On the Activity of Ions and the Junction Potential: Revised Values for All Data

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This work presents an in-depth study of the interrelation between the junction potential E_J and the activity of individual ions. The need to correct for the sign of the junction potential employed in previous publications is used to confirm that the calibration of the ion-selective electrodes largely cancels errors in the estimation of E_J. Revised values of the activity coefficients of individual ions are presented for all systems previously measured. A rederivation of Henderson equation is used to clarify the interpretation of its terms for asymmetric electrolytes. A new analytical equation to calculate E_J is derived and tested. This equation corrects for the nonideality of solutions and for the concentration dependence of the conductivity. The correction for nonideality is only necessary for the ions present in both the sample and the reference electrode solutions. The new equation represents a major improvement over the Henderson equation for E_J calculations. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 445–462, 2004
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Introduction

The possible determination of the activities of single ions has long been a matter of controversy (Guggenheim, 1936). Even today, the field is far from settled, and recent publications maintain the impossibility of measuring such properties (Malatesta, 2000). Thus, it is unfortunate that the junction potential was used with the wrong sign in all publications of the senior author on the subject (Khoshkbarchi and Vera, 1996a, b; Marcos-Arroyo et al., 1996; Rabie et al., 1999; Taghikhani et al., 1999, 2000; Rodil et al., 2001; Rodil and Vera, 2001a,b, 2003). Thanks to Diplom-Ing. Armin C. Schneider (2002), who discussed with us his measurements for the activity of ions in NaCl aqueous solutions, we established that in our computer codes we had consistently used the wrong sign for the junction potential. On the positive side, the detection and correction of this error allows us to demonstrate that, as discussed in a recent publication (Rodil and Vera, 2003), the calibration procedure used for the determination of ionic activities largely compensates for errors in the estimation of the junction potential.

The text of Skoog et al. (1998) opens the section on "Sign Conventions for Electrode Potentials" with the phrase: "It is perhaps not surprising that the choice of sign for electrode potentials has led to much controversy and confusion in the course of the development of electrochemistry." We definitely agree with this statement. Briefly stated, two different conven-

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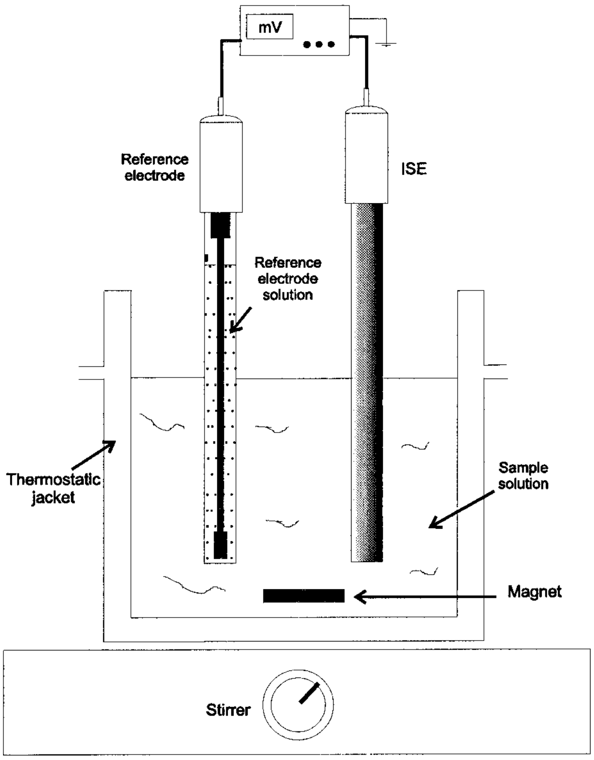

Figure 1. Electrochemical cell used for the measurement of the individual activity of ions.

A thermometer (not shown in the figure) is maintained inside the sample solution to control the temperature of the cell. Water from a thermostatic bath is circulated in the jacket of the cell.

tions are used to write the representation of an electrochemical cell formed by an ion-selective electrode (ISE) and a single junction reference electrode, both immersed in an aqueous electrolyte solution, as shown in Figure 1. To describe the schematics of such a cell, the text of Bates (1965) uses the convention for pH measurements, or "pH-convention" for short, and writes the cell as:

ISE|sample solution (k)||reference electrode solution (r)|
Reference electrode

On the other hand, the text of Skoog and Leary (1992) uses the convention for potentiometry, or "potentiometry-convention" for short, and writes the cell as:

Reference electrode|reference electrode solution (r)||
sample solution (k)|ISE

Both of these texts follow the IUPAC or Stockholm convention for the determination of the sign of the emf between two elements of a cell. In this convention, the emf sign is obtained by subtracting the potential of the element to the left from the potential of the element to the right, with the schematics of the cell as written. In the first publication of the senior author on the subject of the activity of ions (Khoshkbarchi and Vera, 1996a), the Henderson equation for the junction potential (Henderson, 1907, 1908) was used in the form given in the text of Bates (1965), and the equation for the cell was taken from the text of Skoog and Leary (1992) as

$$E = E_{ISE} - E_{ref} + E_J \tag{1}$$

However, in the computer code used to calculate the activity of ions, the necessary change of sign of the junction potential was not implemented. This error in sign was carried on in all successive publications of the group. From here on, we designate by E_J^* the junction potential of the sample solution (k) minus the potential of the solution at the reference electrode (r), as used in the text of Bates, to distinguish it from $E_J = -E_J^*$, as used in Eq. 1. In addition, a closer examination of the Henderson equation showed that its terms were misinterpreted in the literature, and that the tabulated values were in error for asymmetric electrolytes (Bates, 1965, 1973). The proper interpretation of the terms of the Henderson equation is presented in Appendix B. Thus, in addition to the error in sign, the error in interpretation of the terms of the Henderson equation was also present in our calculations of activity coefficients of individual ions for asymmetric electrolytes (Rodil and Vera, 2001a, b, 2003).

In this work we give a detailed consideration to the expressions to calculate the junction potential, and we correct errors on the interpretation of their terms found in the literature. We derive and test a new equation for the calculation of the liquid junction potential with due consideration to the nonideality of the solutions and to the variation of conductivity with composition. Finally, we present revised values for all previously reported activity coefficients of individual ions and propose two new equations to correlate the experimental results.

Relation Between the Activity of Ions and the Reference Electrode Junction Potential

In this treatment, we follow the convention for potentiometry used in the texts of Skoog (Skoog and Leary, 1992; Skoog et al., 1998). For a sample solution at (dimensionless) molality, m_k, of the ion detected by the ISE, the emf of the ISE is related to the activity of the ion, i, by

$$E_{ISE,k} = E_{0,ISE} + S \ln a_{i,k} \tag{2}$$

where $E_{0,ISE}$ is a combination of the standard potential, the junction potential, and the asymmetry potential of the ISE, and S is a general slope used instead of the Nernstian value given by the ratio (RT/z_iF). The sign of the slope, S, is given by the sign of the charge, z_i, of the ion under consideration, and thus it is positive for cations and negative for anions.

From Eqs. 1 and 2, the potential reading E_k obtained for a half-cell ISE vs. a single-junction reference electrode, minus the corresponding value of the junction potential, $E_{J,k}$, is related to the ionic activity by

$$\phi_k = (E_k - E_{J,k}) = E_0 + S \ln a_{i,k} \tag{3}$$

where E_0 is a combination of $E_{0,ISE}$ and E_{ref}. In Eq. 3, the junction potential, $E_{J,k}$, depends on the temperature of the system, the compositions of the two solutions in contact and, for the case of two solutions of different electrolytes in contact, on the geometry of the junction. For the particular geometry of a standard single-junction reference electrode, at 298.15 K, the junction potential is a function of the composition of the two solutions in contact.

The activity of an ion i is obtained from the response E_k of the corresponding half-cell ion-selective electrode against a single-junction reference electrode, both immersed in an aqueous solution at molality m_k of the electrolyte containing the ion i. Then, using a value for the liquid junction potential between the sample solution and the 4-M KCl solution inside the reference electrode, we calculate ϕ_k. The method used to obtain a value for this liquid junction potential is one of the main subjects of this work. The constants E_0 and S in Eq. 3 are evaluated from information on the variation of ϕ_k, calculated as just described, with the values of the activity $a_{i,k}$ $(=m_{i,k}\gamma_{i,k})$ of ion i. Thus information on the activity coefficient of the ion i, $\gamma_{i,k}$, should be provided. For electrolyte concentrations lower than 0.01 m, at 298.15 K, the activity coefficient of the ion is obtained from the Güntelberg equation (Lewis and Randall, 1961)

$$\ln \gamma_{i,k}^{G} = \frac{-1.1762 z_i^2 \sqrt{I_m}}{1 + \sqrt{I_m}} \tag{4}$$

where z_i is the charge of the ionic species i under consideration and the ionic strength I_m at molality m_k, is given by

$$I_m = \frac{1}{2} \sum_i m_{i,k} z_i^2 \tag{5}$$

Thus, from Eq. 3

$$\phi_k^{dilute} = E_0 + S \ln(m_{i,k}\gamma_{i,k}^{G}) \tag{6}$$

Once the values of S and E_0 are known, Eq. 3 is used to obtain the activity coefficients of the individual ion for higher concentrations as

$$\ln \gamma_{i,k} = \frac{\phi_k - E_0}{S} - \ln m_{i,k} \tag{7}$$

For the case of simultaneous measurement of the activities of the cation and the anion of an electrolyte, the upper concentration limit of applicability of Eq. 7 is limited by the need to reproduce the known values of the mean ionic activity coefficient. For the case of measurement of the activity of a single ion, the upper limit of applicability of Eq. 7 is fixed by previous experience regarding the concentration range of reliable operation of the electrode (Rodil and Vera, 2003).

The accuracy of the value of the activity of the ions depends on the reliability of the values used for the junction potential at each point. The most important points are those at high dilution as they determine the values of S and E_0. A recent analysis of the theory supporting this method presented explicit expressions to correct for the error introduced by the use of an erroneous value of the junction potential (Rodil and Vera, 2003). This analysis assumed the existence of the "true" (experimentally measured) value of the junction potential, $E_{J,k}^{T}$, related to the approximated value of the junction potential, $E_{J,k}$, by

$$E_{J,k}^{T} = E_{J,k} + \Delta\epsilon_r + \Delta\epsilon_k \tag{8}$$

with

$$\Delta\epsilon_r = [E_{J,\infty}^{T} - E_{J,\infty}] \tag{9}$$

and

$$\Delta\epsilon_k = [E_{J,\infty} - E_{J,k}] - [E_{J,\infty}^{T} - E_{J,k}^{T}] \tag{10}$$

In the term $\Delta\epsilon_r$, both the true and the approximated liquid junction potentials are those between the most dilute solution measured and the solution in the reference electrode. This term is constant for a set of measurements. For the term $\Delta\epsilon_k$, each of the square brackets on the righthand side of Eq. 10 represents the junction potential that would exist between the most dilute sample solution of the series and the solution of point k, at dimensionless molality m_k, of the series. The largest error is represented by the term $\Delta\epsilon_r$. The term $\Delta\epsilon_k$ represents only a small contribution, and it tends to be zero at high dilution. The analysis of the theory (Rodil and Vera, 2003) demonstrated that the slope S of the ISE would not be affected by an error in the estimate of the junction potential, while the value of the intercept would be displaced by $\Delta\epsilon_r$

$$E_0 = E_0^{T} + \Delta\epsilon_r \tag{11}$$

For the concentrated region, as shown elsewhere (Rodil and Vera, 2003), the effect of this displacement cancels out due to the calibration of the ISE and the only correction required is that coming from $\Delta\epsilon_k$. A "true" value of the activity coefficient of the ion i, $\gamma_{i,k}^{T}$, can be obtained by correcting the value obtained with the approximated junction potential, $\gamma_{i,k}$, using the following equation

$$\gamma_{i,k}^{T} = \gamma_{i,k} \exp\left[-\frac{\Delta\epsilon_k}{S}\right] \tag{12}$$

Although in the present work the same procedure could be used to correct for the error in the sign in the junction potential, the value of the correction term becomes too large due to the addition, instead of subtraction, of the two terms on the righthand side of Eq. 10. Thus, we have preferred to reduce again the raw experimental data of potential readings with the corrected junction potential. These data were kept in our archives. As the analysis of the theory recently presented (Rodil and Vera, 2003) used the equations as written in this work, the conclusions obtained in that study remain unchanged by the change in the sign of the numerical value of the junction potential.

