Re-Evaluation of the Thermodynamic Activity Quantities in Aqueous Sodium and Potassium Chloride Solutions at 25 °C[†]

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The Hückel equation is used to correlate the experimental activities of dilute NaCl and KCl solutions up to a molality of about 1.0 mol·kg^{-1}. The two parameters of this equation are dependent on the electrolyte and are B [which is simply related to the ion-size parameter (a^*) in the Debye−Hückel equation] and b_1 (which is the coefficient of the linear term in molality and related to hydration numbers of the ions of the electrolyte). In more concentrated solutions up the saturation for both electrolytes, an extended Hückel equation was used, and it contains, additionally, a quadratic term with respect to the molality with parameter b_2. The values of parameters B and b_1 for dilute KCl solutions were determined from the cell potential differences measured by Hornibrook et al. on concentration cells with transference (*J. Am. Chem. Soc.* **1942**, *64*, 513−516). With these values of KCl, the corresponding parameter values for NaCl solutions were determined from the isopiestic data of Robinson for NaCl and KCl solutions (*Trans. R. Soc., N. Z.,* **1945**, *75*, 203−217). Only the data points for NaCl molalities less than 1.4 mol·kg^{-1} were included in this determination. The resulting parameter values were successfully tested with all reliable cell potential and isopiestic data in the literature for dilute NaCl and KCl solutions. For more concentrated solutions, new values of parameters b_1 and b_2 were determined for the extended Hückel equations of NaCl and KCl, but the same values of parameter B were used as for dilute solutions. For these more concentrated NaCl solutions, the values of parameters b_1 and b_2 were determined from the vapor pressure data of Olynyk and Gordon (*J. Am. Chem. Soc.* **1943**, *65*, 224−226), which cover the molality range (2.3 to 6.1) mol·kg^{-1}. With these values for NaCl, the corresponding parameter values for more concentrated KCl solutions were determined from the isopiestic data of Robinson for this pair of electrolytes (see the citation above), where all experimental points were included in the determination. The resulting extended Hückel equations were thoroughly tested with all reliable experimental data presented in the literature on the basis of electrochemical, isopiestic, and direct vapor pressure measurements. Most of these data can be reproduced within experimental error by means of the extended Hückel equations up to the saturated solutions. Reliable activity and osmotic coefficients of NaCl and KCl can, therefore, be calculated by using the Hückel and extended Hückel equations determined in this study. The values obtained by these equations are probably the most accurate values available, and they have been tabulated at rounded molalities. The activity and osmotic coefficients obtained from the new equations were compared with the values suggested by Robinson (see citation above), with those calculated by using the Pitzer equations of Pitzer and Mayorga (*J. Phys. Chem.* **1973**, *77*, 2300−2308), with those calculated by using the extended Hückel equations of Hamer and Wu (*J. Phys. Chem. Ref. Data* **1972**, *1*, 1047−1099), and with those calculated by Hückel equations of Partanen and Minkkinen (*Acta Chem. Scand.* **1993**, *47*, 768−776).

Introduction

The activities of sodium and potassium chlorides in aqueous solutions at 25 °C have for a long time been the best known reference values in thermodynamics of electrolyte solutions. In 1945, Robinson[1] presented tables for the activity and osmotic coefficients in NaCl and KCl solutions from a molality of 0.1 mol·kg^{-1} to the value of saturated solution in both cases. The values in these tables were later widely accepted and used, e.g., in the analysis of isopiestic results. Both NaCl and KCl are often used as reference electrolytes in isopiestic determinations.[2] The activity and osmotic coefficients of Robinson's tables[1] are recommended in the well-known book of Robinson and Stokes,[3] and these values were often used in the determination of the activity tables of this book for other electrolytes from isopiestic data. The importance of these tabulated activities is also reflected by the fact that Pitzer and Mayorga mainly used these values when they determined the parameters of the Pitzer equation[4] for various electrolytes in their valuable compilation[5] on thermodynamics of single electrolytes.

In the present study, it is shown that reliable activity values for NaCl and KCl solutions at 25 °C can be obtained with the simple Hückel equation up to a molality of about 1.0 mol·kg^{-1}. In previous studies (see, e.g., refs 6 to 10), the equations of this type have proved to be very useful in the thermodynamic treatment of weak acid solutions (especially those of pH buffer substances[8,10]). Although NaCl and KCl solutions have been

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thermodynamically investigated in many solution chemistry studies (however, the results do not agree well in all cases with each other, see, for example, ref 11), the new values for activity and osmotic coefficients are very important in that they have been tested thoroughly with all relevant experimental data. Additionally, they are fully transparent and traceable because all calculation methods and data sets used in the parameter estimations and tests are presented here in detail. The form of the Hückel equation used in this investigation (see below) contains two parameters dependent on the electrolyte: B [that is related to the ion-size parameter (a^*) in the Debye−Hückel equation] and b_1 (the coefficient of the linear term with respect to the molality, and it is closely related to hydration numbers of the ions). The values of these parameters were obtained in the following way:

1. The values of B and b_1 for KCl in dilute solutions were determined from the cell potential difference (cpd) data measured by Hornibrook et al.[12] on concentration cells with transference. These data extend, however, only up to a molality of 0.1 $\text{mol}\cdot\text{kg}^{-1}$. Therefore, it was checked using the potassium amalgam cell data of Harned and Cook[13] and Giordano et al.[14] that the parameter values apply also well to less dilute solutions.

2. With these new Hückel parameters for KCl, the corresponding parameter values for NaCl solutions were determined from the isopiestic data measured by Robinson[1] for NaCl and KCl solutions, but only the points where the NaCl molality is less than 1.36 $\text{mol}\cdot\text{kg}^{-1}$ (i.e., 52 points) were included in this determination.

3. The resulting parameter values were tested with the data used in the parameter estimation coupled with the isopiestic data of Gordon,[15] Robinson and Sinclair,[16] Janis and Ferguson,[17] and Scatchard et al.[18] for NaCl and KCl solutions up to salt molalities of about 2 $\text{mol}\cdot\text{kg}^{-1}$ (in Gordon's set,[15] however, the strongest salt molality is approximately only 0.1 $\text{mol}\cdot\text{kg}^{-1}$). The parameter values were also tested with the cpd data measured by Janz and Gordon[19] (for NaCl solutions), Brown and MacInnes[20] (NaCl), and Shedlovsky and MacInnes[21] (KCl) on concentration cells with transference and with the measurements of Harned and Nims[22] (NaCl) on amalgam cells.

Additionally, in the present study, it is shown that reliable fitting activity values for NaCl and KCl solutions at 25 °C can be obtained up to a molality of the saturated solution of both electrolytes (i.e., up to 4.803 $\text{mol}\cdot\text{kg}^{-1}$ for KCl solutions and up to 6.144 $\text{mol}\cdot\text{kg}^{-1}$ for NaCl solutions) by extending the Hückel equation with a quadratic term with respect to the molality m. The coefficient multiplying the quantity m^2 in this term is b_2. The extended Hückel equation obtained here for NaCl or KCl solutions does not apply to dilute electrolyte solutions as well as the suggested simpler two-parameter Hückel equation. For most practical applications, however, the former equation is still usable, without change, for these dilute solutions, too. Only in certain applications where the highest precision is needed [such as, for example, in the thermodynamic treatment of weak acids in NaCl and KCl solutions needed for the theoretic acidity (pH) considerations], the latter equation seems to be preferable. The values of the parameters in this extended Hückel equation for NaCl or KCl were obtained in the following way:

1. The same new values were used for parameter B of NaCl and KCl as those determined from dilute solutions.

2. New values of b_1 and b_2 for NaCl were determined from the vapor pressure data of Olynyk and Gordon.[23] These data consist of 15 points at 25 °C and cover the molality range (2.3 to 6.1) $\text{mol}\cdot\text{kg}^{-1}$.

3. With the new values of b_1 and b_2 for concentrated NaCl solutions, the corresponding parameter values for concentrated KCl solutions were determined from the isopiestic data of Robinson[1] for this pair of electrolytes, and all 79 experimental points were included in the determination.

4. The resulting parameter values were tested with both data used in the parameter estimation and the following additional data: isopiestic data of Robinson and Sinclair,[16] Janis and Ferguson,[17] Scatchard et al.,[18] and Kirgintsev and Luk'yanov[24] for NaCl and KCl solutions; vapor pressure data of Negus (NaCl, taken from ref 1), Gibson and Adams (NaCl, taken from ref 1), Pearce and Nelson[25] (NaCl and KCl), Pepela and Dunlop[26] (NaCl), Gibbard et al.[27] (NaCl), Lovelace et al.[28] (KCl, measured at 20 °C), and Brown and MacGregor Delaney[29] (KCl); and amalgam cell data of Harned and Nims[22] (NaCl) and Harned and Cook[13] (KCl).

