. Relationship between Terminology used Herein and Terminologies used Elsewhere

The quantity in the present paper referred to as  $\psi$  has also been called the "outer potential" and the "volta potential".<sup>[38]</sup> The outer potential is a physically meaningful quantity, and it is the only type of electrostatic potential used in this paper.

Guggenheim also discussed another type of potential, the electrostatic potential in the interior of a condensed phase. This is sometimes known as the "inner potential" or "Galvani potential".<sup>[39]</sup> As argued by both Gibbs<sup>[9]</sup> and Guggenheim,<sup>[1]</sup> the electrostatic potential within the interior of a condensed phase has no operational meaning in the sense that it seems impossible to specify a thermodynamically acceptable experiment that can unambiguously measure its value. The inner potential is therefore of dubious physical significance. The inner potential is not used in this paper. Thus, whereas the inner potential may be of interest in certain theoretical discussions, whether or not it has any measurable physical meaning makes no difference to the definition of single-ion activity presented herein.

Some publications use the term "intrinsic" in referring to the thermodynamic properties of ions in condensed phases. This term is tied to the concept of removing electrostatic potential

gradients across phase boundaries. For example, the intrinsic solvation free energy of an ion would be the actual solvation free energy minus the electrostatic energy of the ion crossing a gas-phase/condensed-phase boundary.<sup>[40]</sup> Because the physical meaning of the electrostatic potential gradients across phase boundaries is open to dispute, intrinsic quantities have no part in this paper.

One should not confuse the term "intrinsic" with the term "inherent" used in the present paper. Inherent thermodynamic quantities of an ion in solution include all of the energy contributions, whereas intrinsic thermodynamic quantities would subtract the electrostatic contributions of the ion crossing an electrostatic potential gradient at a gas-phase/condensed-phase boundary. Quantities such as the vapor pressure of ions include all of the energetics and are therefore, in principle, unambiguously physically meaningful, although in some cases the vapor pressure may be too small to measure directly. These quantities are inherent properties, whereas intrinsic quantities exclude part of the energetics and are of doubtful physical meaning. Furthermore, the thermodynamics of processes of ions crossing boundaries between dissimilar materials can be described in terms of inherent thermodynamic functions, whereas intrinsic thermodynamic functions cannot be used to describe the thermodynamics of ions crossing these boundaries. This implies that inherent properties are more useful than intrinsic properties in treating real thermodynamic processes of ions.

"Inherent" properties, as the terminology is used in this paper, are similar to "real" quantities as discussed in certain other publications in the sense that both include all contributions to thermodynamic functions of ions in condensed phases, including any possible contributions from electrostatic potential gradients across interfaces.<sup>[41]</sup> So-called "bulk" quantities, also discussed in Ref. [41] are also apparently synonymous with "intrinsic" quantities.

## 9. Relationship to Guggenheim's Definition of Single-Ion Activity and Its Physical Meaning

Most of the objections to the physical meaning of single-ion activities harken back to Guggenheim's discussion of the problem.<sup>[1]</sup> Guggenheim conceptualized the partial molar Gibbs free energy of an ion in terms of separate "chemical" and "electrostatic" interactions, and he defined the single-ion activity in terms of the chemical portion of the partial molar Gibbs free energy. He noted that there is no unambiguous way of separating "chemical" from "electrostatic" energy for an ion in the interior of a condensed phase, because there is no operational definition for the electrostatic potential in the interior of a condensed phase. This makes the "chemical" portion of the partial molar Gibbs free energy unknowable, and as he himself pointed out, his definition of single-ion activity, therefore, has no thermodynamic meaning. In deference to historical precedent, let us refer to Guggenheim's definition as a "type I" single-ion activity, regardless of whether or not it is thermodynamically meaningful.

Guggenheim's type I definition fails a test proposed earlier for a reasonable definition of single-ion activity, because it is fundamentally incapable of being directly applied to the thermodynamics of ions crossing boundaries between dissimilar materials. This arises from the fact that a type I definition of single-ion activity seeks to remove the electrostatic potential energy across phase boundaries and, therefore, does not account for all of the Gibbs free energy of the process.