One additional important observation to make here is that, while for the evaluation of the activity of individual ions it is required to know the junction potential, the inverse is not necessarily true. For the geometry of the reference electrode,

Table 1. Revised Values of the Activity Coefficients of Individual Ions in Aqueous Solution of KCl, KBr, and KF at 298.15 K

KCl ($\sigma_+ = 0.02$; $\sigma_- = 0.02$)			KBr ($\sigma_+ = 0.03$; $\sigma_- = 0.01$)			KF ($\sigma_+ = 0.04$; $\sigma_- = 0.05$)		
m	γ_{K^+}	γ_{Cl^-}	m	γ_{K^+}	γ_{Br^-}	m	γ_{K^+}	γ_{F^-}
0.003	0.951	0.940	0.01	0.899	0.903	0.01	0.899	0.899
0.006	0.907	0.921	0.02	0.864	0.864	0.05	0.807	0.807
0.01	0.898	0.897	0.03	0.839	0.827	0.1	0.757	0.756
0.05	0.822	0.850	0.05	0.808	0.816	0.3	0.650	0.705
0.1	0.745	0.780	0.1	0.747	0.786	0.5	0.610	0.686
0.2	0.690	0.746	0.2	0.673	0.762	0.8	0.568	0.681
0.3	0.669	0.723	0.5	0.530	0.730	1.0	0.554	0.681
0.4	0.638	0.705	0.8	0.473	0.720	1.2	0.541	0.745
0.5	0.609	0.698	1.0	0.442	0.721	1.5	0.534	0.700
0.6	0.585	0.695	1.2	×	0.721	1.8	0.533	0.712
0.7	0.564	0.684	1.5	×	0.720	2.0	0.536	0.717
0.9	0.545	0.672	2.0	×	0.736	2.5	0.541	0.752
1.0	0.529	0.659	—	—	—	3.0	0.515	0.770
1.2	0.512	0.652	—	—	—	—	—	—
1.4	0.485	0.662	—	—	—	—	—	—
1.6	0.448	0.661	—	—	—	—	—	—
1.8	0.478	0.663	—	—	—	—	—	—
2.0	0.477	0.663	—	—	—	—	—	—
2.5	0.473	0.661	—	—	—	—	—	—
3.0	0.480	0.668	—	—	—	—	—	—
4.0	0.511	0.665	—	—	—	—	—	—
B_x =	39.40	12.81	B_x =	−160.77	49.64	B_x =	56.29	84.66
D_x =	−0.30	0.24	D_x =	−0.242	0.293	D_x =	−0.24	0.13
$(\mathrm{rms})_x$ =	0.035	0.015	$(\mathrm{rms})_x$ =	0.029	0.019	$(\mathrm{rms})_x$ =	0.024	0.036
B_m =	−0.246	0.473	B_m =	−0.288	0.656	B_m =	−0.144	0.404
D_m =	0.146	−0.097	D_m =	−0.168	−0.139	D_m =	0.149	0.029
$(\mathrm{rms})_m$ =	0.033	0.016	$(\mathrm{rms})_m$ =	0.028	0.016	$(\mathrm{rms})_m$ =	0.024	0.035
b_i =	−0.230	0.541	b_i =	−0.026	0.508	b_i =	−0.215	0.249
d_i =	0.006	0.093	d_i =	−0.221	0.166	d_i =	0.042	0.166
(rms) =	0.036	0.018	(rms) =	0.028	0.018	(rms) =	0.024	0.037

Note: The pooled standard deviations σ_+ and σ_- of the activity coefficients obtained from the experimental runs are listed at the top of each column. The parameters for Eqs. 31, 33, and 34, and the corresponding root-mean-square (rms) deviation, are given at the bottom of the table.

the junction potential between the reference solution and the sample solution is, in principle, a measurable quantity at the temperature of the system. Present electrochemical methods require the knowledge of the activity of individual ions to obtain a value for the junction potential (MacInnes, 1961). Therefore, the activity of individual ions and the junction potential are currently considered to be conjugated variables. However, there is no reason to believe that future advances in electronics would not make possible the direct measurement of junction potentials. In the absence of experimental values for the junction potentials of interest, we turn our attention to the consideration of mathematical expressions to calculate such values.

Equations to Calculate Liquid Junction Potentials

The topic of this section is not new. In an inspiring work on the subject, published more than 75 years ago, Harned (1926) stated: "Since the difficulty in estimating liquid junction potentials is the only cause of our not being able to estimate exactly the individual activity coefficients of the ions, an analysis of the problem of liquid junction potentials will be made." Although a recent study (Rodil and Vera, 2003) indicates that the importance of the junction potential on the determination of the activity of ions has been somewhat overemphasized, the difficulty in estimating the junction potential is still largely unsolved. In this work, we derive an analytical equation for the case of a continuous-mixture junction between two concentrated nonideal solutions. As discussed in standard texts (MacInnes, 1961), the general expression for the junction potential E_J is related to the ionic activities by

$$E_J = -\frac{RT}{F}\sum_i \int \frac{t_i}{z_i}\, d\ln a_i \tag{13}$$

In Eq. 13, the transference number of ion i is defined as

$$t_i = \frac{C_i \lambda_i}{\sum_j C_j \lambda_j} \tag{14}$$

where C_i is the molar concentration and λ_i is the molar ionic conductivity of ion i.

Since the junction potential has not been considered important for other applications, it has received, at most, perfunctory attention, except in a few notable works (Plank, 1890a, b; Henderson, 1907, 1908; Harned, 1926; Guggenheim, 1936; Harper, 1985). In order to make some progress, it is necessary to gain a better understanding of the terms appearing in Eq. 13. A thermodynamic derivation of Eq. 13 is presented in standard texts (MacInnes, 1961). This derivation is based on the addition

Table 2. Revised Values of the Activity Coefficients of Individual Ions in Aqueous Solution of NaCl, NaBr, and NaF at 298.15 K

NaCl ($\sigma_+ = 0.004$; $\sigma_- = 0.009$)			NaBr ($\sigma_+ = 0.04$; $\sigma_- = 0.02$)			NaF ($\sigma_+ = 0.001$; $\sigma_- = 0.001$)		
m	γ_{Na^+}	γ_{Cl^-}	m	γ_{Na^+}	γ_{Br^-}	m	γ_{Na^+}	γ_{F^-}
0.003	0.940	0.941	0.005	0.927	0.966	0.01	0.902	0.896
0.006	0.920	0.919	0.006	0.915	0.922	0.05	0.795	0.813
0.01	0.898	0.899	0.008	0.909	0.904	0.1	0.762	0.749
0.1	0.831	0.749	0.1	0.816	0.755	0.3	0.703	0.664
0.2	0.801	0.691	0.2	0.765	0.728	0.5	0.676	0.626
0.3	0.783	0.656	0.3	0.734	0.700	0.8	0.646	0.606
0.4	0.759	0.647	0.4	0.704	0.716	1.0	0.610	0.578
0.5	0.748	0.639	0.5	0.704	0.699	—	—	—
0.7	0.738	0.621	0.6	0.716	0.686	—	—	—
0.9	0.766	0.595	0.8	0.724	0.649	—	—	—
1.0	0.767	0.599	0.9	0.702	0.649	—	—	—
1.2	0.780	0.600	1.0	0.684	0.661	—	—	—
1.5	0.766	0.581	1.2	0.708	0.635	—	—	—
1.8	0.793	0.588	1.5	0.771	0.637	—	—	—
2.0	0.803	0.589	1.8	0.812	0.638	—	—	—
2.5	0.851	0.587	2.0	0.835	0.644	—	—	—
3.0	0.920	0.603	2.5	0.930	0.657	—	—	—
3.5	0.961	0.622	3.0	1.023	0.670	—	—	—
4.0	1.063	0.637	4.0	1.262	0.724	—	—	—
—	—	—	5.0	1.660	0.781	—	—	—
$B_x =$	79.62	70.57	$B_x =$	202.46	58.78	$B_x =$	21.35	46.92
$D_x =$	0.35	−0.136	$D_x =$	−0.05	0.07	$D_x =$	0.08	−0.12
$(\mathrm{rms})_x =$	0.021	0.013	$(\mathrm{rms})_x =$	0.080	0.023	$(\mathrm{rms})_x =$	0.022	0.011
$B_m =$	0.621	0.028	$B_m =$	0.225	0.268	$B_m =$	0.395	−0.011
$D_m =$	−0.008	0.112	$D_m =$	0.278	0.038	$D_m =$	−0.169	0.112
$(\mathrm{rms})_m =$	0.025	0.014	$(\mathrm{rms})_m =$	0.078	0.024	$(\mathrm{rms})_m =$	0.022	0.011
$b_i =$	0.733	−0.095	$b_i =$	0.002	0.306	$b_i =$	0.239	−0.066
$d_i =$	0.193	0.085	$d_i =$	0.260	0.108	$d_i =$	0.078	0.061
(rms) =	0.014	0.013	(rms) =	0.079	0.021	(rms) =	0.022	0.011

Note: The pooled standard deviations σ_+ and σ_- of the activity coefficients obtained from the experimental runs are listed at the top of each column. The parameters for Eqs. 31, 33, and 34, and the corresponding root-mean-square (rms) deviation, are given at the bottom of the table.

of the contributions of the ions to the change of the Gibbs energy between the two liquid solutions forming the junction. A different derivation, based on the potential diffusion of ions across the junction, is presented in Appendix A. This derivation, which is similar to that presented by Koryta (1975), gives a better insight in the terms involved. For the cell written in the potentiometric convention, as discussed in Appendix A, the equation to calculate the junction potential can be written as

$$E_{J,k} = +\frac{RT}{F}\sum_i \tau_i, \tag{15}$$

with τ_i defined as

$$\tau_i = \frac{1}{z_i}\int_k^r \frac{C_i\lambda_i}{\sum_j C_j\lambda_j}\frac{da_i}{a_i} \tag{16}$$

For the type of liquid junction formed between the solution inside the reference electrode (r) and the sample solution (k), the mathematical approximation of Henderson represents closely the physical reality. In this approximation, the concentration of each ion is assumed to change continuously between the concentrations at the two boundary solutions. In addition, Henderson introduced two stringent simplifications to evaluate the integral in Eq. 16. He assumed that the activity of ion i was equal to its molar concentration and that the molar conductivity was independent of concentration and equal to the molar conductivity of the ion at infinite dilution, λ_i^∞. The derivation of the Henderson equation in the potentiometric convention is presented in Appendix B, together with the transformation required to obtain its expression in the pH-convention, as found in the literature (Bates, 1965, 1973). For the purposes of this work, in the potentiometric convention, the Henderson equation takes the form

$$E^H_{J,k} = \frac{RT}{F}\left[\frac{\sum_i \frac{1}{z_i}C_{i,r}\lambda_i^\infty - \sum_i \frac{1}{z_i}C_{i,k}\lambda_i^\infty}{\sum_i C_{i,r}\lambda_i^\infty - \sum_i C_{i,k}\lambda_i^\infty}\right]\ln\frac{\sum_i C_{i,r}\lambda_i^\infty}{\sum_i C_{i,k}\lambda_i^\infty} \tag{17}$$

where C_i and λ_i^∞ are, respectively, the molar concentration and the molar conductivity at infinite dilution of ion i. The subscripts k and r refer to the solution inside the reference electrode and the sample solution, respectively. As explained in Appendix B, following Bates (1965), for work at 298.15 K using a 4-M KCl solution in the reference electrode, Eq. 17 is conveniently rewritten as