All tests of this study were performed on the raw experimental results of appropriate measurements to test whether these could be predicted with the Hückel equations. This method has the advantage that the prediction error can be compared to the experimental error. It is shown below that the Hückel equations are very reliable. In most cases, the measured results can be reproduced within experimental error. The activity coefficients of the electrolyte and the osmotic coefficients and the vapor pressures of water were calculated using the new Hückel equations at rounded molalities of NaCl and KCl, and these values are tabulated as recommended values. These activity and osmotic coefficients were compared to those of the previous investigations (some of which, in addition to Robinson's values,[1] have achieved a wide acceptance). Activity coefficient errors in this comparison are presented as the cell-potential difference errors for galvanic cells without a liquid junction (in the same way as in refs 30–32), and the osmotic coefficient errors are presented as vapor pressure errors.

Theory

In concentrated solutions, the following extended Hückel equation was used in this study for the activity coefficients of NaCl and KCl in aqueous solutions

$$\ln \gamma = -\frac{\alpha\sqrt{m}}{1 + B\sqrt{m}} + b_1(m/m^{\circ}) + b_2(m/m^{\circ})^2 \qquad (1)$$

In this equation, m is the molality; γ is the mean activity coefficient on the molality scale; m° is 1 $\text{mol}\cdot\text{kg}^{-1}$; and α is the Debye−Hückel parameter at 25 °C with the value of 1.1744 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ (see Archer and Wang[33]). The electrolyte parameters in this equation are B, b_1, and b_2. From eq 1, the following equation can be derived for the osmotic coefficient of water (ϕ) in NaCl and KCl solutions by using the Gibbs−Duhem equation

$$\phi = 1 - \frac{\alpha}{B^3 m}\left[(1 + B\sqrt{m}) - 2\ln(1 + B\sqrt{m}) - \frac{1}{1 + B\sqrt{m}}\right] + \frac{1}{2}b_1(m/m^{\circ}) + \frac{2}{3}b_2(m/m^{\circ})^2 \qquad (2)$$

The osmotic coefficient is related to the activity of the solvent (water in this case, a_1) in pure solutions of a uniunivalent electrolyte by the following thermodynamic identity

$$\ln a_1 = -2mM_1\phi \qquad (3)$$

where M_1 is the molar mass of water ($= 0.018015\ \text{kg}\cdot\text{mol}^{-1}$) and the activity of water is related to the vapor pressure of water over the solution (p_1) and to the vapor pressure of pure solvent at the temperature under consideration (p_1^*) by the equation

$$a_1 = \frac{p_1}{p_1^*} \qquad (4)$$

For water at 25 °C, $p_1^* = 3.1686$ kPa (i.e., 23.766 mmHg, see Kell[34]).

In previous studies[11,35] for dilute electrolyte solutions, simplified versions of eqs 1 and 2 (obtained by setting $b_2 = 0$) were used with parameters a^* (related to the ion sizes) and h (related to hydration numbers of ions). These parameters are associated with those in these equations by $B = \beta_{\mathrm{DH}} a^*$ and $b_1 = 2M_1(h - 1)\,m^{\mathrm{o}}$, respectively, where β_{DH} has the value based on the theory of Debye and Hückel [at 25 °C, it is 3.2849 $(\mathrm{mol \cdot kg^{-1}})^{-1/2} \cdot \mathrm{nm}^{-1}$ (see ref 33)]. The equations with a^* and h for activity and osmotic coefficients have been presented by Pan,[36] and they are called the Hückel equations. In ref 35, the parameter values of $a^*(\mathrm{NaCl}) = 0.43$ nm, $h(\mathrm{NaCl}) = 3.01$, $a^*(\mathrm{KCl}) = 0.39$ nm, and $h(\mathrm{KCl}) = 1.42$ were found to apply very well to the thermodynamic properties of NaCl and KCl solutions at 25 °C up to a molality of 2.0 $\mathrm{mol \cdot kg^{-1}}$. The Hückel equations used in the present study (as also in refs 30−32) for dilute solutions were simply obtained from eqs 1 and 2 by setting $b_2 = 0$ and thus have only two electrolyte parameters of B and b_1.

Hamer and Wu[37] suggested the following extended Hückel equations for the activity and osmotic coefficients of NaCl and KCl solutions at 25 °C

$$\log(\gamma) = -\frac{A\sqrt{m}}{1 + B^*\sqrt{m}} + \beta(m/m^{\mathrm{o}}) + C(m/m^{\mathrm{o}})^2 + D(m/m^{\mathrm{o}})^3 \qquad (5)$$

$$\phi = 1 - \ln(10)\left\{\frac{A}{(B^*)^3 m}\left[(1 + B^*\sqrt{m}) - 2\ln(1 + B^*\sqrt{m}) - \frac{1}{1 + B^*\sqrt{m}}\right] - \frac{1}{2}\beta(m/m^{\mathrm{o}}) - \frac{2}{3}C(m/m^{\mathrm{o}})^2 - \frac{3}{4}D(m/m^{\mathrm{o}})^3\right\} \qquad (6)$$

where the Debye−Hückel parameter A has a value of 0.5108 $(\mathrm{mol \cdot kg^{-1}})^{-1/2}$ [$= \alpha/\ln(10)$] and the parameters dependent on the electrolyte are: $B^*(\mathrm{NaCl}) = 1.4495\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $\beta(\mathrm{NaCl}) = 0.020442$, $C(\mathrm{NaCl}) = 5.7927 \cdot 10^{-3}$, $D(\mathrm{NaCl}) = -288.60 \cdot 10^{-6}$, $B^*(\mathrm{KCl}) = 1.295\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $\beta(\mathrm{KCl}) = 0.070 \cdot 10^{-3}$, $C(\mathrm{KCl}) = 3.599 \cdot 10^{-3}$, and $D(\mathrm{KCl}) = -195.40 \cdot 10^{-6}$.

For activity coefficients of a uniunivalent electrolyte, the Pitzer equation[5,38] has the form

$$\ln\gamma = f^{\gamma} + B^{\gamma}(m/m^{\mathrm{o}}) + (3/2)C^{\phi}(m/m^{\mathrm{o}})^2 \qquad (7)$$

where

$$f^{\gamma} = -\frac{\alpha}{3}\left[\frac{\sqrt{m}}{1 + 1.2\sqrt{m/m^{\mathrm{o}}}} + \frac{2\sqrt{m^{\mathrm{o}}}}{1.2}\ln\left(1 + 1.2\sqrt{m/m^{\mathrm{o}}}\right)\right] \qquad (8)$$

$$B^{\gamma} = 2\beta^0 + \frac{\beta^1 m^{\mathrm{o}}}{2m}\left[1 - e^{-2\sqrt{m/m^{\mathrm{o}}}}\left(1 + 2\sqrt{m/m^{\mathrm{o}}} - 2\frac{m}{m^{\mathrm{o}}}\right)\right] \qquad (9)$$

In eqs 7 and 9, β^0, β^1, and C^{ϕ} are the parameters dependent on the electrolyte. Pitzer and Mayorga[5] have presented the following values for these parameters for NaCl and KCl at 25 °C: $\beta^0(\mathrm{NaCl}) = 0.0765$, $\beta^1(\mathrm{NaCl}) = 0.2664$, $C^{\phi}(\mathrm{NaCl}) = 0.00127$, $\beta^0(\mathrm{KCl}) = 0.04835$, $\beta^1(\mathrm{KCl}) = 0.2122$, and $C^{\phi}(\mathrm{KCl}) = -0.00084$. For the osmotic coefficient of water in solutions of a uniunivalent electrolyte, the Pitzer equation[5,38] has the form

$$\phi = 1 - \frac{\alpha}{3}\frac{\sqrt{m}}{1 + 1.2\sqrt{m/m^{\mathrm{o}}}} + \left(\beta^0 + \beta^1 \mathrm{e}^{-2\sqrt{m/m^{\mathrm{o}}}}\right)(m/m^{\mathrm{o}}) + C^{\phi}(m/m^{\mathrm{o}})^2 \qquad (10)$$

Results and Discussion

Determination of Parameters B and b_1 for KCl in Dilute Solutions. The most reliable technique to determine activity coefficients for KCl (as well as for the other alkali metal chlorides) in dilute aqueous solutions is to measure appropriate concentration cells with transference. The precision of the cpd data measured by using this technique can be in the best cases as high as 0.001 mV. However, the calculation of activity coefficients from the cpd data obtained on cells of this kind requires that the transference numbers (t_+ or $t_- = 1 - t_+$) of ions in the electrolyte solutions be known. The most reliable transference numbers for these calculations are obtained using the moving boundary method (see, for example, ref 39).