By contrast, the definition of single-ion activity introduced in the present paper does not separate chemical from electrostatic contributions to the Gibbs free energy. All that matters is that ions in solution have a vapor pressure (or more rigorously, a fugacity), that the vapor pressure is an increasing function of concentration, and that the vapor pressure is proportional to concentration as the concentration approaches zero [Eq. (1)]. Surface potentials (if they can be said to be physically meaningful) are reflected in the fugacity. It is then possible to define a quantity,  $\gamma$ , such that Equation (2) is satisfied. All else follows from this by using well-established thermodynamic principles. Let us refer to this newer definition as a "type II" definition.

It is also notable that Guggenheim used the term "electrochemical potential" equivalently to the partial molar Gibbs free energy of an ion in a condensed phase, and he acknowledged that it is a physically meaningful quantity, whereas he used the term "chemical potential" to refer to the partial molar Gibbs free energy minus the electrostatic energy (for which in this sense "electrostatic energy" refers to the questionable concept of the inner potential), which he acknowledged as a thermodynamically ill-defined quantity. Guggenheim's definition of ionic activity was tied to the chemical potential, which made the type I single-ion activity an ill-defined quantity.

Although the term "electrochemical potential" is now entrenched to refer to the partial molar Gibbs free energy of ions, in retrospect it is probably unnecessary for this term to have been introduced. Given that the "chemical potential" was historically used to refer to the partial molar Gibbs free energy of neutral species, the same terminology could have been carried over to refer to the partial molar Gibbs free energy for ions as well, in which case the additional term "electrochemical potential" would have been unnecessary. As it turns out, Guggenheim applied the term "chemical potential" to a quantity that is not equal to the partial molar Gibbs free energy of ions, which makes the definition of the term "chemical potential" inconsistent between charged and uncharged species, and these choices of definitions may have contributed to the historical controversies and confusion regarding the thermodynamics of ions. Similarly, if Guggenheim would have identified the ionic activity with a thermodynamically meaningful quantity (his "electrochemical potential") instead of a thermodynamically ill-defined quantity (his "chemical potential"), the thermodynamics of ions might have seemed less confusing during the ensuing decades, particularly as it is only the electrochemical potential that relates to the Gibbs free energies of all real processes involving ions.

## 10. Relationship to Extra-thermodynamic Methods

Previous approaches to defining and/or measuring single-ion activities referred to earlier in this paper used extra-thermodynamic assumptions or methods. These may include calculation of single-ion activities by using microscopic theory, assumptions regarding electrostatic potential differences across phase boundaries, devices that contain irreversible components such as salt bridges, methods that rely on kinetic theory or transport parameters, and/or other extra-thermodynamic assumptions or methods. Although one or more of those methods may be useful, or even give numerically correct results, none have been validated by comparison against a truly thermodynamic reference method. Therefore, the validity of none of these methods has been unequivocally established.

The method presented in this paper is purely thermodynamic. It is defined entirely in terms of macroscopic thermodynamic quantities and concepts, and all measurements can be done under conditions that approach thermodynamic reversibility. It can, therefore, serve as a thermodynamic gold standard or reference method to validate other methods of determining single-ion activities.

## 11. Reversibility of the Measurement Process

There are three unknowns that need to be measured to determine single-ion activities, temperature, concentration, and contact potential. Clearly, temperature and concentration can be measured by thermodynamically acceptable methods.

This leaves the reversibility of contact potential for consideration. Measuring the contact potential requires moving of electrode N. This is a macroscopic process that does not involve heat, and as such, it can be performed arbitrarily close to reversible conditions.

Next, consider the bias voltage. The bias voltage is applied to an open circuit, so there is no dc current to introduce irreversibility. In principle, the voltage from the bias supply can be applied by a reversible source, for example, an electrochemical cell with the cell parameters (cell type and electrolyte concentrations) selected so the voltage of the cell matches the bias voltage required to produce a null. As a practical matter, one would likely use either a resistive voltage divider coupled to a standard voltage source or a variable power supply to supply the bias voltage. These are irreversible devices. However, the potential difference across the terminals of the bias supply does not depend on whether the potential source is reversible or irreversible, so the contact potential difference measurement does not depend on the reversibility of the bias supply.

The measurement also requires determining the null point of an ac current. Given that the ac current is zero at the null condition, there is no entropy produced by the ac current, and that aspect of the measurement is, therefore, thermodynamically reversible.