Table 3. Revised Values of the Activity Coefficients of Individual Ions in Aqueous Solution of LiCl, LiBr, and CsCl at 298.15 K

LiCl ($\sigma_- = 0.02$)			LiBr ($\sigma_- = 0.02$)			CsCl ($\sigma_- = 0.005$)		
m	$\gamma_{Li^+}^{calc.}$	γ_{Cl^-}	m	$\gamma_{Li^+}^{calc.}$	γ_{Br^-}	m	$\gamma_{Cs^+}^{calc.}$	γ_{Cl^-}
0.01	0.908	0.900	0.01	0.907	0.903	0.003	0.937	0.941
0.02	0.883	0.865	0.02	0.922	0.858	0.006	0.917	0.919
0.03	0.873	0.835	0.03	0.916	0.839	0.01	0.872	0.899
0.05	0.844	0.810	0.05	0.855	0.810	0.1	0.720	0.754
0.1	0.824	0.755	0.1	0.804	0.791	0.2	0.696	0.702
0.2	0.810	0.706	0.2	0.759	0.774	0.3	0.656	0.670
0.5	0.858	0.637	0.5	0.763	0.746	0.4	0.619	0.647
0.8	0.936	0.611	0.8	0.805	0.752	0.5	0.590	0.631
1.0	0.993	0.605	1.0	0.848	0.761	0.7	0.553	0.604
1.2	1.061	0.600	1.2	0.901	0.772	0.9	0.526	0.586
1.5	1.234	0.593	1.5	1.066	0.782	1.0	0.510	0.579
2.0	1.442	0.592	2.0	1.282	0.799	1.2	0.495	0.565
2.5	1.766	0.600	2.5	1.645	0.827	1.5	0.484	0.550
3.0	2.177	0.615	3.0	2.153	0.859	1.8	0.473	0.539
—	—	—	—	—	—	2.0	0.462	0.533
—	—	—	—	—	—	2.5	0.453	0.522
—	—	—	—	—	—	3.0	0.451	0.508
B_x =	292.66	65.33	B_x =	413.63	51.41	B_x =	17.46	4.102
D_x =	0.464	−0.098	D_x =	−0.115	0.401	D_x =	−0.304	−0.044
(rms)$_x$ =	0.024	0.011	(rms)$_x$ =	0.044	0.023	(rms)$_x$ =	0.012	0.004
B_m =	0.890	0.064	B_m =	0.184	0.740	B_m =	−0.248	0.114
D_m =	0.284	0.099	D_m =	0.685	−0.118	D_m =	0.107	−0.026
(rms)$_m$ =	0.024	0.011	(rms)$_m$ =	0.040	0.020	(rms)$_m$ =	0.012	0.004
b_i =	0.616	−0.033	b_i =	−0.416	0.722	b_i =	−0.233	0.102
d_i =	0.489	0.087	d_i =	0.512	0.182	d_i =	−0.023	0.024
(rms) =	0.025	0.011	(rms) =	0.045	0.025	(rms) =	0.014	0.004

Note: The pooled standard deviations σ_- of the activity coefficients obtained from the experimental runs are listed at the top of each column. Activity coefficients for Li^+ and Cs^+ were calculated from the mean ionic activity coefficients using Eq. 37. The parameters for Eqs. 31, 33, and 34, and the corresponding root-mean-square (rms) deviation, are given at the bottom of the table.

$$E^H_{J,k} = 25.693\left[\frac{\left(\frac{1}{z_+}C_{+,k}\lambda_+^\infty - \frac{1}{|z_-|}C_{-,k}\lambda_-^\infty\right) + 11.6}{(C_{+,k}\lambda_+^\infty + C_{-,k}\lambda_-^\infty) - 623}\right] \times \ln\frac{623}{(C_{+,k}\lambda_+^\infty + C_{-,k}\lambda_-^\infty)} \qquad (18)$$

where $E^H_{J,k}$ is in milivolts.

Two notable attempts have been made to improve Henderson's equation for the calculation of the liquid junction potential. Harned (1926) proposed a modification that corrects for the variation of the ionic conductivity with concentration, and Harper (1985) included the correction for nonideality of the solutions and for the variation of ionic conductivity. While the method of Harned resulted in an analytical solution that does not correct for activities, the method of Harper produced complex expressions that required numerical solutions.

In this work, we propose a new analytical equation to calculate the value of the liquid junction potential that includes corrections for nonideality and for the variation of conductivity with concentration. For the integration of Eq. 16, we employ a mathematical artifice similar to that used by Henderson, as discussed in Appendix B. Here we follow an integration path in which there is a linear variation of the product $(C\lambda)_i$ with α. Thus, we write

$$C_i\lambda_i = (C\lambda)_{i,k} + \alpha\Delta(C\lambda)_i \qquad (19)$$

with

$$\Delta(C\lambda)_i = (C\lambda)_{i,r} - (C\lambda)_{i,k} \qquad (20)$$

Because the integral in Eq. 16 depends only on the two limiting solutions, the only condition for the dummy variable α is to be zero at the conditions of solution k and unity at the conditions of the reference solution r. Thus, to continue, we define the auxiliary variable α by the following expression

$$\alpha = \frac{a_i - a_{i,k}}{\Delta a_i} \qquad (21)$$

with

$$\Delta a_i = a_{i,r} - a_{i,k} \qquad (22)$$

With these definitions, Eq. 16 can be written as

$$\tau_i = \frac{\Delta a_i}{z_i}\int_0^1 \frac{[(C\lambda)_{i,k} + \alpha\Delta(C\lambda)_i]\, d\alpha}{[a_{i,k} + \alpha\Delta a_i][\beta_k + \alpha\Delta\beta]}, \qquad (23)$$

with

$$\beta_k = \sum_j C_{j,k}\lambda_{j,k} \qquad (24)$$

Table 4. Revised Values of the Activity Coefficients of Individual Ions in Aqueous Solution of NaOH, KOH, and HCl at 298.15 K

NaOH ($\sigma_+ = 0.04$)			KOH ($\sigma_+ = 0.02$)			HCl ($\sigma_- = 0.02$)		
m	γ_{Na^+}	$\gamma_{OH^-}^{calc.}$	m	γ_{K^+}	$\gamma_{OH^-}^{calc.}$	m	$\gamma_{H^+}^{calc.}$	γ_{Cl^-}
0.002	0.957	0.945	0.002	0.952	0.950	0.003	0.930	0.955
0.004	0.935	0.931	0.004	0.933	0.933	0.005	0.948	0.909
0.006	0.918	0.922	0.006	0.929	0.923	0.008	0.920	0.908
0.008	0.910	0.916	0.007	0.912	0.918	0.01	0.882	0.909
0.009	0.899	0.911	0.01	0.898	0.882	0.03	0.850	0.867
0.03	0.818	0.883	0.03	0.793	0.914	0.05	0.800	0.870
0.05	0.781	0.861	0.06	0.739	0.895	0.07	0.792	0.844
0.07	0.754	0.851	0.08	0.699	0.914	0.1	0.785	0.806
0.1	0.729	0.805	0.1	0.665	0.896	0.3	0.798	0.740
0.2	0.670	0.815	0.2	0.581	0.965	0.5	0.821	0.713
0.3	0.637	0.804	0.3	0.530	1.007	0.7	0.853	0.710
0.4	0.616	0.793	0.4	0.483	1.071	0.9	0.892	0.725
0.5	0.605	0.782	0.5	0.449	1.138	1.2	0.955	0.753
0.7	0.589	0.776	0.7	0.412	1.246	1.7	1.064	0.812
1.0	0.586	0.780	0.8	0.377	1.378	2.0	1.166	0.913
1.2	0.591	0.776	1.0	0.341	1.614	—	—	—
1.6	0.606	0.791	1.3	0.310	1.935	—	—	—
2.0	0.631	0.821	1.6	0.286	2.324	—	—	—
—	—	—	1.9	0.274	2.669	—	—	—
$B_x =$	206.57	−24.83	$B_x =$	−55.16	385.26	$B_x =$	199.13	173.53
$D_x =$	−0.491	0.688	$D_x =$	−0.999	1.227	$D_x =$	0.438	0.103
$(\mathrm{rms})_x =$	0.036	0.047	$(\mathrm{rms})_x =$	0.021	0.087	$(\mathrm{rms})_x =$	0.031	0.029
$B_m =$	−0.512	1.195	$B_m =$	−1.515	2.077	$B_m =$	0.909	0.314
$D_m =$	0.578	−0.451	$D_m =$	0.551	0.032	$D_m =$	0.064	0.255
$(\mathrm{rms})_m =$	0.037	0.049	$(\mathrm{rms})_m =$	0.020	0.088	$(\mathrm{rms})_m =$	0.028	0.030
$b_i =$	−0.668	1.041	$b_i =$	−1.084	1.282	$b_i =$	0.545	0.125
$d_i =$	0.157	0.182	$d_i =$	−0.289	0.831	$d_i =$	0.384	0.269
(rms) =	0.036	0.047	(rms) =	0.020	0.086	(rms) =	0.031	0.029

Note: The pooled standard deviations σ_+ and σ_- of the activity coefficients obtained from the experimental runs are listed at the top of each column. The activity coefficients of OH^- and H^+ were calculated from the mean ionic activity coefficients using Eq. 37. The parameters for Eqs. 31, 33, and 34, and the corresponding root-mean-square (rms) deviation, are given at the bottom of the table.

and

$$\Delta\beta = \beta_r - \beta_k, \tag{25}$$

where

$$\beta_r = \sum_j C_{j,r}\lambda_{j,r} \tag{26}$$

The integration of Eq. 23 is analytical and, after rearrangement, it produces the following general expression for τ_i for the case when ion i is present in both solutions k and r:

$$\tau_i = \frac{1}{z_i}\left[\frac{[a_{i,k}(C\lambda)_{i,r} - a_{i,r}(C\lambda)_{i,k}]}{[a_{i,k}\beta_r - a_{i,r}\beta_k]}\ln\frac{a_{i,r}}{a_{i,k}} + \frac{\Delta a_i}{\Delta\beta}\frac{[(C\lambda)_{i,k}\beta_r - (C\lambda)_{i,r}\beta_k]}{[a_{i,k}\beta_r - a_{i,r}\beta_k]}\ln\frac{\beta_r}{\beta_k}\right]. \tag{27}$$

As expected, the integrated form of the term τ_i is only a function of the compositions of the end solutions and it is independent of the integration path. If an ion, i, is not present in one of the two solutions, the first term inside the brackets on the righthand side of Eq. 27 vanishes. For the case of ion i, present only in the reference electrode solution r, its composition and activity are equal to zero in solution k, and Eq. 27 simplifies to

$$\tau_{i,r} = +\frac{1}{z_i}\frac{C_{i,r}\lambda_{i,r}}{\Delta\beta}\ln\frac{\beta_r}{\beta_k} \tag{28}$$

Similarly, for the case of ion i, present only in the sample solution k, Eq. 27 simplifies to

$$\tau_{i,k} = -\frac{1}{z_i}\frac{C_{i,k}\lambda_{i,k}}{\Delta\beta}\ln\frac{\beta_r}{\beta_k} \tag{29}$$