Parameters B and b_1 for eq 1 with $b_2 = 0$ were determined here from data measured on concentration cells with transference as follows (see also ref 32). The cell used in the measurements of KCl solutions can be written as

$$\mathrm{Ag(s)|AgCl(s)|MCl(aq,}\ m_1\mathrm{)|MCl(aq,}\ m_2\mathrm{)|AgCl(s)|Ag(s)} \qquad (11)$$

where M is in this case $\mathrm{K^+}$. In the data sets measured with cell 11 for the determination of activity coefficients, the molality of solution 1 ($= m_1$) is often exactly, or almost, constant within each set, and molality m_2 is varied. Theoretically, the cpd of this cell (E) can be expressed by the following equation

$$E = -\frac{2RT}{F}\int_1^2 t_+ d\ln(\gamma m/m^{\mathrm{o}}) \qquad (12)$$

where t_+ is the transference number of the cation ($\mathrm{K^+}$). In the subsequent calculations, the treatment of Longsworth (see, e.g., refs 20 and 40) is followed. Transference number t_+ is first divided into two parts

$$t_+ = t_{+,1} + \Delta t_+ \qquad (13)$$

where $t_{+,1}$ is the transference number of $\mathrm{K^+}$ at molality m_1. Using eqs 12 and 13, the following equation can be derived

$$\Delta\ln(\gamma) = \ln(\gamma_2) - \ln(\gamma_1) = \frac{-FE}{2RTt_{+,1}} - \ln(m_2/m_1) - \frac{1}{t_{+,1}}\int_{m_1}^{m_2}\Delta t_+(dm/m) - \frac{1}{t_{+,1}}\int_0^{\Delta\ln\gamma}\Delta t_+ d[\Delta\ln(\gamma)] \qquad (14)$$

where, for example, m_2 is the molality of solution 2. According to this equation, it is possible to calculate the value of quantity $\Delta\ln(\gamma)$ for each experimental point. These values will be used below to determine the parameters B and b_1 for eq 1 with $b_2 = 0$. The evaluation of the third term on the right-hand side requires a mathematical expression for the dependence of $t_+ = t_+(m)$. This expression can be obtained by using curve fitting from results of appropriate moving boundary experiments. The evaluation of the fourth term on the right-hand side of eq 14 requires, on the other hand, a mathematical expression for $t_+ = t_+(\gamma)$. Because γ is the quantity to be determined, this evaluation requires iterative calculations (see ref 40). In the case of dilute KCl solutions, the fourth term is, however, small, and it can be omitted from the calculations.

After the final values of $\Delta\ln(\gamma)$ have been determined from eq 14 using the procedure explained in the previous paragraph, the parameters B and b_1 for eq 1 with $b_2 = 0$ can be obtained

Table 1. Experimental Data Measured by Hornibrook et al.[12] on Concentration Cells of Type 11 for KCl Solutions and Values of Quantity Δln(γ) (See Equation 14) Obtained from These Data

m_1/mol·kg^{-1}	m_2/mol·kg^{-1}	E/int. mV^a	$(e_E/\text{mV})^b$	Δln(γ)
0.049845	0.009922	38.141	0.006	0.09900
0.049941	0.010015	37.961	0.005	0.09874
0.049791	0.020015	21.372	0.005	0.06226
0.049941	0.020032	21.437	0.020	0.06183
0.049831	0.020105	21.295	0.016	0.06163
0.050179	0.030000	12.005	0.002	0.03742
0.049919	0.070304	−7.894	0.019	−0.02876
0.050056	0.080010	−10.804	0.018	−0.03972
0.050164	0.085368	−12.260	−0.001	−0.04453
0.049845	0.099554	−15.920	0.005	−0.05921
0.049856	0.099516	−15.901	0.010	−0.05936

[a] 1 int. V = 1.00034 V. [b] e_E = E(observed) − E(predicted), and the latter value was calculated from eq 20.

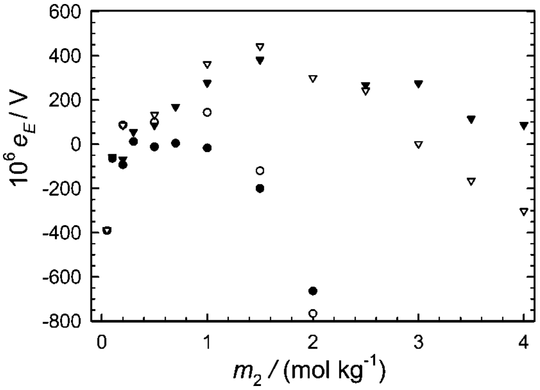

Figure 1. Deviation, e_E in eq 21, between the observed and predicted cell potential difference (cpd) from the data measured by Harned and Cook[13] (HaCo37, m_1 = 0.05 mol·kg^{-1}) in KCl solutions and by Harned and Nims[22] (HaNi32, m_1 = 0.1 mol·kg^{-1}) in NaCl solutions on cell 22 as a function of molality m_2. The predicted cpd was calculated by using eq 23 where the Hückel equation (H, eq 1 with b_2 = 0) or the extended Hückel equation (EH, eq 1) with the suggested parameter values was used for the activity coefficients. ●, HaCo37, KCl, H; ○, HaNi32, NaCl, H; ▼, HaCo37, KCl, EH; ▽, HaNi32, NaCl, EH.

from these values as follows. The equation used in this determination is derived by the following reasoning

$$\Delta\ln(\gamma) = \ln(\gamma_2) - \ln(\gamma_1) = -\frac{\alpha\sqrt{m_2}}{1 + B\sqrt{m_2}} + b_1(m_2/m^\circ) - \ln(\gamma_1) \Rightarrow \Delta\ln(\gamma) + \frac{\alpha\sqrt{m_2}}{1 + B\sqrt{m_2}} = f_1 = -\ln(\gamma_1) + b_1(m_2/m^\circ) \tag{15}$$

When parameter B has been fixed, eq 15 represents an equation of the straight line f_1 versus (m_2/m°). The slope of the straight line is b_1, and the intercept with the $f_1$axis is $-\ln(\gamma_1)$. These values can be determined by using linear regression analysis. Parameter B can be determined by requiring that the straight line has the best possible linearity. Hence, the value of B is sought that gives the minimum for standard deviation about regression (s) in the fitting with eq 15.

For KCl, two important sets measured by this technique (cell 11) are available in the literature, i.e., those of Shedlovsky and MacInnes[21] and Hornibrook et al.[12] The latter of these sets is probably slightly more reliable, and it is used here in the parameter estimation. The relationship $t_+ = t_+(m)$ for eq 14 was determined in this case from the moving boundary results of Longsworth[39] and Allgood et al.,[41] and the following general equation was used for this relationship (see refs 39 and 40)

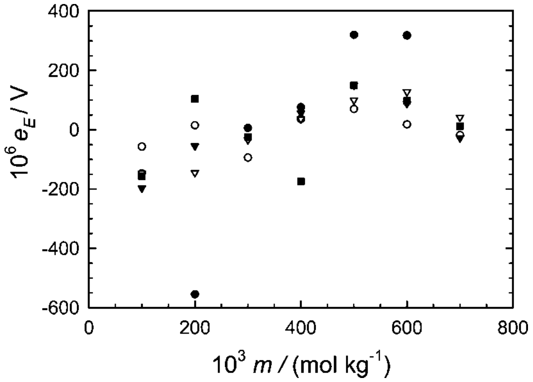

Figure 2. Deviation, e_E in eq 21, between the observed and predicted cell potential difference (cpd) from the data measured by Giordano et al.[14] in KCl solutions on cell 24 as a function of molality m. The predicted cpd was calculated by using eq 25 where the Hückel equation (eq 1 with b_2 = 0) with the parameter values of B = 1.3 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.011 was used for the activity coefficients and the following values were used for the standard cell potential differences: ●, x = 0.004148, E° = 2.06436 V; ○, 0.01469, 2.11551; ▼, 0.01925, 2.13176; ▽, 0.02919, 2.15891; ■, 0.04014, 2.18652.

$$t_+ = t_+^\infty - u_1\sqrt{m/m^\circ} + u_2(m/m^\circ) \tag{16}$$

where t_+^∞, u_1, and u_2 are parameters depending on the electrolyte. The transference number data have been reported on the concentration (molarity, c) scale. For the conversion of the data on the molality (m) scale, the following equation was used

$$\frac{m}{m^\circ} = 1.00288\frac{c}{c^\circ} + 0.028275\left(\frac{c}{c^\circ}\right)^2 \tag{17}$$

where c° = 1 mol·dm^{-3}. It was obtained from the accurate density data measured by Jones and Talley,[42] and it applies to a molarity of 0.2 mol·dm^{-3}. The two moving-boundary studies[39,41] give almost identical transference numbers for KCl solutions at different concentrations. Therefore the results of these two studies can be unified, and the following parameters were estimated from the unified set for the cationic transference number of KCl for eq 16: t_+^∞ = 0.49049, u_1 = 0.0042, and u_2 = 0.0079. The experimental data in these two t_+ studies covered the concentration range from (0.001 to 0.1) mol·dm^{-3}, and the transference numbers are reported in these data to four digits. Equation 16 predicts the reported values always within 0.0003. This error is so small that the uncertainty in t_+ values does not have a significant influence on the activity coefficients obtained from the cpds of cell 11. Below, the same is also true for NaCl results of this cell. This equation for KCl also reveals that the transference number of K$^+$ ions is almost constant at the concentrations considered.