In summary, it is possible to perform all aspects of the measurement under conditions that either approach thermody-

namic reversibility or are functionally indistinguishable from thermodynamic reversibility

## 12. Molar Balance versus Electrical Balance and the Independent Variation of Ion and Counterion Composition of Electrolytes

We normally think of the anion and cation concentrations as being constrained by electrical neutrality to be balanced. However, in the strictest sense perfect electrical neutrality is not a physical requirement, and independent variation of charge carriers can take place to a certain degree, that is, a small quantity of a charged species may move from one material to another. This can only continue until the charge difference builds up to the point at which the outer potential differences of the materials prevent further transfer. At equilibrium, these outer potential differences constitute the contact potential.

A sample calculation can be instructive. Consider two solutions containing a singly charged ion, such as sodium ions in a sodium chloride solution, one solution of 1.0 M and the other of 0.5 M. Assume the volume of each solution is 1 L. Assume the samples are in the form of cubes facing each other, separated by a distance of 1 mm. Assume for sake of discussion that the activity coefficients for the ions are the same in each of the two solutions and that the temperature is 300 K. Let the ion but not the counterion equilibrate between the materials. From Equation (11), the contact potential is 0.0179 V. The system has a capacitance of  $8.85 \times 10^{-11}$  farad. From this capacitance and the contact potential of 0.0179 V, we calculate the charge transferred to be  $1.58 \times 10^{-12}$  coulomb, which is equivalent to  $1.64 \times 10^{-17}$  moles, an utterly negligible amount relative to the number of moles of the ion in either solution. Even if one were to assume that the excess amount of ions was concentrated in a 0.1 nm layer on one face of the cube, the excess ion concentration in that thin slice of solution would be only  $1.64 \times 10^{-8}$  M, which is a negligible amount relative to the bulk concentration of either solution. Thus, for most purposes we can assume virtual molar equivalence of ion and counterion, even if there is a significant outer potential difference between the materials.

Similarly, if the concentrations of the two solutions were 1 M and  $5 \times 10^{-4}$  M then the contact potential would be 0.196 V, and the excess ion concentration would be  $1.80 \times 10^{-7}$  M in a thin 0.1 nm slice, which is orders of magnitude less than  $5 \times 10^{-4}$  M. One can reasonably conclude that even rather high levels of charge imbalance are negligible in terms of concentration imbalance. Thus, we are safe in assuming that one does not normally need to take concentration changes into account in dealing with electrochemical contact potentials.

Considering the issue of electrical balance further, there are numerous examples that demonstrate that an electrical imbalance is possible in systems undergoing electrochemical or analogous processes. For example, in the field of mass spectrometry a technique known as electrospray has become, arguably, the most widely used ionization method. In this technique, an electrical voltage is applied to an ion-containing solution flowing from a capillary. This causes accumulation of an

excess amount of charge on the solution, with an opposite charge accumulated on a counter electrode external to the solution. The counter electrode is typically a conductive plate forming the entrance to a mass spectrometer. In positive-mode electrospray, the excess amount of charge on the solution consists of positive ions, and the excess amount of charge on the conductive plate consists of electrons, and there is clearly a charge separation that takes place between components of the system.

In fact, it is possible to draw the schematic of an electrospray ion source to look very much like Figure 4 of this paper, with electrode N taking the place of the external conductive plate in an electrospray ion source, the liquid in the capillary taking the place of the electrolyte in Figure 4, and the bias supply (which in principle could take the form of a stack of reversible electrochemical cells) taking the place of the electrospray voltage source. Prior to the onset of spraying, this system is highly analogous to the type of system discussed in this paper, except that the bias supply is set to a high voltage rather than the relatively low voltage needed to cancel  $\Delta\psi$ . After the onset of spraying, the system undergoes irreversible processes, and the analogy is less perfect. However, the existence of a spray of charged droplets is an unequivocal demonstration that charge separation has taken place.