Notably, these two expressions are independent of the activity of the ions. Equations 15 and 27 suffice for the calculation of the liquid junction potential to be used in the measurement of the activity of individual ions. All that is required is to have experimentally determined values of the molar conductivity λ_i of the ions and good initial estimates of the activity of the individual ions present in both solutions forming the liquid junction. Normally, a 4-M KCl solution is used in the reference electrode. Thus, only for the measurement of the activity of the ions of chloride or potassium containing salts in aqueous solutions, the activity coefficient of the chloride or potassium ion will be required. As suggested by Harper (1985), a first esti-

Table 5. Revised Values of the Activity Coefficients of Individual Ions in Aqueous Solution of $NaNO_3$, KNO_3, Na_2SO_4, and K_2SO_4 at 298.15 K

$NaNO_3$ ($\sigma_+ = 0.03$; $\sigma_- = 0.03$)			KNO_3 ($\sigma_- = 0.05$)		Na_2SO_4 ($\sigma_- = 0.003$)			K_2SO_4 ($\sigma_- = 0.005$)	
m	γ_{Na^+}	$\gamma_{NO_3^-}$	$\gamma_{K^+}^{calc.}$	$\gamma_{NO_3^-}$	m	γ_{Na^+}	$\gamma_{SO_4^=}^{calc.}$	γ_{K^+}	$\gamma_{SO_4^=}^{calc.}$
0.002	—	—	0.949	0.949	0.01	0.841	0.452	0.845	0.429
0.004	0.948	0.929	—	—	0.02	0.794	0.416	0.792	0.395
0.005	—	—	0.914	0.930	0.03	0.751	0.379	0.749	0.354
0.008	0.905	0.910	—	—	0.05	0.719	0.292	0.721	0.262
0.01	0.887	0.895	0.868	0.896	0.10	0.658	0.167	0.662	0.140
0.02	0.866	0.857	0.834	0.876	0.20	—	—	0.596	0.121
0.1	0.779	0.722	0.711	0.721	0.30	0.560	0.116	0.559	0.096
0.2	0.748	0.633	0.703	0.637	0.40	—	—	0.531	0.077
0.3	0.724	0.567	0.671	0.580	0.50	0.515	0.076	0.505	0.065
0.4	0.721	0.551	0.620	0.548	0.60	—	—	0.485	0.057
0.6	0.714	0.465	0.567	0.482	0.69	—	—	0.476	0.049
0.8	0.714	0.466	0.537	0.429	0.80	0.472	0.051	—	—
0.9	—	—	0.569	0.372	1.00	0.452	0.039	—	—
1.0	0.712	0.426	0.519	0.368	1.25	0.440	0.034	—	—
1.2	0.714	0.402	0.456	0.369	1.50	0.426	0.029	—	—
1.4	0.707	0.387	0.412	0.352	1.75	0.416	0.025	—	—
1.6	0.716	0.365	0.417	0.325	2.00	0.414	0.022	—	—
1.8	0.741	0.367	0.415	0.302	2.50	0.415	0.018	—	—
2.0	0.718	0.309	0.393	0.277	3.00	0.426	0.015	—	—
2.5	0.723	0.271	0.368	0.239	—	—	—	—	—
3.0	0.725	0.259	0.325	0.226	—	—	—	—	—
3.5	0.719	0.257	0.272	0.222	—	—	—	—	—
B_x =	17.33	−66.99	−88.15	−153.51	B_x =	7.496	−108.14	−35.58	32.64
D_x =	0.342	−0.550	−0.201	−0.421	D_x =	−0.192	−0.135	−0.074	−0.840
$(rms)_x$ =	0.024	0.025	0.047	0.049	$(rms)_x$ =	0.009	0.022	0.004	0.029
B_m =	0.619	−0.628	−0.115	−0.533	B_m =	−0.084	0.462	0.073	−0.623
D_m =	−0.132	0.069	−0.134	−0.088	D_m =	0.027	−0.334	−0.104	0.333
$(rms)_m$ =	0.022	0.024	0.047	0.048	$(rms)_m$ =	0.007	0.022	0.004	0.029
b_i =	0.665	−0.550	0.036	−0.291	b_i =	−0.087	0.649	0.093	−0.450
d_i =	0.125	−0.179	−0.129	−0.252	d_i =	−0.004	−0.083	−0.032	−0.063
(rms) =	0.028	0.024	0.047	0.048	(rms) =	0.011	0.022	0.004	0.029

Note: The pooled standard deviations σ_+ and σ_- of the activity coefficients obtained from the experimental runs are listed at the top of each column. The activity coefficients of K^+ in KNO_3 and of SO_4^{2-} were calculated from the mean ionic activity coefficients using Eq. 37. The parameters for Eqs. 31, 33, and 34, and the corresponding root-mean-square (rms) deviation, are given at the bottom of the table.

mate of the activity coefficients of the ions can be obtained from the mean ionic activity coefficient of the electrolyte at the concentration of the solution by direct application of the Debye-Hückel equation. For the cation ($i = +$) or the anion ($i = -$) of the electrolyte in a single-electrolyte sample solution, one obtains

$$\ln \gamma_i = \frac{z_i^2}{|z_+ z_-|} \ln \gamma_\pm \tag{30}$$

For 1:1 electrolytes, Eq. 30 is equivalent to considering that the activity coefficient of the cation and of the anion are equal to the mean ionic activity coefficient of the electrolyte.

Before concluding this section, one last word of warning is in order. While Eq. 18 can be obtained directly from Eqs. 15 and 27, for numerical calculations with the Henderson equation it is not advisable to use the general form of Eq. 27 with Henderson's simplifications. Although, analytically, the first term inside the brackets on the righthand side of Eq. 27 cancels out and the second term gives exactly the form of Eq. 18, working with numerical values can produce a factor close (or equal) to zero in the denominator on the righthand side of Eq. 27.

Correlation of the Activity Coefficients of Individual Ions

The equation proposed by Khoshkbarchi and Vera (1996) has proved to correlate well the activity coefficients of the individual ions. This equation has the form

$$\ln \gamma_i = \frac{-A_x z_i^2 I_x^{1/2}}{1 + 9I_x^{1/2}} + B_{x,i} \frac{I_x^{3/2}}{1 + 9I_x^{1/2}} + D_{x,i} \ln(1 + 9I_x^{2/3}) \tag{31}$$

where, in aqueous solutions at 298.15 K, $A_x = 8.766$, $B_{x,i}$, and $D_{x,i}$ are adjustable parameters and the ionic strength, I_x, expressed in terms of mole fraction x_i of the ions in the solution, can be written as:

$$I_x = \frac{1}{2} \sum_i x_i z_i^2 \tag{32}$$

The basis for this equation has been explained elsewhere (Rabie et al., 1999). In this work, the values of B_i and D_i were recalculated for all ions for which activity coefficients had been measured and, in addition, two new correlations were tested.

Table 6. Revised Values of the Activity Coefficients of Individual Ions in Aqueous Solution of $BaCl_2$, $MgCl_2$, and $CaCl_2$ at 298.15 K

$BaCl_2$ ($\sigma_- = 0.009$)			$MgCl_2$ ($\sigma_- = 0.008$)			$CaCl_2$ ($\sigma_- = 0.009$)		
m	$\gamma^{calc}_{Ba^{+2}}$	γ_{Cl^-}	m	$\gamma^{calc}_{Mg^{+2}}$	γ_{Cl^-}	m	$\gamma^{calc}_{Ca^{+2}}$	γ_{Cl^-}
0.01	0.472	0.845	0.01	0.506	0.842	0.01	0.494	0.842
0.02	0.454	0.789	0.02	0.486	0.796	0.02	0.475	0.792
0.04	0.363	0.748	0.03	0.468	0.752	0.03	0.453	0.748
0.05	0.341	0.723	0.05	0.399	0.723	0.05	0.375	0.723
0.1	0.228	0.680	0.1	0.317	0.667	0.1	0.277	0.672
0.2	0.217	0.634	0.3	0.341	0.585	0.3	0.269	0.600
0.4	0.195	0.580	0.5	0.369	0.563	0.5	0.268	0.577
0.6	0.195	0.550	0.8	0.478	0.554	0.8	0.318	0.563
0.8	0.207	0.532	1.0	0.683	0.560	1.0	0.409	0.568
1.0	0.225	0.520	1.2	0.929	0.571	1.2	0.515	0.574
1.1	0.237	0.515	1.5	1.322	0.592	1.5	0.657	0.595
1.2	0.250	0.511	1.8	1.955	0.621	1.8	0.886	0.615
1.3	0.265	0.506	2.0	3.061	0.646	2.0	1.249	0.633
1.4	0.280	0.504	2.5	8.165	0.701	2.5	2.648	0.678
—	—	—	3.0	23.589	0.765	3.0	6.231	0.719
B_x =	176.26	1.702	B_x =	364.17	59.20	B_x =	1.568	0.059
D_x =	0.556	−0.009	D_x =	1.021	−0.178	D_x =	0.195	0.063
$(\text{rms})_x$ =	0.021	0.012	$(\text{rms})_x$ =	0.097	0.009	$(\text{rms})_x$ =	0.040	0.009
B_m =	1.468	0.156	B_m =	1.777	−0.011	B_m =	269.22	46.13
D_m =	−0.052	−0.041	D_m =	0.336	0.097	D_m =	0.857	−0.103
$(\text{rms})_m$ =	0.020	0.012	$(\text{rms})_m$ =	0.065	0.010	$(\text{rms})_m$ =	0.038	0.008
b_i =	1.336	0.160	b_i =	2.927	−0.191	b_i =	2.787	−0.019
d_i =	0.439	0.024	d_i =	0.732	0.069	d_i =	0.570	0.062
(rms) =	0.022	0.013	(rms) =	0.096	0.011	(rms) =	0.035	0.008

Note: The pooled standard deviations σ_- of the activity coefficients obtained from the experimental runs are listed at the top of each column. The activity coefficients of the cations were calculated from the mean ionic activity coefficients. The parameters for Eqs. 31, 33, and 34, and the corresponding root-mean-square (rms) deviation, are given at the bottom of the table.