The cpd data of Hornibrook et al.[12] consisted of 11 points, and the molality of the reference solution 1 was not exactly constant in this set but varied slightly around a value of 0.05 mol·kg^{-1}. The experimental data are shown in Table 1. The Δln(γ) values obtained from these data using eq 14 are also shown in this table. When the Δln(γ) values in Table 1 were used to obtain parameters B and b_1 for KCl for eq 1 with b_2 = 0, eq 15 must be somewhat modified because of the slightly different values used in these data for molality m_1. The parameters were estimated by using linear regression analysis from the equation deduced by the following reasoning: The reference molality m_1 in cell 11 was approximately $\overline{m_1}$, and for these data, it was chosen that $\overline{m_1}$ = 0.05 mol·kg^{-1}. Then, the definition of Δln(γ) in eq 14 gives

$$\Delta\ln(\gamma) = \ln\gamma(m_2) - \ln\gamma(m_1) = \ln\gamma(m_2) - \ln\gamma(\overline{m_1}) + \ln\gamma(\overline{m_1}) - \ln\gamma(m_1) \Rightarrow \Delta\ln(\gamma) + \frac{\alpha\sqrt{m_2}}{1+B\sqrt{m_2}} + \frac{\alpha\sqrt{\overline{m_1}}}{1+B\sqrt{\overline{m_1}}} - \frac{\alpha\sqrt{m_1}}{1+B\sqrt{m_1}} = f_2 = -\ln\gamma(\overline{m_1}) + b_1[m_2 - (m_1 - \overline{m_1})]/m^{\mathrm{o}} = -\ln\gamma(\overline{m_1}) + b_1 m_{\mathrm{corrected}}/m^{\mathrm{o}} \quad (18)$$

where $m_{\mathrm{corrected}} = m_2 - (m_1 - \overline{m_1})$. Parameters B and b_1 can be determined from this equation in the same way as suggested for the original eq 15. After the best value of parameter B has been found and fixed, it is possible to calculate for each experimental point the value of quantity f_2. The resulting values of f_2 are presented as a function of the variable ($m_{\mathrm{corrected}}/m^{\circ}$). The slope of the best straight line is an estimate of parameter b_1. When the $\Delta\ln(\gamma)$ values from the set of Hornibrook et al. in Table 1 were used to obtain parameters B and b_1 of KCl for eq 1 with $b_2 = 0$, the value of $B = 1.3\ (\mathrm{mol\cdot kg^{-1}})^{-1/2}$ was obtained from these data. With this value, the following straight line was determined

$$f_2 = (0.20254 \pm 0.00016) + (0.011 \pm 0.003)(m_{\mathrm{corrected}}/m^{\mathrm{o}}) \quad (19)$$

where the standard deviations for the estimated parameters are also given. From this equation, a b_1 value of 0.011 can be deduced for KCl in dilute solutions. Here the following parameter values are suggested for dilute KCl solutions for eqs 1 and 2: $B = 1.3\ (\mathrm{mol\cdot kg^{-1}})^{-1/2}$, $b_1 = 0.011$, and $b_2 = 0$. The resulting equations are called the Hückel equations of KCl for activity and osmotic coefficients, respectively.

To test the suggested parameter values, the data of Hornibrook et al.[12] (see Table 1) were predicted by means of these values. The equation used to predict the cpd values has the following form

$$E = -\frac{2RTt_{+,1}}{F}\ln(m_2/m_1) - \frac{2RTt_{+,1}}{F}\ln(\gamma_2/\gamma_1) - \frac{2RT}{F}\int_{m_1}^{m_2}\Delta t_{+}(dm/m) - \frac{2RT}{F}\int_{\ln\gamma_1}^{\ln\gamma_2}\Delta t_{+}d[\ln(\gamma)] \quad (20)$$

where the integral in the last term on the right-hand side must be evaluated numerically. The cpd errors are defined by the equation

$$e_{\mathrm{E}} = E(\mathrm{observed}) - E(\mathrm{predicted}) \quad (21)$$

and are shown in Table 1. They are very small, and thus the data support well the suggested Hückel equation.

Tests of the Resulting Hückel Equation for KCl with Cell Potential Difference Data. As can be seen in Table 1, the KCl data used in the parameter estimation for the new Hückel equation extend only up to a molality of 0.1 mol·kg^{-1}. It can be immediately shown, however, that this equation applies well to cpd data measured in much stronger KCl solutions. For KCl, the amalgam cell data of Harned and Cook[13] and Giordano et al.[14] at 25 °C are precise, and these data are used here to show the importance of the new parameters for KCl in less dilute solution.

Harned[43] and Harned and Cook[13] have measured on the following concentration cell without transference

$$\mathrm{Ag(s)|AgCl(s)|MCl(aq,}\ m_1\mathrm{)|M(Hg)|MCl(aq,}\ m_2\mathrm{)|\times AgCl(s)|Ag(s)} \quad (22)$$

where M is K^{+} and M(Hg) refers to the alkali metal amalgam electrode (potassium amalgam electrode in this case). The older data of Harned[43] agree quite well with those of Harned and Cook[13] (see ref 32) but are less precise, and the latter set is only considered here. In that set, the molality of solution 1 was constant in a value of $m_1 = 0.05$ mol·kg^{-1}. The cpd of this cell is given by

$$E = -\frac{2RT}{F}\ln(m_2/m_1) - \frac{2RT}{F}\ln(\gamma_2/\gamma_1) \quad (23)$$

These data were predicted by means of the suggested Hückel equation for KCl, and the results are shown as an error plot (see eq 21) in Figure 1. Measurements on cells with an amalgam electrode are usually not as precise as those on cells with transference, but in this case the agreement is very good up to a molality of 1.5 mol·kg^{-1}. Therefore, the amalgam data support well the suggested model up to this molality.

Giordano et al.[14] have measured directly KCl solutions on amalgam cells of the following type at 25 °C

$$\mathrm{M(Hg,}\ x\mathrm{)|MCl(aq,}\ m\mathrm{)|AgCl(s)|Ag(s)} \quad (24)$$

where M is K^{+} and again M(Hg, x) refers to the alkali metal amalgam electrode. The data consisted of eight series of measurements. The mole fraction (x) of potassium in the amalgam was constant in each series, and the molality of KCl (m) varied up to a molality of 0.7 mol·kg^{-1}. The cpd for these cells can be calculated from the following equation

$$E = E^{\mathrm{o}} - (2RT/F)\ln(\gamma m/m^{\mathrm{o}}) \quad (25)$$

where E° is the standard cpd, and now it depends on x. These data were predicted with the new Hückel equation for KCl, and the best value of E° was used in the calculation of errors (see eq 21) for each series. The most important results, obtained from the series where x is 0.004148, 0.01469, 0.01925, 0.02919, and 0.04014, support very well the suggested model, and the errors of these series are shown in Figure 2 of the present study. In these series, the number of different KCl solutions studied is the largest (i.e., usually 7), and the measurements were probably carried out in the most accurate way. Other data series[14] support the new model quite well (not shown in this figure because of the clarity), but there the precision of the measurements was not as good (see ref 32).