A second example demonstrating charge separation is the charging of the plates of a capacitor. This can be arranged to be a pure reversible system. For example, suppose the electrochemical cell uses two electrodes composed of liquid amalgams at two different mole fractions. More than a century ago, Richards et al. performed a series of painstaking experiments on the electrochemical thermodynamics of metals doped into mercury and found that amalgam electrodes can be reversible for a number of different metals.<sup>[42]</sup> If two capacitor plates are connected to the terminals of the cell then a charge separation will occur, and the plate connected to the negative terminal of the cell will become negatively charged and the plate connected to the positive terminal of the cell will become positively charged. The charging process can be made to be reversible by initially positioning the plates far apart and then slowly bringing them closer together.

The amount of charge imbalance can be determined by integrating the current as the plates are brought closer together. Alternatively, in a thought experiment one could draw Gaussian boxes around the electrodes and calculate the charges by integration of the electric field components normal to the surfaces. A capacitor charged by using a battery is similar to the systems described in the present paper in the sense that the charge separation can develop reversibly and also by the fact that it is electrochemical in origin, but it differs in the sense that it employs a full electrochemical cell (i.e. two half-cells) rather than the systems illustrated in the figures in this paper, which correspond more closely to individual half cells.

A third example showing charge separation is if dissimilar metals are electrically connected by a thin wire. Due to the difference in the Fermi levels of the metals (equivalent to the difference in electrochemical potentials of electrons in the metals, which is in turn equivalent to the work function differ-

ence) electrons are transferred from one metal to the other. This produces a contact potential that is equal in magnitude to the difference in Fermi levels for the uncharged metals. Assuming the dissimilar metals are of the form of two plates separated by a gap, the charge imbalance is given by the integral of the current in the wire as the electrons equilibrate between the metals. Alternatively, in a thought experiment by employing Gauss's law, the charge on a plate is given by the integral of the electric field normal to a box drawn around an electrode. At a conceptual level, the development of a charge imbalance in this system is very similar to the charge imbalance between the solution and the external electrode in the systems discussed in the present paper, and the transfer of ions between the solution and the electrode metal take the place of electron transfer between the dissimilar conductors. This is the physical basis of the well-established Kelvin probe technique of measuring differences between work functions of dissimilar metals.

### 13. Single-Ion Activities of Counterions

There are at least two methods that could be used to determine single-ion activities of a counterion. The first is to use two different ion-selective electrodes and to measure the single-ion activity coefficients separately. This has the feature that the results can be substituted into the equation for mean ionic activity coefficient, for example, for a uni-univalent electrolyte [Eq. (50)]:

$$\gamma_{\pm} = (\gamma_{+}\gamma_{-})^{1/2} \quad (50)$$

and the results are compared to experimentally determined mean ionic activity coefficients. This enables checking for internal consistency of the theory presented herein. This method would use an ion-selective electrode in an unconventional way, that is, there would be no reference electrode to complete an electric circuit, but rather it would be arranged in an apparatus similar to that shown in Figure 4, and a Kelvin probe technique would be applied. The other approach would be to measure the single-ion activity coefficient of one species and then solve Equation (50) to determine the single-ion activity coefficient of the other.

### 14. On the Vapor Pressure of Ions

The concept that every material has a vapor pressure underlies the concept of fugacity.<sup>[23,24]</sup> Fundamentally, in this respect ions are no different from any other solute, including nominally nonvolatile electrically uncharged solutes. In each case, they are bound to a solution by a finite energy, which implies that a certain fraction of the nonvolatile species may populate the gas phase, though the fraction may be exceedingly small. This concept also underlies the understanding of thermionic emission, and it has long been recognized that ions may undergo thermionic emission.<sup>[43]</sup> The same physics must apply at lower temperature, differing only in degree but not in kind. Fermi

has given a statistical mechanical treatment of an electron gas in equilibrium with a metal.<sup>[44]</sup> The same basic physics must apply to ions as well as to electrons, which implies that ions must also have a vapor pressure, though that pressure may be exceedingly small. All of these lines of thought justify that the concept of ionic vapor pressure is valid, which in turn justifies a fugacity-based treatment of the single-ion activity problem.

### 15. Single-Ion Activities Depend on the Properties of the Counterion

The term "single-ion activity" does not mean that a single-ion activity is independent of the identity or properties of the counterion. These properties can affect the vapor pressure of the solution-phase ion (or more strictly, the fugacity of the solution-phase ion), which leads to a nonlinear relationship between the fugacity of an ion and the concentration of the electrolyte. In an alternative but equivalent point of view, the electrochemical potential of an ion is affected by the properties of the counterion.