Table 7. Revised Values of the Activity Coefficients of Individual Ions in Aqueous Solution of $BaBr_2$, $MgBr_2$, and $CaBr_2$ at 298.15 K

$BaBr_2$ ($\sigma_- = 0.009$)			$MgBr_2$ ($\sigma_- = 0.007$)			$CaBr_2$ ($\sigma_- = 0.009$)		
m	$\gamma^{calc}_{Ba^{+2}}$	γ_{Br^-}	m	$\gamma^{calc}_{Mg^{+2}}$	γ_{Br^-}	m	$\gamma^{calc}_{Ca^{+2}}$	γ_{Br^-}
0.01	0.481	0.849	0.01	0.513	0.836	0.01	0.525	0.830
0.02	0.481	0.781	0.02	0.485	0.798	0.02	0.511	0.781
0.03	0.425	0.766	0.03	0.459	0.761	0.03	0.475	0.752
0.05	0.352	0.737	0.05	0.405	0.723	0.05	0.428	0.705
0.1	0.261	0.682	0.10	0.328	0.678	0.10	0.360	0.638
0.3	0.276	0.584	0.30	0.386	0.607	0.30	0.441	0.531
0.5	0.284	0.550	0.50	0.480	0.583	0.50	0.534	0.489
0.8	0.317	0.545	0.80	0.739	0.580	0.80	1.185	0.457
1.0	0.363	0.545	1.00	1.258	0.588	1.00	1.228	0.449
1.2	0.413	0.554	1.25	1.845	0.615	1.25	1.752	0.448
1.5	0.527	0.564	1.50	2.852	0.654	1.50	3.065	0.448
1.8	0.689	0.579	1.75	4.546	0.705	1.75	4.443	0.452
2.0	0.851	0.586	2.00	7.672	0.757	2.00	4.905	0.459
2.3	1.093	0.610	2.50	23.90	0.863	2.50	12.13	0.470
—	—	—	3.00	100.28	0.916	3.00	64.83	0.490
B_x =	201.83	39.48	B_x =	393.74	74.75	B_x =	366.74	28.99
D_x =	1.032	−0.119	D_x =	1.597	−0.161	D_x =	1.724	−0.272
$(\text{rms})_x$ =	0.079	0.044	$(\text{rms})_x$ =	0.099	0.053	$(\text{rms})_x$ =	0.069	0.026
B_m =	1.788	0.023	B_m =	2.393	0.058	B_m =	2.620	−0.116
D_m =	0.014	0.062	D_m =	0.297	0.099	D_m =	0.153	0.057
$(\text{rms})_m$ =	0.080	0.046	$(\text{rms})_m$ =	0.106	0.043	$(\text{rms})_m$ =	0.077	0.023
b_i =	2.824	−0.029	b_i =	3.042	−0.180	b_i =	4.423	−0.286
d_i =	0.513	0.051	d_i =	0.945	0.092	d_i =	0.871	0.016
(rms) =	0.085	0.046	(rms) =	0.108	0.053	(rms) =	0.087	0.031

Note: The pooled standard deviations σ_- of the activity coefficients obtained from the experimental runs are listed at the top of each column. The activity coefficients of the cations were calculated from the mean ionic activity coefficients using Eq. 37. The parameters for Eqs. 31, 33, and 34, and the corresponding root-mean-square (rms) deviation, are given at the bottom of the table.

Because the ionic strength is expressed in the form of Eq. 5 for reducing the data, it is somewhat awkward to use a different definition of ionic strength, as in Eq. 32, for the correlation of the resulting activity coefficients. Thus, additionally, the following two correlations were tested in this work

$$\ln \gamma_i = \frac{-A_m z_i^2 I_m^{1/2}}{1 + I_m^{1/2}} + \frac{B_{m,i} I_m + D_{m,i} I_m^{3/2}}{1 + I_m^{1/2}} \tag{33}$$

and

$$\ln \gamma_i = \frac{-A_m z_i^2 I_m^{1/2}}{1 + I_m^{1/2}} + \frac{b_i I_m}{(1 + 1.5 I_m)^2} + d_i I_m \tag{34}$$

where, for aqueous solutions at 298.15 K, $A_m = 1.1762$ and $B_{m,i}$, $D_{m,i}$, b_i, and d_i are adjustable parameters. For the case of $B_{m,i} = D_{m,i}$, Eq. 33 gives the form of the Davies equation (Davies, 1938) for the mean ionic activity coefficient. For the case of $b_i = 0.06\ (1 + 10 d_i)$, Eq. 34 gives the form of the Bromley equation (Bromley, 1973) for the mean ionic activity coefficients of 1:1 electrolytes.

Results and Discussion

Before presenting numerical results, it is necessary to make one further clarification with respect to the sign convention for potentials and the experimental results reported in this work. In the potentiometric convention, the expression for the potential of the cell, formed by an ISE and a reference electrode, is obtained from Eq. 3 as

$$E_k = E_0 + S \ln a_{i,k} + E_{J,k} \tag{35}$$

On the other hand, in the pH convention, the expression for the potential is written as

$$E_k^* = E_0^* - S \ln a_{i,k} + E_{J,k}^* \tag{36}$$

Due to the fact that the way of writing the schematics of the cell is arbitrary, whether the reading of a high-resistance voltmeter is giving E_k or E_k^* only depends on how the ISE and the reference electrode are connected to the terminals of the meter. Skoog et al. (1998) warn that instrument manufacturers use different ways of connecting the electrodes to the meter, depending on the application. Since the slope S is positive for cations and negative for anions, and the activity of an ion increases with its concentration, the variation of the measured emf with concentration indicates the connection in use in a particular instrument. If the potential measured increases with the increase of concentration for cations and decreases for anions, the voltmeter is connected according to the potentiometry convention and Eq. 35 must be used. Otherwise, it is connected according to the pH-convention, and Eq. (36) must be used.

Table 8. Effect of a Change of Sign in the Junction Potential on the Activity of the Ions for Some Typical Systems

KCl

m	ΔE_J	E_{K^+}	$(\gamma_{K^+})^*$	γ_{K^+}	E_{Cl^-}	$(\gamma_{Cl^-})^*$	γ_{Cl^-}
0.1	3.56	154.2	0.75	0.75	44.6	0.78	0.78
0.5	2.04	188.3	0.62	0.61	6.8	0.69	0.70
1.0	1.40	203.0	0.53	0.53	−7.4	0.66	0.66
2.0	0.70	215.8	0.49	0.48	−26.8	0.66	0.66

NaCl

m	ΔE_J	E_{Na^+}	$(\gamma_{Na^+})^*$	γ_{Na^+}	E_{Cl^-}	$(\gamma_{Cl^-})^*$	γ_{Cl^-}
0.1	2.95	110.8	0.84	0.83	93.0	0.73	0.75
0.3	0.94	141.5	0.82	0.78	70.0	0.62	0.66
0.5	−0.29	155.1	0.80	0.75	58.5	0.59	0.64
0.7	−1.22	164.6	0.81	0.74	51.4	0.56	0.62
1.0	−2.35	176.1	0.87	0.77	44.0	0.52	0.60
1.2	−2.98	182.3	0.88	0.78	39.6	0.51	0.60
1.5	−3.80	188.5	0.89	0.77	35.5	0.49	0.58
2.0	−4.95	198.5	0.96	0.80	28.3	0.48	0.59

$CaCl_2$

m	ΔE_J	E_{Cl^-}	$(\gamma_{Cl^-})^*$	γ_{Cl^-}
0.1	1.33	74.7	0.67	0.67
0.3	−1.43	51.4	0.56	0.60
0.5	−3.13	40.1	0.52	0.58
0.8	−4.96	30.1	0.48	0.57
1.0	−5.97	24.8	0.47	0.57
1.3	−6.83	20.5	0.47	0.63

$BaCl_2$

m	ΔE_J	E_{Cl^-}	$(\gamma_{Cl^-})^*$	γ_{Cl^-}
0.1	1.54	72.6	0.67	0.68
0.4	−1.72	42.9	0.54	0.58
0.6	−3.02	34.2	0.50	0.55
0.8	−4.01	28.3	0.47	0.53
1.0	−4.86	23.5	0.45	0.52
1.2	−5.57	19.7	0.43	0.51

$MgCl_2$

m	ΔE_J	E_{Cl^-}	$(\gamma_{Cl^-})^*$	γ_{Cl^-}
0.1	1.10	75.1	0.65	0.67
0.3	1.57	56.1	0.54	0.59
0.5	−3.90	40.5	0.50	0.56
0.8	−6.01	30.3	0.46	0.55
1.0	−7.21	24.9	0.45	0.56
1.2	−8.17	20.6	0.45	0.57
1.5	−9.44	14.9	0.45	0.59

Note: $\Delta E_J = (E_J^H)^* - E_J^H$; E_J(mv) is the emf measured between the reference electrode and the ISE for ion i for a single run; the asterisk indicates the value of the activity coefficient of the ion obtained with Henderson equation using the sign in the pH convention. As discussed in Appendix B, for asymmetric electrolytes $(E_J^H)^*$ was calculated following Bates (1973).

Tables 1 to 7 present revised values for the activity coefficient for the ions calculated with the junction potential obtained from Eq. 18, Henderson's equation in the potentiometric convention. With the exception of the data for the KBr, LiBr, and LiCl systems, all emf data used in this work were the same as used in the previous publications (Khoshkbarchi and Vera, 1996a,b; Marcos-Arroyo et al., 1996; Rabie et al., 1999; Taghikhani et al., 1999, 2000; Rodil et al., 2001; Rodil and Vera, 2001a,b, 2003). The data for the KBr system, available from previous measurements, gave large deviations for the mean ionic activity coefficients, thus suggesting a malfunction of one of the electrodes. New measurements for this system reproduce well the mean ionic activity coefficient up to molality 1.0. At higher molality, the potassium ISE gave a decrease in the emf response with an increase in the concentration of the electrolyte. Different potassium electrodes were tested with similar results. Thus Table 1 reports results for both ionic activity coefficients up to molality 1 only. For higher molality,

Table 9. Comparison of Experimentally Measured Values of pH with Values Calculated from the Revised Activity Coefficients of Na^+ in NaOH, of K^+ in KOH, and of Cl^- in HCl Aqueous Solutions at 298.15 K

NaOH			KOH			HCl		
m	$pH_{Corr.}$	pH from γ_{Na^+}	m	$pH_{Corr.}$	pH from γ_{K^+}	m	$pH_{Corr.}$	pH from γ_{Cl^-}
0.002	11.27	11.23	0.002	11.31	11.22	0.003	2.54	2.63
0.004	11.59	11.54	0.004	11.59	11.53	0.005	2.32	2.32
0.006	11.77	11.72	0.006	11.68	11.70	0.008	2.13	2.16
0.008	11.90	11.84	0.007	11.83	11.82	0.01	2.04	2.05
0.009	12.00	11.93	0.01	11.98	11.94	0.03	1.62	1.59
0.03	12.46	12.42	0.03	12.44	12.47	0.05	1.41	1.40
0.05	12.65	12.64	0.06	12.72	12.70	0.07	1.26	1.24
0.07	12.77	12.80	0.08	12.83	12.86	0.1	1.09	1.10
0.1	12.89	12.90	0.1	12.91	12.97	0.3	0.56	0.62
0.2	13.09	13.21	0.2	13.17	13.28	0.5	0.33	0.38
0.3	13.20	13.38	0.3	13.32	13.47	0.7	0.19	0.22
0.4	13.27	13.49	0.4	13.43	13.62	0.9	0.08	0.09
0.5	13.32	13.59	0.5	13.52	13.75	1.2	−0.06	−0.07
0.7	13.39	13.76	0.7	13.67	13.95	1.7	−0.25	−0.25
1.0	13.46	13.89	0.8	13.73	14.05	2.0	−0.36	−0.37
1.2	13.49	13.99	1.0	13.84	14.23	—	—	—
1.6	13.54	14.12	1.3	13.97	14.43	—	—	—
1.9	13.58	14.23	1.6	14.09	14.60	—	—	—
—	—	—	1.9	14.19	14.73	—	—	—

only the activity coefficient of bromide is reported. The activity coefficient of the potassium ion can be calculated from the mean ionic activity coefficients. The original emf data for the systems LiBr and LiCl were lost, therefore, we measured again these systems here. Results shown in Table 3 are those obtained with the new emf data. All the previously and newly measured emf data are available from the Depository of Unpublished Data of Canada, listed in the references.

The pooled standard deviations of the activity coefficients measured, reported at the tops of Tables 1 to 7, indicate that the activity coefficients of the ions are measured with a precision of about ±0.03. For the cases in which the activity of only one of the ions was measured, say of ion i, the activity coefficient of its counterion j was obtained from the exact relation

$$\gamma_j^{calc.} = (\gamma_{\pm}^{(\nu_i+\nu_j)}/\gamma_i^{\nu_i})^{1/\nu_j} \tag{37}$$

where ν_i and ν_j are the stoichiometric numbers of ions i and j, respectively. The values for the corresponding mean ionic activity coefficients were obtained from the literature (Zaytsev and Aseyev, 1992). The parameters and root-mean-square deviation for the fitting of the data with Eqs. 31, 33, and 34 are presented at the bottoms of Tables 1 to 7. For the $CaCl_2$, $MgCl_2$, $CaBr_2$, and $MgBr_2$ systems, the correlations fail to reproduce the data for the activity coefficients of the cations at molality higher than 2. For the cations in these systems, data at molality higher than 2 were not included in the fitting procedure. Comparison of the values of the root-mean-square deviation for the three equations tested here shows Eq. 31 to be slightly superior.