Determination of Parameters B and b_1 for NaCl in Dilute Solutions. The parameter values suggested above for dilute KCl solutions also proved to apply to molalities much higher than those used in their estimation. These values were, therefore, accepted for the Hückel equation of KCl. The most reliable values for parameters B and b_1 for NaCl can probably be determined from the isopiestic results of Robinson[1] for dilute NaCl and KCl solutions. In this determination, KCl can be regarded as the reference electrolyte (x) because the activities in the solutions of this salt are now known. The activity of water in dilute KCl solutions can be calculated from the isopiestic molality of the KCl solution (m_{x}) using eq 3 and eq 2 with $b_2 =$ 0 and with the suggested values of B [$= 1.3\ (\mathrm{mol\cdot kg^{-1}})^{-1/2}$] and b_1 ($= 0.011$). The molality of the isotonic NaCl solution can then be regarded as the response variable (m_{y}). In isopiestic equilibrium, the condition that $a_{1,\mathrm{x}} = a_{1,\mathrm{y}}$ is valid, and thus the following equation can be derived by using eq 3 and eq 2 with $b_2 = 0$ for the determination of B and b_1 for NaCl

$$\ln a_{1,\mathrm{x}} = \ln a_{1,\mathrm{y}} = -2M_1 m_\mathrm{y} + \frac{2\alpha M_1}{B_\mathrm{y}^3}\left[(1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}) - 2\ln(1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}) - \frac{1}{1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}}\right] - b_{1,\mathrm{y}}M_1(m_\mathrm{y}^2/m^\mathrm{o}) \Rightarrow f_3 = \ln a_{1,\mathrm{x}} + 2M_1 m_\mathrm{y} - \frac{2\alpha M_1}{B_\mathrm{y}^3}\left[(1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}) - 2\ln(1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}) - \frac{1}{1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}}\right] = f_0 - b_{1,\mathrm{y}}M_1(m_\mathrm{y}^2/m^\mathrm{o}) = f_0 + k_3 m_\mathrm{y}^2 \quad (26)$$

where $k_3 = -b_{1,\mathrm{y}}M_1/m^\mathrm{o}$. When parameter B_y has been fixed, eq 26 represents an equation of the straight line f_3 versus m_y^2. The slope of the straight line is k_3, and parameter $b_{1,\mathrm{y}}$ can be calculated from the slope. The straight line should go through the origin, and therefore, parameter B_y must now be determined so that the value of intercept f_0 is zero.

In the determination of the Hückel parameters for NaCl, the points from Robinson's data[1] where the molalities are less than 1.5 mol·kg^{-1} could be included. This means that 52 (out of 79) points were taken into account in the least-squares fitting with eq 26. The following results were obtained: $B_\mathrm{y} = 1.4$ (mol·kg^{-1})$^{-1/2}$ and $b_{1,\mathrm{y}} = 0.0716 \pm 0.0002$ where the standard deviation is also given. The estimated parameters can be tested in a reliable way by predicting the vapor pressures of water over the isotonic sodium and potassium chloride solutions in this data set. The vapor pressures of both solutions can be calculated using eqs 3 and 4 and eq 2 with $b_2 = 0$ and with the suggested activity parameters. The results are shown in graph A of Figure 3 where the isopiestic vapor pressure error (e_ip) is defined by

$$e_\mathrm{ip} = p_\mathrm{x} - p_\mathrm{y} \quad (27)$$

and presented as a function of the molality m_y. For solutions where $m \le 1.5$ mol·kg^{-1}, the largest absolute error is in these tests less than 0.13 Pa (= 0.001 mmHg), and the errors form an almost random pattern. Thus, the errors support very well the suggested parameter values. Here, the following parameter values are suggested for dilute NaCl solutions for eqs 1 and 2: $B = 1.4$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.072$, and $b_2 = 0$. The resulting equations are called the Hückel equations of NaCl for activity and osmotic coefficients, respectively. The suggested Hückel equations for KCl and NaCl will now be tested against other thermodynamic data.

Tests of the New Hückel Equations with Isopiestic Data. The new parameter values for the Hückel equations of NaCl and KCl were first tested with the existing isopiestic data. The tests were performed exactly in the same way as the above tests with Robinson's data. The test results from the very dilute isotonic solutions of Gordon[15] are shown in graph A of Figure 3, and the results from dilute solution data of Robinson and Sinclair,[16] Janis and Ferguson,[17] and Scatchard et al.[18] are shown in graph B of this figure. Only the solutions where the NaCl molality is less than 2.0 mol·kg^{-1} were included in graph B. All errors in graph B and in Gordon's set in graph A of Figure 3 are small and thus support well the suggested Hückel parameters up to molalities of about 1.5 mol·kg^{-1} for both electrolytes.

Tests of the New Hückel Equations with Cell Potential Difference Data. Measurements on concentration cells of type 11 have been made at 25 °C by Shedlovsky and MacInnes[21] (M = K$^+$ and $m_1 = 0.100571$ mol·kg^{-1}), Janz and Gordon[19] (M = Na$^+$ and $m_1 \cong 0.05$ mol·kg^{-1}), and Brown and MacInnes[20] (M = Na$^+$ and $m_1 = 0.10000$ mol·kg^{-1}), in addition to those made by Hornibrook et al.[12] in dilute KCl solution (see above). In the set of Janz and Gordon,[19] the molality of the reference solution varied slightly around a value of 0.05 mol·kg^{-1} similarly as in the set of Hornibook et al. (see Table 1). The data in these three sets were predicted with the Hückel equations by using eq 20 as the data of Hornibrook et al. above. In the set of Shedlovsky and MacInnes,[21] the compositions of the solutions were reported as concentrations (molarities), and they were converted into the molalities by using eq 17. For the transference number of K$^+$ ions in KCl solutions, eq 16 with the above-mentioned parameters was used. For the NaCl sets of Brown and MacInnes[20] and Janz and Gordon,[19] the transference numbers were determined from the moving boundary data of Longsworth[39] and of Allgood and Gordon,[44] and these data were converted on the molality scale by the equation

$$\frac{m}{m^\mathrm{o}} = 1.00291\frac{c}{c^\mathrm{o}} + 0.01791\left(\frac{c}{c^\mathrm{o}}\right)^2 \quad (28)$$

The parameters for this equation were obtained from the concentrations and molalities reported by Brown and MacInnes for their cpd data.[20] The following parameter values were obtained for eq 16 from these t_+ data for NaCl solutions: $t_+^\infty = 0.39629$, $u_1 = 0.04928$, and $u_2 = 0.04681$. These parameters apply to the experimental data as well as to the corresponding KCl parameters above. The results of the Hückel equation tests are shown as error plots in Figure 4. In these plots, all errors are small and form an almost random pattern, and thus also

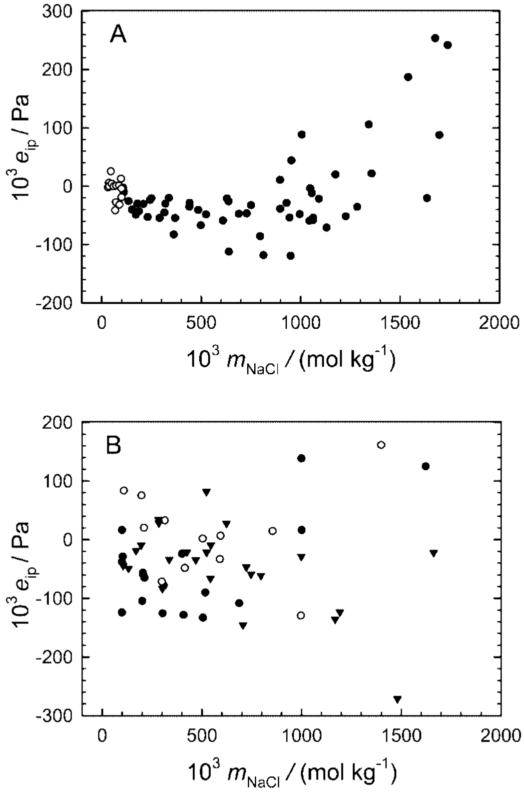

Figure 3. Difference, e_ip in eq 27, between the vapor pressure of water over the tested solution (y) and that over the reference solution (x) as a function of the molality of the tested solution (m_NaCl) in the isotonic KCl (x) and NaCl (y) solutions reported by ●, Robinson[1] (graph A); ○, Gordon[15] (A); ●, Scatchard et al.[18] (B); ○, Janis and Ferguson[17] (B); and ▼, Robinson and Sinclair[16] (B). The vapor pressures have been calculated by eqs 3 and 4 using the Hückel equation (eq 2 with $b_2 = 0$) with the following parameter values for the osmotic coefficients: $B_\mathrm{KCl} = 1.3$ (mol·kg^{-1})$^{-1/2}$, $b_{1,\mathrm{KCl}} = 0.011$, $B_\mathrm{NaCl} = 1.4$ (mol·kg^{-1})$^{-1/2}$, and $b_{1,\mathrm{NaCl}} = 0.072$.