This concept is most easily illustrated by using microscopic theory, such as Debye–Hückel theory. In Debye–Hückel theory the single-ion activity coefficient depends on the ionic strength, but two solutions of equal concentration do not necessarily have the same ionic strength, because there is a term in the definition of ionic strength that depends on the square of the counterion charge. For example, if one considers two solutions, one solution containing the solute NaCl and the other containing the solute Na<sub>2</sub>SO<sub>4</sub>, and if both solutions have the same Na<sup>+</sup> concentration, then the single-ion activity coefficient for Na<sup>+</sup> calculated by Debye–Hückel theory will be different for the two solutions, because the counterion charge is different for the two solutions. Furthermore, at higher concentrations there are other (incompletely understood) contributions to nonideal behavior of the ion, and these properties no doubt depend on the properties of the counterion as well. Thus, in general a single-ion activity depends on the properties of the counterion.

If a single-ion activity depends on the properties of a counterion, then in what sense can it be considered a "single-ion" property? It is a single-ion quantity in the sense that it ultimately relates to the change in Gibbs free energy of a phase if a small number of ions are added to or removed from the phase without simultaneously adding or removing counterions.

In another way of looking at the same issue, the situation is analogous to a mixed solution of neutral compounds. Consider two solutions, one that is 1 M in sucrose and 1 M in glucose and the other that is 1 M in sucrose and 1 M in acetone. Because sucrose molecules interact differently with glucose than they do with acetone, the fugacity of sucrose in the two solutions will not necessarily be the same, and furthermore, the nonlinearity of the fugacity/concentration relationship will not necessarily be the same for the two cases. Therefore, the activity coefficients of sucrose will likely differ in the two cases, even though the concentrations are the same. Similarly, the fugacity of an ion will, in the general case, depend on the identity of

the counterion, and furthermore, the nonlinearity of the fugacity/concentration relationship will in general depend on the identity of the counterion. Thus, the single-ion activity coefficient will depend on the identity and properties of the counterion.

## 16. Relationship between the Concepts of “Thermodynamically Well Defined” and “Thermodynamically Well Measurable”

This paper has emphasized the concepts of both defining and measuring single-ion activities in a thermodynamically rigorous way. Although closely related, these two concepts are not identical, and both play an important role in the practical utility of single-ion activities. It is possible for a quantity to be thermodynamically well definable in a formal sense but not thermodynamically well measurable in a practical sense. Clearly, for a thermodynamic quantity to be useful it must satisfy both criteria.

To illustrate the distinction between thermodynamic meaning and thermodynamic measurability, consider two concrete examples. The first is the vapor pressure of a nonvolatile electrically neutral solute. For concreteness, it could be a large soluble molecule, such as a cyclodextrin or a protein at its isoelectric point. The vapor pressure is thermodynamically well defined, but the vapor pressure of a nonvolatile component is so low it cannot be measured directly. This is the case for which something is thermodynamically well defined but not amenable to direct thermodynamic measurement. Even the vapor pressure of a slightly volatile solute might not be amenable to direct thermodynamic measurement, though it might be measurable by extra-thermodynamic methods, such as optical spectroscopy or mass spectrometry.

It is, however, possible to determine the ratio between two vapor pressures (or fugacities) of a nonvolatile solute. This is, in fact, the conceptual basis of relative vapor pressures (or relative fugacities) of nonvolatile solutes, more commonly known as activities. For nonvolatile solutes, measurement of relative vapor pressure is not done by direct measurements but rather by indirect means, such as by using the Gibbs–Duhem relationship.

The partial molar heat capacity of electrons in a conductor is another example of something that is thermodynamically well defined. It is the differential between two heat capacities of the same sample, differing only in that a different number of electrons have been added for one of the two heat-capacity measurements. However, as a practical matter it is impossible to add enough electrons to directly observe the difference in heat capacity. Hence, the partial molar heat capacity of electrons in a conductor is well defined in a formal sense, but as a practical matter it is not measurable by using the methods of equilibrium thermodynamics.