An interesting observation is provided by the fact that previously reported values for the activity coefficients of ions (Khoshkbarchi and Vera, 1996a, b; Marcos-Arroyo et al., 1996; Rabie et al., 1999; Taghikhani et al., 1999, 2000; Rodil et al., 2001; Rodil and Vera, 2001a, b, 2003), and those reported in Tables 1 to 7, were obtained with exactly the reversed junction potential. As discussed earlier, a previous analysis of the theory (Rodil and Vera, 2003) concluded that an error in the estimation of the junction potential would be largely absorbed by the calibration of the ion-selective electrodes used in this method. Moreover, the analysis showed that the effect of an error on the junction potential would increase with an increase in the concentration of the sample solution. Thus, the comparison of results is quite illustrative, as it is hard to think of a larger error in the estimate of the junction potential than the one obtained by reversing its sign, as happened here. Since both sets of results are now available, there is no need to produce long tables with comparisons, and a short sample suffices. Table 8 gives the comparison of both sets of results for a single experimental run for some selected systems. For completeness, in

Table 10. Comparison of Observed Values of Junction Potential E_J at 298.15 K with Values Calculated by Harper's Method, Henderson Equation, Eq. 18, and by the New Analytical Form Proposed in this Work, Eqs. 15 and 27

			E_J (mV)			
Electrolyte	m_A	m_B	Observed*	Harper (1985)	Henderson Eq. 18	Eqs. 15 and 27**
HCl	0.1005	0.0035	53.9	53.8	55.5	54.3
HCl	0.0587	2.9919	−75.6	−76.5	−63.9	−76.8
HCl	0.0587	5.5843	−99.6	−99.0	−73.3	−98.4
$CaCl_2$	0.0985	0.0019	−39.6	−39.5	−35.0	−41.1
$MgCl_2$	0.0986	1.7768	39.5	38.9	28.9	41.9

Note: The two aqueous solutions A and B in contact are of the same electrolyte at two different concentrations characterized by their molality.

*Values compiled by Harper (1985).

**For HCl and $CaCl_2$ systems, the equivalent conductances and the corresponding transference numbers at 298.15 K were taken from Harned and Owen (1958) and Zaytsev and Aseyev (1992), and for $MgCl_2$ system from Phang and Stokes (1980). For high concentrations of the HCl system, this information was complemented with transference numbers data collected by Kaimakov and Varshavskaya (1966). The values of mean activity coefficients, $\gamma_{\pm}$, at 298.15 K, were taken from Harned and Owen (1958) and from Zaytsev and Aseyev (1992). The activity coefficients of individual ions were estimated using Eq. 30. To convert the different concentration scales used by different data sources, the density data were taken from the *CRC Handbook of Chemistry and Physics* (1985–1986).

Table 11. Effect of the Junction Potential on the Activity of the Ions for Some Typical Systems at 298.15 K

KCl

	E_J^H	$E_J a$	γ_{K^+}		γ_{Cl^-}	
m	Eq. 18	Eq. 15 and 27	Eq. 18	Eq. 15 and 27	Eq. 18	Eq. 15 and 27
0.003	−3.46	−3.29	0.951 [0.95]	0.951 [0.95]	0.940 [0.94]	0.940 [0.94]
0.006	−3.13	−2.98	0.907 [0.91]	0.907 [0.91]	0.921 [0.92]	0.922 [0.92]
0.01	−2.89	−2.76	0.898 [0.90]	0.898 [0.90]	0.897 [0.90]	0.897 [0.90]
0.05	−2.12	−2.05	0.822 [0.82]	0.822 [0.82]	0.850 [0.85]	0.850 [0.85]
0.1	−1.78	−1.78	0.745 [0.75]	0.746 [0.75]	0.780 [0.78]	0.775 [0.78]
0.2	−1.45	−1.49	0.690 [0.69]	0.691 [0.69]	0.746 [0.75]	0.740 [0.74]
0.3	−1.26	−1.32	0.669 [0.67]	0.671 [0.67]	0.723 [0.72]	0.719 [0.72]
0.4	−1.12	−1.20	0.638 [0.64]	0.640 [0.64]	0.705 [0.70]	0.701 [0.70]
0.5	−1.02	−1.10	0.609 [0.61]	0.611 [0.61]	0.698 [0.70]	0.694 [0.70]
0.6	−0.93	−1.01	0.585 [0.58]	0.587 [0.59]	0.695 [0.69]	0.691 [0.69]
0.7	−0.86	−0.94	0.564 [0.56]	0.566 [0.57]	0.684 [0.68]	0.681 [0.68]
0.9	−0.74	−0.83	0.545 [0.54]	0.547 [0.55]	0.672 [0.67]	0.668 [0.67]
1.0	−0.69	−0.79	0.529 [0.53]	0.530 [0.53]	0.659 [0.66]	0.655 [0.66]
1.2	−0.61	−0.70	0.512 [0.51]	0.514 [0.51]	0.652 [0.65]	0.649 [0.65]
1.4	−0.54	−0.61	0.485 [0.48]	0.486 [0.49]	0.662 [0.66]	0.658 [0.66]
1.6	−0.47	−0.54	0.448 [0.45]	0.449 [0.45]	0.661 [0.66]	0.658 [0.66]
1.8	−0.42	−0.47	0.478 [0.48]	0.479 [0.48]	0.663 [0.66]	0.661 [0.66]
2.0	−0.37	−0.42	0.477 [0.48]	0.478 [0.48]	0.663 [0.66]	0.661 [0.66]
2.5	−0.27	−0.30	0.473 [0.47]	0.474 [0.47]	0.661 [0.66]	0.659 [0.66]
3.0	−0.19	−0.20	0.480 [0.48]	0.480 [0.48]	0.668 [0.67]	0.667 [0.67]
4.0	−0.07	−0.05	0.511 [0.51]	0.510 [0.51]	0.665 [0.67]	0.664 [0.66]

NaCl

	E_J^H	$E_J a$	γ_{Na^+}		γ_{Cl^-}	
m	Eq. 18	Eq. 15 and 27	Eq. 18	Eq. 15 and 27	Eq. 18	Eq. 15 and 27
0.003	−3.52	−6.11	0.940 [0.94]	0.940 [0.94]	0.941 [0.94]	0.941 [0.94]
0.006	−3.17	−5.93	0.920 [0.92]	0.920 [0.92]	0.919 [0.92]	0.919 [0.92]
0.01	−2.91	−5.81	0.898 [0.90]	0.898 [0.90]	0.899 [0.90]	0.898 [0.90]
0.1	−1.48	−5.55	0.831 [0.83]	0.847 [0.85]	0.749 [0.75]	0.732 [0.73]
0.2	−0.88	−5.39	0.801 [0.80]	0.824 [0.82]	0.691 [0.69]	0.669 [0.67]
0.3	−0.47	−5.22	0.783 [0.78]	0.810 [0.81]	0.656 [0.66]	0.631 [0.63]
0.4	−0.14	−4.68	0.759 [0.76]	0.777 [0.78]	0.647 [0.65]	0.630 [0.63]
0.5	0.14	−4.23	0.748 [0.75]	0.760 [0.76]	0.639 [0.64]	0.627 [0.63]
0.7	0.61	−3.59	0.738 [0.74]	0.744 [0.74]	0.621 [0.62]	0.615 [0.62]
0.9	1.00	−3.31	0.766 [0.77]	0.773 [0.77]	0.595 [0.60]	0.588 [0.59]
1.0	1.17	−2.78	0.767 [0.77]	0.764 [0.76]	0.599 [0.60]	0.601 [0.60]
1.2	1.49	−1.97	0.780 [0.78]	0.762 [0.76]	0.600 [0.60]	0.614 [0.61]
1.5	1.90	−1.36	0.766 [0.77]	0.742 [0.74]	0.581 [0.58]	0.600 [0.60]
1.8	2.26	−0.15	0.793 [0.79]	0.744 [0.74]	0.588 [0.59]	0.628 [0.63]
2.0	2.47	0.53	0.803 [0.80]	0.741 [0.74]	0.589 [0.59]	0.640 [0.64]
2.5	2.95	2.00	0.851 [0.85]	0.758 [0.76]	0.587 [0.59]	0.662 [0.66]
3.0	3.37	3.83	0.920 [0.92]	0.779 [0.78]	0.603 [0.60]	0.719 [0.72]
3.5	3.73	5.62	0.961 [0.96]	0.774 [0.77]	0.622 [0.62]	0.783 [0.78]
4.0	4.05	7.16	1.063 [1.06]	0.819 [0.82]	0.637 [0.64]	0.840 [0.84]

$CaCl_2$

	E_J^H	$E_J a$	γ_{Cl^-}	
m	Eq. 18	Eq. 15 and 27	Eq. 18	Eq. 15 and 27
0.01	−2.38	−5.98	0.842 [0.84]	0.849 [0.85]
0.02	−1.91	−6.28	0.792 [0.79]	0.782 [0.78]
0.03	−1.46	−5.91	0.748 [0.75]	0.744 [0.74]
0.05	−1.12	−5.38	0.723 [0.72]	0.730 [0.73]
0.1	−0.30	−4.86	0.672 [0.67]	0.679 [0.68]
0.3	1.59	−3.32	0.600 [0.60]	0.609 [0.61]
0.5	2.77	−1.72	0.577 [0.58]	0.603 [0.60]
0.8	4.15	0.37	0.563 [0.56]	0.613 [0.61]
1.0	4.88	1.86	0.568 [0.57]	0.642 [0.64]
1.2	5.51	3.29	0.574 [0.57]	0.674 [0.67]
1.5	6.35	5.50	0.595 [0.59]	0.746 [0.75]
1.8	7.06	7.53	0.615 [0.62]	0.821 [0.82]
2.0	7.51	8.99	0.633 [0.63]	0.886 [0.89]
2.5	8.44	12.23	0.678 [0.68]	1.054 [1.05]
3.0	9.24	15.08	0.719 [0.72]	1.229 [1.23]

Table 11. Effect of the Junction Potential on the Activity of the Ions for Some Typical Systems at 298.15 K

	MgCl$_2$			
	E_J^H	$E_J{}^a$	γ_{Cl^-}	
m	Eq. 18	Eq. 15 and 27	Eq. 18	Eq. 15 and 27
0.01	−2.44	−4.85	0.842 [0.84]	0.843 [0.84]
0.02	−1.93	−4.46	0.796 [0.80]	0.795 [0.80]
0.03	−1.45	−3.99	0.752 [0.75]	0.752 [0.75]
0.05	−1.12	−3.61	0.723 [0.72]	0.723 [0.72]
0.1	−0.24	−2.62	0.667 [0.67]	0.672 [0.67]
0.3	1.74	0.14	0.585 [0.59]	0.609 [0.61]
0.5	3.07	2.29	0.563 [0.56]	0.605 [0.61]
0.8	4.55	4.97	0.554 [0.55]	0.623 [0.62]
1.0	5.34	6.76	0.560 [0.56]	0.656 [0.66]
1.2	6.05	8.31	0.571 [0.57]	0.691 [0.69]
1.5	6.96	10.47	0.592 [0.59]	0.752 [0.75]
1.8	7.78	12.58	0.621 [0.62]	0.829 [0.83]
2.0	8.23	13.91	0.646 [0.65]	0.891 [0.89]
2.4	9.28	16.47	0.701 [0.70]	1.026 [1.03]
3.0	10.23	18.41	0.765 [0.77]	1.164 [1.16]

Note: Henderson's junction potential E_J^H is calculated with Eq. 18, and the junction potential with correction for nonideality and effect of concentration in conductivity E_J is calculated with Eqs. 15 and 27. Values of the activity coefficients rounded to two significant figures are given in brackets.