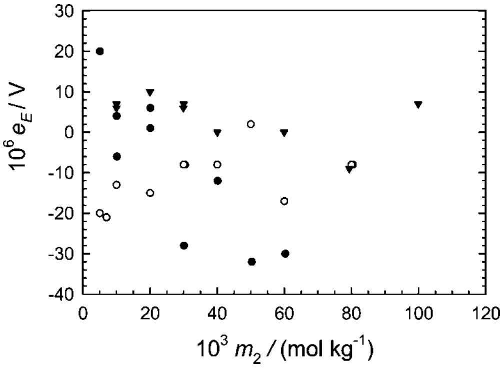

Figure 4. Deviation, e_E in eq 21, between the observed and predicted cell potential difference (cpd) from the data measured ●, by Shedlovsky and MacInnes[21] (M = K^+, $m_1 = 0.100571$ mol·kg^{-1}); ○, by Brown and MacInnes[20] (M = Na^+, $m_1 = 0.1$ mol·kg^{-1}); and ▼, by Janz and Gordon[19] (M = Na^+, $m_1 \cong 0.05$ mol·kg^{-1}) on cell 11 as a function of molality m_2. The predicted cpd was calculated by using eq 20 where the Hückel equation (eq 1 with $b_2 = 0$) with the parameter values of $B_{KCl} = 1.3$ (mol·kg^{-1})$^{-1/2}$ and $b_{1,KCl} = 0.011$, $B_{NaCl} = 1.4$ (mol·kg^{-1})$^{-1/2}$ and $b_{1,NaCl} = 0.072$ were used for the activity coefficients. The point where $m_1 = 0.049826$ mol·kg^{-1}, $m_2 = 0.019978$ mol·kg^{-1}, and $E = 0.017112$ int. V in the set of Janz and Gordon[19] was omitted as a probable outlier.

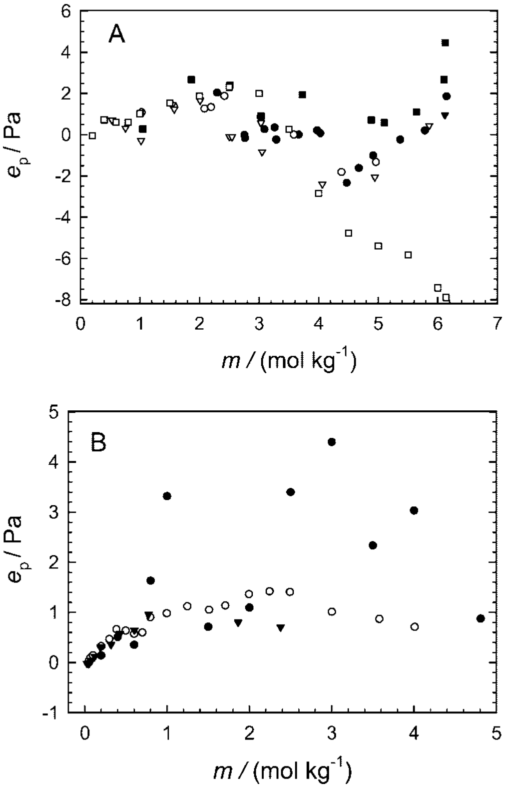

Figure 5. Difference, e_p in eq 30, between the observed and predicted vapor pressure of water over the NaCl (graph A) and KCl (B) solutions as a function of molality m. The vapor pressures have been predicted by eqs 3 and 4 using the extended Hückel equation (eq 2) with the suggested parameter values for the osmotic coefficients. The following data were used (see text): ●, Olynyk and Gordon[23] (graph A), Pearce and Nelson[25] (B); ○, Negus (taken from ref 1, A), Lovelace et al.[28] (measured at 20 °C, B); ▼, Gibson and Adams (taken from ref 1, A), Brown and MacGregor Delaney[29] (B); ▽, Pepela and Dunlop[26] (A); ■, Gibbard et al.[27] (A); □, Pearce and Nelson[25] (A).

these data support well the suggested Hückel parameters. The NaCl data from Gordon's group (see ref 19) seem to be exceptionally precise (as the corresponding KCl data in Table 1). It is important to emphasize that the new Hückel equation for NaCl (where the parameters were estimated above only from the isopiestic vapor pressure data) predicts all cpds in this set within ± 0.01 mV.

Harned,[43] Harned and Nims,[22] and Caramazza[45] measured on the concentration cell of type 22 where M is Na^+ and the sodium amalgam electrode was used. The data of Harned and of Caramazza agree satisfactorily with those of Harned and Nims (see ref 32) but are usually less precise, and the latter set is only considered here. In that set, the molality of solution 1 was constant in a value of $m_1 = 0.1$ mol·kg^{-1}. The cpd of this cell is given by eq 23, and these data were predicted by means of the suggested Hückel equation for NaCl. The results are shown as an error plot (see eq 21) in Figure 1. These data support well the suggested model up to the molality of 1.5 mol·kg^{-1}. Mussini et al.[46] measured directly at 25 °C NaCl solutions on amalgam cells of the type 24 (where in this case M = Na^+). These data resemble those of Giordano et al.[14] but are usually slightly less precise. These data can be predicted within experimental error with the new Hückel equation for NaCl as well as with another Hückel equation with the slightly different parameter values in ref 32.

Determination of Parameters b_1 and b_2 for NaCl in Concentrated Solutions. The most reliable direct technique to determine osmotic coefficients of alkali metal chlorides in concentrated aqueous solutions is to measure vapor pressures of these solutions. Because the solute is not volatile, the vapor pressure resulted only from water. Vapor pressure in NaCl solutions is better known than that in KCl solutions (see above). Probably, the most precise study in NaCl solutions is that measured by Olynyk and Gordon[23] containing 15 vapor pressure points from a molality of 2.3 mol·kg^{-1} to the saturated solution. Here, the parameters b_1 and b_2 were estimated for the extended Hückel equation (eq 1 or 2) of NaCl from this set. The following equation was used in the estimation (compare to eq 26)

$$f_4 = \ln a_{1,\text{exptl}} + 2M_1 m - \frac{2\alpha M_1}{B^3}\left[(1 + B\sqrt{m}) - 2\ln(1 + B\sqrt{m}) - \frac{1}{1 + B\sqrt{m}}\right] + \frac{4M_1 b_2 m^3}{3(m^\circ)^2} = f_0 - b_1 M_1 (m^2/m^\circ) = f_0 + k_4 m^2 \quad (29)$$

where k_4 is $-b_1M_1/m^\circ$; the experimental values were used for the activity of water ($a_{1,\text{exptl}}$, see eqs 3 and 4); and the same value of parameter B was used as above [= 1.4 (mol·kg^{-1})$^{-1/2}$]. When parameter b_2 has been fixed, eq 29 represents an equation of the straight line f_4 versus m^2. The slope of the straight line is k_4, and parameter b_1 can be calculated from the slope. The straight line should again go through the origin, and therefore, parameter b_2 must be determined so that the value of the intercept f_0 is zero.

In the determination of the parameters for the extended Hückel equation of NaCl, the following results were obtained from the set of Olynyk and Gordon: $b_2 = 0.0062$ and $b_1 = 0.0699 \pm 0.0007$ where the standard deviation is also given. The estimated parameters can be tested by predicting the vapor pressures in this set with the parameter values. The vapor pressures were calculated using eqs 2, 3, and 4. The results are shown in graph A of Figure 5 where the vapor pressure error (e_p) is defined by

$$e_p = p(\text{observed}) - p(\text{predicted}) \qquad (30)$$

and presented as function of the molality m. The vapor pressure errors for the direct measurements are considerably larger than those of the isopiestic determinations (compare to Figure 3).

The largest absolute error from the data of Olynyk and Gordon[23] is less than 2.7 Pa (= 0.02 mmHg), and the errors were found to support well the suggested parameters. Thus, the following parameter values are suggested for less dilute NaCl solution up to the saturated solution for eqs 1 and 2: $B = 1.4\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.0699$, and $b_2 = 0.0062$. The resulting equations are called the extended Hückel equations of NaCl for activity and osmotic coefficients, respectively.

Tests of the Resulting Extended Hückel Equation for NaCl with Vapor Pressure and Cell Potential Difference Data. The suggested parameters for the extended Hückel equation of NaCl can be tested by predicting with these values the other vapor pressures existing in the literature for NaCl solutions (see above). The vapor pressure errors (see eq 30) were calculated as for the set of Olynyk and Gordon, and the results are shown in graph A of Figure 5. In the calculation of the errors for the sets of Pearce and Nelson[25] and of Pepela and Dunlop,[26] the values of (3.1667 and 3.1695) kPa (i.e., (23.752 and 23.773) mmHg) were used for the vapor pressure of pure water at 25 °C, respectively, as in the original papers. All errors except that of the strongest solution in the set of Gibbard et al.[27] and those of the five strongest solutions in the set of Pearce and Nelson[25] support at least satisfactorily the suggested model. The suggested Hückel parameters for concentrated NaCl solutions can also be tested with the cpd data measured by Harned and Nims[22] on cell 22 up to a molality of 4 mol·kg^{-1}. These data were predicted with the new extended Hückel equation (eq 1) by using eq 23. The results are shown in Figure 1, and the cpd errors in this figure support very satisfactorily the suggested model.