Of the examples discussed, the single-ion activity is most similar to the determination of the activity of a nonvolatile neutral species by using indirect thermodynamic methods, such as the Gibbs–Duhem relation. However, in the case of single-ion activity coefficients, the relevant relationship is not

the Gibbs–Duhem equation, but rather, the relationship between activity coefficients and contact potentials, which are themselves measurable by using thermodynamically reversible methods. Thus, the single-ion activity coefficient, which is defined by Equation (2), is not just thermodynamically well defined in a formal theoretical sense, but it is also a thermodynamically well-measurable quantity in a practical sense.

Interestingly, returning to the example of the partial molar electronic heat capacity of a conductor, and by implication the partial molar entropy of electrons in a conductor, these are quantities that are well defined in a formal sense but not measurable in a practical sense. However, by using the methods of nonequilibrium thermodynamics they can be determined by using thermoelectric measurements.

Complicating the thermodynamic interpretation of this method of determining electronic entropies, thermoelectric measurements ultimately depend on the measurement of Thomson coefficients, which cannot be measured under thermodynamically reversible conditions. Consequently, determining the partial molar heat capacity and partial molar entropy of electrons in a conductor by using thermoelectric measurements depends on an extension of the principles of thermodynamics, wherein certain quantities from equilibrium thermodynamics would be equivalent to certain quantities from irreversible thermodynamics. If this extension of thermodynamic principles is valid, then it becomes possible to determine the partial molar entropy of ions in solution by using electrochemical Peltier experiments,<sup>[35,44,45]</sup> which brings us back to single-ion thermodynamics of ionic solutes.

The presentation in this paper is based on equilibrium thermodynamics, a rigorous and exact science, and it may therefore seem to have an air of inevitability or infallibility to it. However, its correctness depends on the soundness of the underlying assumptions and the correctness of the logic connecting one relationship to another. For example, one assumption made in this paper is that the inherent fugacity of an ion (roughly speaking the ionic vapor pressure near the surface of the solution) does not change if the solution is placed in a region of different potential or if the solution becomes electrically charged. This assumption was examined, at least in part, in another section of this paper by considering whether the molar imbalance between ion and counterion during charging is enough to significantly alter the concentration of ion or counterion, and on the basis of sample calculations, this does not seem to be a problem under normal laboratory conditions.

Another issue is whether the use of a one-chambered apparatus based on Figure 3 or 4 is valid. As with any scientific argument, this point is open to additional discussions. Fortunately, this issue is open to experimental validation. On the basis of a discussion earlier in this paper, one could perform the single-ion activity measurements by using a one-chambered apparatus based on Figure 3 or 4 and repeat the experiments by using a two-chambered apparatus based on Figure 1 or 2. Comparing the results would validate or invalidate the proposed equivalence. Of course, one would need to insert bias voltages into both the left- and right-hand sides of a two-

chambered apparatus. Additionally, one would need to make provision for modulating the distances ( $D_1$  and  $D_2$ ) independently in each of the two sides of the apparatus and for detecting a null in the ac currents as the distances are modulated. If the validation of the one-chambered scheme were to fail then the measurements could be performed by using a two-chambered device.

There are also practical experimental factors to consider. One is already addressed in the present work, the issue of whether the uncertainty in contact potential measurements is small enough to allow useful results to be obtained, and on the basis of projections from companies that market Kelvin probe equipment, it appears that sufficiently accurate measurements of contact potentials are feasible, although additional unforeseen experimental uncertainties or difficulties could also arise.

There could also be other unforeseen problems, either in the theoretical development or in the experimental realization of the technique described herein. These possibilities should be discussed by the wider scientific community, particularly as they deal with a topic of such long-standing controversy as single-ion activities.

## 17. On the Equilibrium versus Nonequilibrium of System Components

In Figure 1, the ion under study ( $M^+$ ) equilibrates between two solutions, but the counterion ( $X^-$ ) does not. The fact that one component has not reached equilibrium does not invalidate the possibility that another component has reached equilibrium. This concept is, in fact, the basis of separation of solution components by using equilibrium dialysis. A small molecule, such as testosterone, may be separated from large components, such as sex hormone binding globulin (SHBG) and the testosterone/SHBG complex, by using dialysis membranes with an appropriate cutoff for molecular size. Provided that the diffusion rate of testosterone across the membrane is sufficiently fast, and provided that the diffusion rate of the large components across the membrane is sufficiently slow as to be negligible, then one component may achieve equilibrium between the two dialysis compartments, despite the fact that other components might not equilibrate across the membrane. Similarly, an ion may equilibrate between two solutions without a requirement that the counterion must also equilibrate between the solutions.