[a] Values of conductivities of potassium and chloride ions and activity coefficient of chloride ions used for the solution in the reference electrode are given in the text. Value for the activity coefficient of chloride ion in the sample solutions were taken from Tables 1, 2, and 6, depending on the system. Values for conductivities of the ions in the sample solutions were taken from data reported by Braun and Weingaertner (1985) for NaCl; from data reported by Kaimakov and Varshavskaya (1966), Chambers et al. (1956), and MacInnes and Dole (1931) for KCl; and for CaCl$_2$ and MgCl$_2$, from data reported by Harned and Owen (1958) and by Kaimakov and Varshavskaya (1966).

Table 8 we have included the values of the error in the junction potential and the measured emf response for each of the ion-selective electrodes. Surprisingly, for KCl the results are hardly changed up to a molality as high as 2. The NaCl system was one for which the effect of reversing the junction potential was larger. As can be seen from Table 8, the effect of the major error in the junction potential is far from catastrophic. For both the KCl and the NaCl systems, the relative magnitudes of the activity coefficient of the cation with respect to that of the anion are maintained. The activity coefficient of potassium is smaller than the activity coefficient of chloride. For the NaCl system, the activity coefficient of the cation is larger than that of the anion. The comparison of results for the CaCl$_2$, BaCl$_2$, and MgCl$_2$ systems is also presented in Table 8. For these systems the error in the junction potential was larger, as it not only had the sign reversed but, following Bates (1973), the value was wrongly calculated using both the concentrations and the conductivities in terms of equivalents. The discussion of this erroneous interpretation of terms in the Henderson equation is presented in Appendix B. Table 8 shows that again for the CaCl$_2$ and BaCl$_2$ systems, the effect of the error in the junction potential is negligible at low concentrations and significant, but not disastrous, at higher concentrations. For MgCl$_2$ the effect of the error in the junction potential is more important. It is worth noticing that for these systems only the activity of chloride ion was measured and that the molality of chloride is twice the molality of the electrolyte reported in Table 8. Thus the difference in activity coefficient of chloride produced by the change in junction potential around molality 0.5 for the CaCl$_2$ and BaCl$_2$ systems should be compared with the values at molality unity for NaCl.

Perhaps one of the most interesting results presented in previous publications was the calculation of pH from measurements of the activity of chloride in HCl solutions or from measurements of the activity of the cation in aqueous solutions of NaOH or KOH (Rodil et al., 2001). Because these results were obtained using the wrong sign for the Henderson equation, it is of interest to see the effect of the correction of the sign on the calculation of pH. Table 9 shows the comparison of the experimentally measured value of pH (Rodil et al., 2001) with the values calculated from the revised activity coefficients reported in Table 4. The fact that the results for pH are not affected by the error in the sign of the junction potential in the range of pH from zero (or even negative values) to 13.4, confirms once again the conclusions obtained from the analysis of the theory of the measurements. Values of pH in the range just given correspond to changes of concentration in the dilute region of the acid or the base. In this range, the calibration of the chloride electrode, or of the sodium or potassium electrodes, absorbs errors in the value of the junction potential.

All the results just discussed are based on the use of the Henderson equation, in the potentiometric convention, to estimate the value of the junction potential. Before exploring the effect of using the newly derived equation for the junction potential, Eqs. 15 and 27, we present a test of its capabilities. As discussed by Harper (1985), the Henderson equation gives reliable results for the junction potential between two dilute solutions, even if both are aqueous solutions of the same electrolyte. In addition, according to Eqs. 27 to 29, only in the case where the same ion is present in both solutions, the activities of the ion in question need to be considered for the calculation of the junction potential. Thus, the most stringent test of the ability of the new equation to give realistic values of the junction potential is obtained using data of the junction potential between two solutions of the same electrolyte at two different concentrations. Fortunately, these are exactly the data from the literature compiled by Harper (1985). Table 10 presents a comparison between experimentally measured values of the junction potential, as given by Harper (1985), with those calculated by Harper's method, by the Henderson equation, and by the new equation given by Eqs. 15 and 27. In order to have a fair comparison, for the new equation we used the same *a* *priori* information used by Harper (1985), and obtained the activities of the ions from the mean ionic activity coefficients using Eq. 30. Notably, the new equation for the junction potential presented in this work represents a major improvement over the Henderson equation, as its results are comparable with those obtained with the much more complex graphical and numerical method of Harper (1985). It should be noticed that in this comparison there are several independent experimental measurements involved: the junction potential, the mean ionic activity coefficient of the electrolyte, and the molar conductivities of each ion.

Clearly, the new equation proposed here to calculate the junction potential represents a definite improvement over the Henderson equation. Thus, it is of interest to determine to what extent its use would change the values of the activity coefficients reported in Tables 1 to 7. The main problem, however, is the lack of experimental values of the ionic conductivities in concentrated aqueous solutions. In this work we test the effect caused by the new equation for four aqueous solutions for which the necessary data are available: KCl, NaCl, $CaCl_2$, and $MgCl_2$. Table 11 presents a comparison of the values of the junction potentials calculated with the Henderson equation and with the new equation for these systems. The aim of these calculations was to obtain the best possible estimate for the junction potential with the use of Eqs. 15 and 27. For the 4-M, or equivalently 4.6-m, KCl solution at 298.15 K, employed in the reference electrode, the calculations were made using $\lambda_{K^+} = 45.42$ [S cm^2 mol^{-1}], $\lambda_{Cl^-} = 47.12$ [S cm^2 mol^{-1}], and $\gamma_{Cl^-} = 0.64$. The values of conductivity were obtained from conductivity data for KCl reported by Chambers et al. (1956) and transference numbers for the ions reported by MacInnes and Dole (1931). The value of the activity coefficient of the chloride ion was obtained by extrapolation of the data for KCl presented in Table 1. For the sample solutions, the sources for the values of conductivity used are indicated in the footnote to Table 11. The activity coefficients of the chloride ion in the sample solutions were obtained from Tables 1, 2, or 6, depending on the system. In addition to the junction potentials, Table 11 includes the values of the activity coefficients of the individual ions obtained with these junction potentials using the same emf values measured for the corresponding ISE. To facilitate the comparison, in Table 11 we have included in brackets the values of the activity coefficients rounded to two significant places. Most notably, the activity coefficients of the ions in the KCl system hardly change with a change in the junction potential. This is the same conclusion that was obtained from the results presented in Table 8. Since the KCl aqueous solution is the one used in the reference electrode for all other sample systems, this is a very fortunate finding. The NaCl system was one of the most sensitive to the change of sign of Henderson's junction potential, and it was highlighted in Table 8. From Table 11 one can conclude that up to a molality of 1.5 the results are not much changed by the use of the improved junction potential. Similarly for the $CaCl_2$ and $MgCl_2$ systems, up to a molality of 1.6 of the ion chloride (molality of 0.8 of the electrolyte), the differences of results obtained with both potentials are within acceptable limits. This is another confirmation of the conclusions obtained in a previous analysis of the theory of measurements (Rodil and Vera, 2003): the effect of an error in the junction potential is largely compensated by the calibration of the electrode and it only shows in the concentrated region of the sample solution.

Conclusions

The correction of an error in previous publications has provided a valuable opportunity to test the validity of the conclusions obtained in a recent analysis of the theory of measurements of the activities of individual ions (Rodil and Vera, 2003). Values of the activity coefficient of the ions measured with ion-selective electrodes are not significantly affected in the dilute region by reasonable errors in the estimation of the junction potential. Large errors in the estimation of the junction potential only affect the values of the activity of ions at molality higher than 1.5 molal. Most aqueous solutions of practical interest in biotechnology, biological studies, or environmental work hardly ever have to deal with ions at concentrations higher than 1.5 molal. A detailed consideration of the derivation of the Henderson equation for the calculation of the junction potential has shown that the terms of this equation were erroneously interpreted in the literature (Bates, 1965, 1973). A new equation for the calculation of the junction potential, including the effect of nonideality of the solutions and the effect of concentration on the conductivities, has been developed and tested. This analytical equation reproduces well experimental values of the junction potential between two solutions of the same electrolyte at different concentrations, which is the most demanding case. For the junction of two electrolyte solutions without a common ion, it takes the form of the Henderson equation, but including the correction for the concentration dependence of the conductivity. For the measurement of the activity of ions, as the reference electrode contains a 4-M aqueous solution of KCl, only sample solutions containing chloride or potassium ions require a knowledge of the activity of the ions to calculate the junction potential. A good estimate of the activity of ions can be obtained using the Henderson equation for the junction potential. Future work to evaluate the activity of ions requires either direct measurements of the junction potentials of interest or information on the conductivity of salts and the transport numbers of the ions in concentrated solutions.

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Notation

A_m, A_x = Debye-Hückel constant; the subscript m or x indicates whether it is on a molality or a mole fraction base, Eqs. 31, 33, 34
a_i = activity of ionic species i
B, D = adjustable parameters; the subscript m or x indicates whether it is on molality or mole fraction base
b, d = adjustable parameters
C_i = concentration of species i, moles per liter
$\tilde{C}_i$ = concentration of species i, in equivalents per liter
$\mathcal{D}_i$ = diffusivity
E = Potential
F = Faraday constant

I_m, I_x = Ionic strength. The subscript m or x indicates whether it is on molality or mole fraction base. Eqs. 5 or 32 respectively
ISE = ion-selective electrode
J_i = molar flux of ions i across the junction
ℓ = thickness of the liquid junction
k = refers to the sample solution at dimensionless molality m_k
m = dimensionless molality
R = universal gas constant
r = refers to the reference electrode, or solution in the reference electrode
rms = root-mean-square deviation
S = slope of the electrode potential vs. the logarithm of the ion activity
s_i = drift speed of ion i
T = absolute temperature
t_i = transference number of species i
u_i = electrical mobility of ion i
x = mole fraction
Y_1, Y_2 = functions defined by Eqs. B7 and B8
z_i = charge of ion i

Greek letters

α = dummy integration variable
β_k, β_r = functions defined by Eqs. 24 and 26, respectively
γ = activity coefficient
Δ = difference
$\Delta\epsilon$ = error in junction potential estimation
λ_i = molar ionic conductance of species i
$\tilde{\lambda}_i$ = equivalent ionic conductivity of species i
μ_i = electrochemical potential of species i
μ_i^0 = standard state chemical potential of species i
ν_i = stoichiometric number of ion i per mol of electrolyte
σ = pooled standard deviation of the data
τ_i = contribution of species i to the junction potential
ϕ = difference between the measured potential and the junction potential, Eq. 3
Ψ = electric potential

Subscripts and superscripts

$Corr$ = value of the measured pH corrected following instrument instructions
ISE = value for the ion-selective electrode
ref = value for the reference electrode
i, j = ionic species
J = junction
k = refers to sample solution at dimensionless molality m_k
r = refers to the KCl solution in the reference electrode
$+$ = cation
$-$ = anion
$\pm$ = mean ionic
0 = constant term in the equation for the potential, Eqs. 2 and 3
∞ = value for the most diluted sample in the series of measurements
$calc$ = calculated value
G = Güntelberg contribution to the activity coefficient of an ion, Eq. 4
H = refers to Henderson equation
$*$ = value of the function in the pH-convention
T = true value
∞ = property at infinite dilution

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Appendix A: A Complete Derivation of the Equation to Calculate the Junction Potential