Determination of Parameters b_1 and b_2 for KCl in Concentrated Solutions. The Hückel parameters suggested above for concentrated NaCl solutions proved to apply almost within experimental error up to the saturated solution, and these values are, therefore, accepted for the extended Hückel equation of NaCl. The most reliable values for parameters b_1 and b_2 of KCl can then be determined from the isopiestic results of Robinson[1] for NaCl and KCl solutions. In this determination, NaCl must be regarded as the reference electrolyte (x) because the activities of this salt are now known. Thus, the activity of water in NaCl solutions can be calculated from the isopiestic molality of the NaCl solution (m_x) from eqs 2 and 3 with $B = 1.4\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.0699$, and $b_2 = 0.0062$. The molality of the isotonic KCl solution is then regarded as the response variable (m_y). (Above, in the estimation of the parameters for the two-parameter Hückel equation of NaCl from the dilute solutions of this data set, the reverse was true, and m_{NaCl} was the response variable.) Again, in isopiestic equilibrium, the condition that $a_{1,x} = a_{1,y}$ is valid, and the parameter value of $B = B_y = 1.3\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ is used for KCl. Thus, the following equation can be derived for the determination of b_1 and b_2 of KCl (compare to eqs 26 and 29)

$$f_5 = \ln a_{1,x} + 2M_1 m_y - \frac{2\alpha M_1}{B_y^3}\left[\left(1 + B_y\sqrt{m_y}\right) - 2\ln\left(1 + B_y\sqrt{m_y}\right) - \frac{1}{1 + B_y\sqrt{m_y}}\right] + \frac{4M_1 b_{2,y} m_y^3}{3(m^{\circ})^2} = f_0 - b_{1,y}M_1(m_y^2/m^{\circ}) = f_0 + k_5 m_y^2 \quad (31)$$

where $k_5 = -b_{1,y}M_1/m^{\circ}$. When parameter $b_{2,y}$ has been fixed, eq 31 represents an equation of the straight line f_5 versus m_y^2. Parameter $b_{1,y}$ can be calculated from the slope k_5. The straight line should again go through the origin and, therefore, parameter $b_{2,y}$ must be determined so that the value of intercept f_0 is zero (as for eqs 26 and 29).

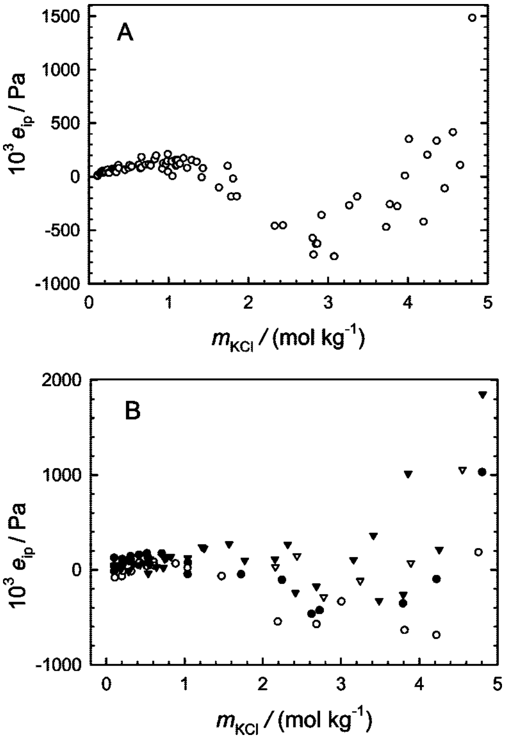

Figure 6. Difference, e_{ip} in eq 27, between the vapor pressure of water over the tested solution (y) and that over the reference solution (x) as a function of the molality of the tested solution (m_{KCl}) in the isotonic NaCl (x) and KCl (y) solutions reported by ○, Robinson[1] (graph A); ●, Scatchard et al.[18] (B); ○, Janis and Ferguson[17] (B); ▼, Robinson and Sinclair[16] (B); and ▽, Kirgintsev and Luk'yanov[24] (B). The vapor pressures have been calculated by eqs 3 and 4 using the extended Hückel equation (eq 2) with the suggested parameter values for the osmotic coefficients.

All points from Robinson's data[1] (i.e., 79 points) could be included in the least-squares fitting with eq 31. The following results were obtained, $b_{2,y} = 0.0036$ and $b_{1,y} = 0.01324 \pm 0.00010$, where the standard deviation is also given. The estimated parameters can again be tested by predicting the vapor pressures of this data set (see above). The vapor pressures of both solutions can be calculated using eqs 2 to 4 with the suggested activity parameters. The results are shown in graph A of Figure 6 where the isopiestic vapor pressure error (defined by eq 27) is presented as a function of the molality m_y. The largest absolute error in these tests is about 1.5 Pa (i.e., 0.01 mmHg), and the small trends observed in the plot are approximately of the same order as the precision of the measurements in the concentrated solutions. Thus, the results of Robinson's set[1] support well the suggested parameters. Here, the following parameter values are, therefore, suggested for less dilute KCl solution up to the saturated solution for eqs 1 and 2: $B = 1.3\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.01324$, and $b_2 = 0.0036$. The resulting equations are called the extended Hückel equations of KCl for activity and osmotic coefficients, respectively. The extended Hückel equations for NaCl and KCl will then be tested with the existing thermodynamic data not used so far in the tests.

Tests of the New Extended Hückel Equations with Thermodynamic Data. The new parameter values for the extended Hückel equations of NaCl and KCl were first tested with the isopiestic data. The tests were performed exactly in the same way as the tests with Robinson's data. In these tests, all points of Robinson and Sinclair,[16] Janis and Ferguson,[17] and

Table 2. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Sodium Chloride Solutions at 25 °C as a Function of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.2	0.734	0.924	3.1476
0.4	0.694	0.922	3.1268
0.6	0.676(0.675)	0.926(0.925)	3.1058(3.1059)
0.8	0.666(0.664)	0.932(0.930)	3.0846(3.0848)
1.0	0.662(0.659)	0.940(0.937)	3.0631(3.0635)
1.2	0.660(0.656)	0.948(0.943)	3.0413(3.0419)
1.4	0.662	0.957	3.0192
1.6	0.665	0.967	2.9968
1.8	0.669	0.977	2.9740
2.0	0.675	0.988	2.9509
2.2	0.682	0.999	2.9274
2.4	0.690	1.010	2.9035
2.6	0.699	1.022	2.8793
2.8	0.709	1.034	2.8547
3.0	0.720	1.046	2.8298
3.2	0.732	1.059	2.8044
3.4	0.744	1.072	2.7786
3.6	0.758	1.085	2.7525
3.8	0.772	1.099	2.7259
4.0	0.787	1.113	2.6989
4.2	0.803	1.128	2.6716
4.4	0.820	1.142	2.6438
4.6	0.838	1.157	2.6156
4.8	0.857	1.172	2.5871
5.0	0.877	1.188	2.5581
5.2	0.898	1.204	2.5287
5.4	0.920	1.220	2.4990
5.6	0.943	1.237	2.4688
5.8	0.968	1.254	2.4383
6.0	0.993	1.271	2.4074
6.144[b]	1.012	1.284	2.3849

[a] See text. [b] The molality of the saturated solution.

Scatchard et al.[18] and also the new points presented by Kirgintsev and Luk'yanov[24] for concentrated solutions were taken into account. The test results are shown in graph B of Figure 6. All errors in this graph are small, and thus the data support well the suggested Hückel parameters.

The KCl parameters were then tested with the vapor pressure data. The vapor pressure errors (see eq 30) were calculated as for the NaCl sets above, and the results are shown in graph B of Figure 5. In the calculation of the errors for the set of Pearce and Nelson,[25] the value 3.1667 kPa was used for the vapor pressure of pure water at 25 °C (see above). Despite that the data of Lovelace et al.[28] were measured at 20 °C, the activity parameters for 25 °C can be used for these data. At 20 °C, the vapor pressure of pure water and the Debye−Hückel parameter are 2.3384 kPa (= 17.539 mmHg, see Kell[34]) and 1.1646 (mol·kg^{-1})$^{-1/2}$ (Archer and Wang[33]), respectively, and these values were used for this set. The vapor pressure data in this graph support at least satisfactorily the new parameters for the extended Hückel equation of KCl. The suggested Hückel parameters for concentrated KCl solutions can also be tested with the cpd data measured by Harned and Cook[13] using molalities up to 4 mol·kg^{-1}. These data were predicted with the new extended Hückel equation by using eq 23. The results are shown in Figure 1, and the cpd errors support in this figure very satisfactorily the suggested model.