As an aside, if one were to drill a hole through the metal plate that separates the two solutions in Figure 1 and cover the hole with a membrane that is selectively permeable only to  $M^+$  then the equilibrium concentrations of  $M^+$  in the modified system would be the same as that in the original system. Alternatively, one could completely replace the metal plate separating the solutions with a selectively permeable membrane to achieve equilibrium of  $M^+$  between the chambers. This is the basis for Donnan equilibrium. However, if one wishes to measure single activity coefficients, there would still be a need for at least one electrode to interact electrochemically with the liquid phase(s) to facilitate the measure-

ment of contact potentials by the Kelvin probe method, even if a selectively permeable membrane were used to equilibrate  $M^+$  between the two chambers of the device.

## 18. Summary

Going back to first principles and considering the thermodynamic relationships between concentration, vapor pressure (or, more rigorously, the relationship between concentration and fugacity), and the Gibbs free energy of transfer of charged objects between points in the gas phase, one can derive a relationship between contact potentials and single-ion activity coefficients. The steps in the derivation involve only thermodynamically reversible steps. Contact potentials are measurable by using thermodynamically reversible processes. Consequently, single-ion activity coefficients can be determined without the use of any extra-thermodynamic assumptions for either definition or measurement.

In this approach to single-ion activities there is no need to know the electrostatic potential gradient across a boundary between dissimilar materials. Similarly, there is no need to know the electrostatic energy across the interface between a gas phase and the interior of a condensed phase. This avoids the principal historical objection to the physical meaning of single-ion activities.

One consequence of defining single-ion activities in the way presented in the present paper (a "type II definition") is that they relate directly to the thermodynamics processes in which ions cross boundaries between dissimilar materials, whereas single-ion activities under a type I definition do not, nor do other approaches that seek to remove the surface potential. Furthermore, the approach presented in this paper does not require knowledge of any microscopic properties of the system, nor does it require the presence of any devices that may introduce thermodynamic irreversibility into the system, such as salt bridges. Because of the close relationship between single-ion activities and the energetics of transfer of ions across boundaries between dissimilar materials, it stands at a crossroads between physics, chemistry, biology, geology, and engineering. It also places the concept and measurement of pH on a valid thermodynamic foundation, and lastly, it enables the thermodynamic determination of the Gibbs free energy for the transfer of ions between dissimilar materials.

## Acknowledgements

Support from ARUP Institute for Clinical and Experimental Pathology is gratefully acknowledged.

**Keywords:** charge transfer · contact potential · Gibbs free energy · single-ion activity · thermodynamics

- [1] E. A. Guggenheim, *J. Phys. Chem.* **1929**, *33*, 842. M. Klotz, *Chemical Thermodynamics, revised ed.*, Benjamin, New York **1964**, pp. 390–419.
- [2] W. J. Moore, *Physical Chemistry, 4th ed.*, Prentice Hall, Englewood Cliffs, NJ, **1972**, pp. 440, 534.
- [3] <http://goldbook.iupac.org/P04524.html>.