The equation to calculate the junction potential between two solutions of different concentrations is obtained considering that no net electric current is transported by the ions through the junction. Since the current would be carried by ions in solution, we consider first the molar flux of ions i, J_i, through a unit surface area. This flux is proportional to the molar concentration of ions i, C_i, and to the negative of the gradient of the electrochemical potential of species i, μ_i, over the path ℓ, that is, the thermodynamic force acting over the ions i. Thus, we write

$$J_i = \frac{\mathcal{D}_i}{RT} C_i \left(- \frac{\partial \mu_i}{\partial \ell} \right) \tag{A1}$$

In Eq. A1, $\mathcal{D}_i$ is the diffusion coefficient of i, R is the gas constant, and T is the absolute temperature. The electrochemical potential of species i has the form

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F \Psi \tag{A2}$$

where a_i and z_i are the activity and the charge of ion i, respectively, F is the Faraday constant, and Ψ is the electric potential of the liquid phase. Thus the gradient of the electrochemical potential takes the form

$$\frac{\partial \mu_i}{\partial \ell} = RT \frac{\partial \ln a_i}{\partial \ell} + z_i F \frac{\partial \Psi}{\partial \ell} \tag{A3}$$

To continue, it is necessary to express the diffusion coefficient in terms of the molar ionic conductivity of ions moving under the effect of an electric potential only. For this, it is useful to define the drift speed, s_i, attained by ion i when the drag forces balance the forces acting over the ion. This drift speed is proportional to the gradient of the applied electrical field, thus

$$s_i = \frac{|J_i|}{C_i} = u_i \left| \frac{\partial \Psi}{\partial \ell} \right| \tag{A4}$$

The proportionality constant u_i, known as the electrical mobility of ion i, represents the limiting steady-state velocity attained by ion i under a unit of potential gradient. From Eqs. A1 and A3, for an ion moving under the effect of an electric field only, in the absence of a concentration gradient in the solution, the drift speed takes the form

$$s_i = \frac{|J_i|}{C_i} = \frac{\mathcal{D}_i}{RT} |z_i| F \left| \frac{\partial \Psi}{\partial \ell} \right| \tag{A5}$$

Hence, combining Eqs. A4 and A5 gives

$$u_i = \frac{\mathcal{D}_i}{RT} |z_i| F \tag{A6}$$

Equation A6 is known as the Einstein relation (Atkins, 1986). In electrochemistry, the molar ionic conductivity, λ_i, is defined as the electric current transported per mole of species i, per unit electrical potential gradient, through a unit cross section. Thus

$$\lambda_i = |z_i| F u_i \tag{A7}$$

Combining Eqs. A6 and A7 gives

$$\frac{\mathcal{D}_i}{RT} = \frac{\lambda_i}{|z_i|^2 F^2} \tag{A8}$$

Equation A8 is known as the Nernst-Einstein relation (Atkins, 1986). Combining Eqs. A1, A3, and A8, after rearrangement, gives an expression for the current density ($z_i F J_i$) transported by ions of type i

$$z_i F J_i = - \left[\frac{RT}{F} \frac{C_i \lambda_i}{z_i} \frac{\partial \ln a_i}{\partial \ell} + C_i \lambda_i \frac{\partial \Psi}{\partial \ell} \right] \tag{A9}$$

For the calculation of the junction potential between two solutions of different composition, the sum of the current densities transported by all ions is set to zero. Thus, setting to zero the sum over all ions on the righthand side of Eq. A9 gives

$$\frac{\partial \Psi}{\partial \ell} = - \frac{RT}{F} \sum_i \frac{1}{z_i} \frac{C_i \lambda_i}{\sum_j C_j \lambda_j} \frac{\partial \ln a_i}{\partial \ell} \tag{A10}$$

Finally, integrating Eq. A10 over the thickness, ℓ, of the liquid junction gives

$$E_J = - \frac{RT}{F} \sum_i \int \frac{t_i}{z_i} d \ln a_i \tag{A11}$$

where, to follow the conventional nomenclature, we have used the symbol E_J to indicate the potential difference $\Delta\Psi$ across the junction and introduced the symbol t_i for the transference number of ion i, defined as

$$t_i = \frac{C_i \lambda_i}{\sum_j C_j \lambda_j} = \frac{\tilde{C}_i \tilde{\lambda}_i}{\sum_j \tilde{C}_j \tilde{\lambda}_j} = \frac{|z_i| C_i \tilde{\lambda}_i}{\sum_j |z_j| C_j \tilde{\lambda}_j} \tag{A12}$$

It is interesting to note that the transference number, t_i, has naturally appeared in Eq. A10. This term, which has caused some confusion in the literature, can be written in alternative ways. In Eq. A12, the equivalent conductivity $\tilde{\lambda}_i$ and the concentration of ions i, $\tilde{C}_i$, in equivalent per litter, are related to the corresponding molar quantities, λ_i and C_i, by

$$\lambda_i = |z_i|\tilde{\lambda}_i \tag{A13}$$

and

$$C_i = \frac{\tilde{C}_i}{|z_i|} \tag{A14}$$

The erroneous interpretation of these terms that can be found in the literature (Bates, 1965, 1973) is discussed in Appendix B.

The next step is to obtain an integrated form of the equation for the junction potential. For the purposes of this work, we follow the potentiometric convention. In this convention the ISE electrode is written at the right and the reference electrode at the left. In agreement with the Stockholm convention, the junction potential in this case corresponds to the potential of the sample solution (k) minus the potential of the solution at the reference electrode (r). Thus, the lower limit of the integral in Eq. A11 is the state of the ion at the reference solution and the upper limit is the state of the ion in the sample solution. Hence, Eq. A11 takes the form

$$E_{J,k} = \Psi_k - \Psi_r = -\frac{RT}{F}\sum_i \int_r^k \frac{1}{z_i}\frac{C_i\lambda_i}{\sum_j C_j\lambda_j}\frac{da_i}{a_i} \tag{A15}$$

For simplicity rewrite Eq. A15 as

$$E_{J,k} = +\frac{RT}{F}\sum_i \tau_i \tag{A16}$$

with τ_i defined as

$$\tau_i = \frac{1}{z_i}\int_k^r \frac{C_i\lambda_i}{\sum_j C_j\lambda_j}\frac{da_i}{a_i} \tag{A17}$$

The key problem in determining the activity of ions is the evaluation of τ_i. Appendix B gives the details of the derivation of the Henderson equation and discusses some errors in the interpretation of terms found in the literature. The derivation of a new equation to calculate the junction potential is presented in the text.

Appendix B: Henderson's Approximation for the Junction Potential

The Henderson approximation is the best-known equation for the junction potential. Thus, we now discuss its relation with the equations presented in Appendix A. In order to avoid the problem of the indefiniteness of terms in the case where ion i is not present at one of the two solutions, Henderson introduced the auxiliary variable, α, and considered a linear variation of the concentration of the ions with α across the junction

$$C_i = C_{i,k} + \alpha\Delta C_i, \tag{B1}$$

with

$$\Delta C_i = C_{i,r} - C_{i,k}. \tag{B2}$$

In addition, Henderson introduced two stringent simplifications. He assumed that the activity of ion i was equal to its molar concentration and that the molar conductivity was independent of concentration and equal to the molar conductivity of the ion at infinite dilution, λ_i^∞. Thus, setting $a_i = C_i$ and also $\lambda_{i,k} = \lambda_{i,r} = \lambda_i^\infty$ in Eq. A17 gives

$$\tau_i^H = \frac{\lambda_i^\infty \Delta C_i}{z_i\left[\sum_i C_{i,r}\lambda_i^\infty - \sum_i C_{i,k}\lambda_i^\infty\right]}\ln\frac{\sum_i C_{i,r}\lambda_i^\infty}{\sum_i C_{i,k}\lambda_i^\infty} \tag{B3}$$

Thus, for the schematics of the electrochemical cell written in the potentiometric convention, as considered in Appendix A, we write

$$E_{J,k}^H = \frac{RT}{F}\left[\frac{\sum_i \frac{1}{z_i}C_{i,r}\lambda_i^\infty - \sum_i \frac{1}{z_i}C_{i,k}\lambda_i^\infty}{\sum_i C_{i,r}\lambda_i^\infty - \sum_i C_{i,k}\lambda_i^\infty}\right]\ln\frac{\sum_i C_{i,r}\lambda_i^\infty}{\sum_i C_{i,k}\lambda_i^\infty} \tag{B4}$$

The usual form for the Henderson equation found in the literature (Bates, 1965, 1973), is written for the "pH convention" that considers the ISE to be written at the left and the reference electrode at the right. In addition, it is normally written in terms of the equivalent limiting conductivity, $\tilde{\lambda}_i$, of the ion instead of the molar limiting activity conductivity, λ_i. These two limiting conductivities are related by Eq. A13. Hence, the form of the Henderson equation found in the literature is as follows

$$\begin{aligned}(E_{J,k}^H)^* &= -E_{J,k}^H \\ &= \frac{RT}{F}\left[\frac{\sum_i \frac{|z_i|}{z_i}C_{i,k}\tilde{\lambda}_i^\infty - \sum_i \frac{|z_i|}{z_i}C_{i,r}\tilde{\lambda}_i^\infty}{\sum_i |z_i|C_{i,k}\tilde{\lambda}_i^\infty - \sum_i |z_i|C_{i,r}\tilde{\lambda}_i^\infty}\right]\ln\frac{\sum_i |z_i|C_{i,k}\tilde{\lambda}_i^\infty}{\sum_i |z_i|C_{i,r}\tilde{\lambda}_i^\infty}\end{aligned} \tag{B5}$$

The ratio of the absolute value of the charge over the value of the charge of ion i, appearing in the numerator inside the brackets of the righthand side of Eq. B5, is $+1$ for cations and -1 for anions. Hence, this term is usually not explicitly written, and the sum over all ions is written as the sum over the cations minus the sum over the anions

$$(E^H_{J,k})^* = \frac{RT}{F} \frac{[\sum C_+\tilde{\lambda}^\infty_+ - \sum C_-\tilde{\lambda}^\infty_-]_k - Y_1}{[\sum C_+\tilde{\lambda}^\infty_+|z_+| + \sum C_-\tilde{\lambda}^\infty_-|z_-|]_k - Y_2} \times \ln \frac{[\sum C_+\tilde{\lambda}^\infty_+|z_+| + \sum C_-\tilde{\lambda}^\infty_-|z_-|]_k}{Y_2} \tag{B6}$$

In Eq. B6, the symbols Y_1 and Y_2 represent numerical values that depend on the solution r used in the reference electrode. In Henderson's approximation, these constants are obtained as

$$Y_1 = C_{+,r}\tilde{\lambda}^\infty_{+,r} - C_{-,r}\tilde{\lambda}^\infty_{-,r} \tag{B7}$$

and

$$Y_2 = C_{+,r}\tilde{\lambda}^\infty_{+,r}|z_+|_r + C_{-,r}\tilde{\lambda}^\infty_{-,r}|z_-|_r \tag{B8}$$

At 298.15 K, for a 4-M KCl reference electrode solution, $Y_1 = -11.6$ and $Y_2 = 623$. At this temperature, the value of the ratio (RT/F) is 25.693 (mV). It is more important, however, to note that the terms in each sum contain the product of the molar concentration times the equivalent limiting conductivity. Standard references in the literature are in error here. In some places it is indicated that in Eq. B6 both the concentration and the conductivity are in molar units (Bates, 1965), while in others it is stated that both the concentration and the conductivity are in terms of equivalents (Bates, 1973). Both of these statements are wrong. Although these errors do not affect the value of the junction potential for 1:1 electrolytes, they give incorrect results for 1:2 and 2:1 electrolytes. Values tabulated in the literature for these latter cases are in error.

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