- [4] Y. C. Wu, W. F. Koch, W. A. Durst, *Standard Reference Materials: Standardization of pH Measurement*, U.S. Department of Commerce/National Bureau of Standards, NBS Special Publication 260–53 (1988 Edition).
- [5] A. K. Covington, R. G. Bates, R. A. Durst, *Pure Appl. Chem.* **1985**, *57*, 531–542.
- [6] <http://goldbook.iupac.org/I03244.html>.
- [7] J. Darnell, H. Lodish, D. Baltimore, *Molecular Cell Biology, 2nd ed.*, Scientific American Books, New York **1990**, pp. 584, 771, 772, 870, 871.
- [8] J. W. Gibbs, *Collected Works of J. Willard Gibbs, Vol. 1*, Yale University Press, New Haven **1906**, p. 429.
- [9] Y. M. Joshi, J. C. T. Kwak, *J. Phys. Chem.* **1979**, *83*, 1978–1983.
- [10] P. Sloth, T. S. Soerensen, *J. Phys. Chem.* **1990**, *94*, 2116–2123.
- [11] T. S. Soerensen, *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 1815–1843.
- [12] P. Sloth, *J. Chem. Phys.* **1993**, *98*, 7319–7337.
- [13] C. Li, Y. Li, J. Lu, L. Yang, *Fluid Phase Equilib.* **1996**, *124*, 99–110.
- [14] M. K. Khoshkbarchi, J. H. Vera, *AIChE J.* **1996**, *42*, 249–258.
- [15] A. Ferse, H. Müller, *J. Solid State Electrochem.* **2011**, *15*, 2149–2167.
- [16] D. Fraenkel, *J. Phys. Chem. B* **2011**, *115*, 557–568.
- [17] G. Wilczek-Vera, J. H. Vera, *Fluid Phase Equilib.* **2011**, *312*, 79–84.
- [18] D. P. Zarubin, *J. Chem. Thermodyn.* **2011**, *43*, 1135–1152.
- [19] D. P. Zarubin, *J. Chem. Thermodyn.* **2012**, *47*, 451–452.
- [20] D. Fraenkel, *J. Phys. Chem. B* **2012**, *116*, 3603–3612.
- [21] H. Sakaida, T. Kakiuchi, *J. Phys. Chem. B* **2011**, *115*, 13222–13226.
- [22] G. N. Lewis, M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw Hill, New York **1923**, p. 192.
- [23] G. N. Lewis, M. Randall, K. S. Pitzer, L. Brewer, *Thermodynamics, 2nd ed.*, McGraw Hill, New York **1961**, p. 154.
- [24] L. F. Kelvin, *Philos. Mag.* **1898**, *46*, 82–120.
- [25] W. N. Hansen, G. J. Hansen, *Phys. Rev. A* **1987**, *36*, 1396–1402.
- [26] R. Gomer, G. J. Tryson, *J. Chem. Phys.* **1977**, *66*, 4413–4424.
- [27] C. D. Kinloch, A. I. McMullen, *J. Sci. Instrum.* **1959**, *36*, 347–349.
- [28] KP Technology Ltd., Caithness, Scotland, <http://www.airphotoemission.com/systems.html>
- [29] McCallister Technical Services, Coeur d'Alene, Idaho, USA, <http://www.mcallister.com/kpfaq.html>
- [30] D. Himmel, S. K. Goll, I. Leito, I. Krossing, *Angew. Chem. Int. Ed.* **2010**, *49*, 6885–6888; *Angew. Chem.* **2010**, *122*, 7037–7040.
- [31] A. L. Rockwood, *Phys. Rev. A* **1986**, *33*, 554–559.
- [32] J. E. Bartmess, *J. Phys. Chem.* **1994**, *98*, 6420–6424.
- [33] A. L. Rockwood, *Phys. Rev. A* **1984**, *30*, 2843–2844.
- [34] A. L. Rockwood, *Electrochim. Acta* **2013**, *112*, 706–711.
- [35] A. L. Rockwood, *J. Phys. Chem.* **1987**, *91*, 3116–3116.
- [36] A. L. Rockwood, *Phys. Rev. A* **1987**, *36*, 1525–1526.
- [37] a) <http://goldbook.iupac.org/C01293.html>; b) <http://goldbook.iupac.org/O04349.html>.
- [38] a) <http://goldbook.iupac.org/G02574.html>; b) <http://goldbook.iupac.org/I03046.html>.
- [39] C. P. Kelly, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2006**, *110*, 16066–16081.
- [40] T. P. Pollard, T. L. Beck, *J. Chem. Phys.* **2014**, *141*, 18C512.
- [41] T. W. Richards, J. H. Wilson, R. N. Garrod-Thomas, *Electrochemical Investigations of Liquid Amalgams of Thallium, Indium, Tin, Zinc, Cadmium, Lead, Copper, and Lithium*, The Lord Baltimore Press, Baltimore, **1909**.
- [42] O. W. Richardson, *Thermionic Phenomena and the Laws which Govern Them*, Nobel Lecture, Dec 12, **1929**.
- [43] E. Fermi, *Thermodynamics*, Dover, New York, **1956**, p. 155.
- [44] A. L. Rockwood, *Electrochim. Acta* **2013**, *107*, 686–690.

Received: January 15, 2015

Published online on April 27, 2015