Recommended Activity and Osmotic Coefficients at 25 °C. From the evidence indicated in the tests of the present study (see Figures 1 to 6), it can be concluded that the new Hückel equations for dilute solutions and the new extended Hückel equations for more concentrated solutions are very reliable. New tables for the activity and osmotic coefficients of NaCl and KCl solutions at 25 °C have been calculated on this basis. For NaCl solutions, the new values are given in Table 2 and for KCl solutions in Table 3. Vapor pressures of water are also included in these tables. The values of all activity quantities have been calculated in these tables by using the parameter values

Table 3. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Potassium Chloride Solutions at 25 °C as a Function of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.2	0.719	0.915(0.914)	3.1478
0.4	0.669(0.668)	0.905(0.904)	3.1275(3.1276)
0.6	0.641(0.640)	0.902(0.900)	3.1074(3.1075)
0.8	0.623(0.621)	0.902(0.899)	3.0873(3.0875)
1.0	0.610(0.607)	0.902(0.899)	3.0672(3.0676)
1.2	0.601(0.596)	0.904(0.899)	3.0471(3.0477)
1.4	0.593	0.907	3.0270
1.6	0.588	0.909	3.0068
1.8	0.584	0.913	2.9865
2.0	0.580	0.916	2.9662
2.2	0.578	0.920	2.9458
2.4	0.576	0.924	2.9253
2.6	0.575	0.928	2.9048
2.8	0.575	0.932	2.8841
3.0	0.575	0.937	2.8634
3.2	0.576	0.942	2.8425
3.4	0.576	0.947	2.8215
3.6	0.578	0.952	2.8004
3.8	0.580	0.958	2.7792
4.0	0.582	0.963	2.7579
4.2	0.584	0.969	2.7364
4.4	0.587	0.975	2.7148
4.6	0.590	0.981	2.6930
4.8	0.593	0.988	2.6711
4.803[b]	0.593	0.988	2.6708

[a] See text. [b] The molality of the saturated solution.

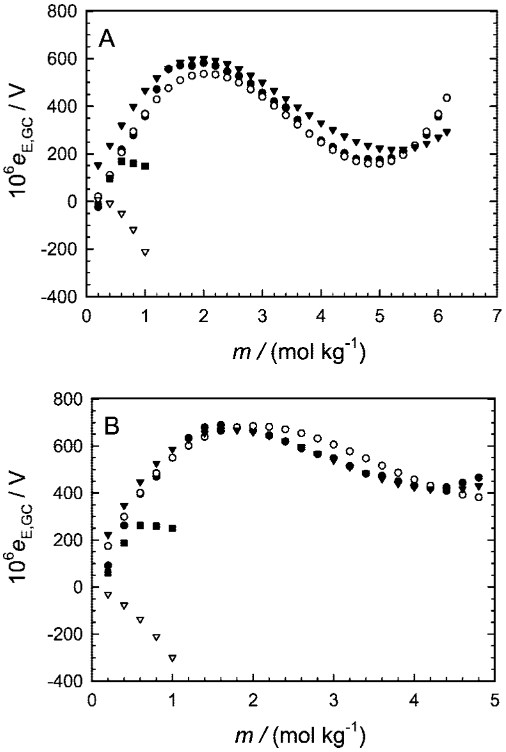

Figure 7. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 32, between the literature activity coefficients of ●, Robinson;[1] ○, Hamer and Wu[37] (eq 5); and ▼, Pitzer and Mayorga[5] (eq 7) and those obtained in this study using the extended Hückel equation (eq 1, see Tables 2 and 3) and deviation, expressed in the same way, between the activity coefficients from the extended Hückel equation (EH, see eq 34 and Tables 2 and 3, ▽) and from Robinson[1] (■) and those obtained using the suggested Hückel equation (H) as a function of molality m in NaCl (graph A) and KCl (B) solutions.

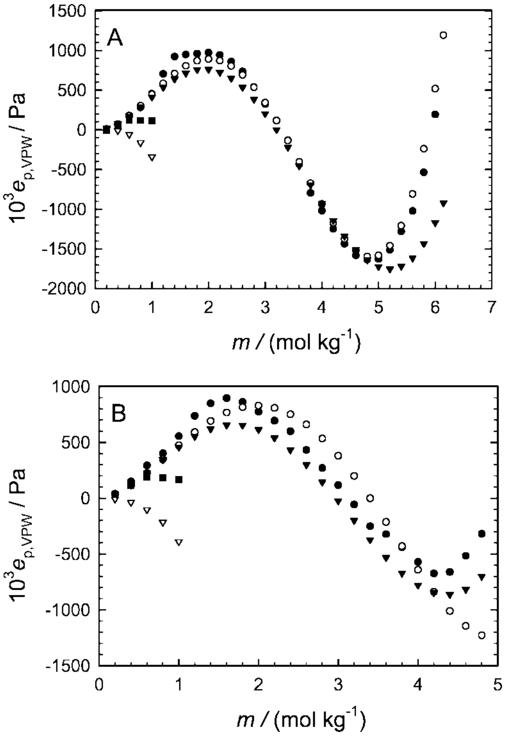

Figure 8. Deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 33, between the literature osmotic coefficients of ●, Robinson;[1] ○, Hamer and Wu[37] (eq 6); and ▼, Pitzer and Mayorga[5] (eq 10) and those obtained in this study using the extended Hückel equation (eq 2, see Tables 2 and 3) and deviation, expressed in the same way, between the osmotic coefficients from the extended Hückel equation (EH, see eq 35 and Tables 2 and 3, ▽) and from Robinson[1] (■) and those obtained using the suggested Hückel equation (H) as a function of molality m in NaCl (graph A) and KCl (B) solutions.

suggested for the extended Hückel equations. In dilute solutions (i.e., when $m \le 1$ mol·kg^{-1}), the values obtained with the suggested Hückel equations are given in parentheses when they differ significantly from those presented in the tables. The absolute difference between the two values is always small (less than about 0.004 for both γ and ϕ).

Comparison of the Recommended Activity Values to the Literature Values. The values in Tables 2 and 3 were compared to the activity and osmotic coefficients presented by Robinson,[1] Hamer and Wu,[37] Pitzer and Mayorga,[5] and Partanen and Minkkinen.[35] Pitzer parameters for NaCl and KCl (and for other electrolytes) have been also suggested, e.g., by Kim and Frederick[47] and Marshall et al.[48] The parameter values from these two studies are close to those of Pitzer and Mayorga (see above), and they were estimated from the tables of Hamer and Wu.[37] Therefore, they are not considered separately here. Equations of activity quantities for NaCl solutions covering wide ranges of temperatures (and possibly also pressures) have been presented by Pitzer et al.,[49] Clarke and Glew,[50] and Archer.[51] For KCl solutions, such equations are given by Archer.[52] These general equations have to be much more complicated than those considered so far, and they are not treated here.

The comparison of the activity coefficients with the literature values is shown in two graphs of Figure 7. Graph A shows the results for NaCl solutions, and graph B for KCl solutions, in the following way: The quantity presented on the y axis is the cell potential difference error [$e_{E,GC}$ where GC refers to the appropriate galvanic cell without a liquid junction containing electrodes reversible to the cation and anion of the electrolyte (i.e., in this case, GC refers to the cell of type 24)] that resulted from the use of the literature activity coefficients of various sources [i.e., γ(literature)] when compared to the recommended values [i.e., γ(recd)] shown in Tables 2 or 3. Thus, $e_{E,GC}$ is defined by

$$e_{E,GC} = -\frac{2RT}{F} \ln \frac{\gamma(\text{literature})}{\gamma(\text{recd})} \qquad (32)$$

For the recommended activity coefficients, the values obtained from the extended Hückel equation (eq 1) for NaCl or KCl are used (see above).

The comparison of the osmotic coefficients in Tables 2 and 3 with the literature values is shown in two graphs of Figure 8. Graph A shows the results for NaCl solutions, and graph B for KCl solutions, in the following way: The quantity presented on the y axis is the vapor pressure error ($e_{p,VPW}$ where VPW refers to the vapor pressure of water) that resulted from the use of the literature osmotic coefficients [i.e., ϕ(literature)] when compared to the recommended values [i.e., ϕ(recd)] shown in Tables 2 or 3. Literature vapor pressure p(literature) and recommended vapor pressure p(recd) have been calculated from these osmotic coefficients by using eqs 3 and 4 and the errors in Figure 8 by using the following equation

$$e_{p,VPW} = p(\text{literature}) - p(\text{recd}) \qquad (33)$$

For the recommended osmotic coefficients, the values obtained from the extended Hückel equation (eq 2) for NaCl or KCl were used (see above).

It can be seen in Figures 7 and 8 that the activity and osmotic coefficients obtained from the equations of Hamer and Wu[37] and of Pitzer and Mayorga[5] are practically the same as those suggested by Robinson.[1] Only near to the saturated solution of both electrolytes do the osmotic coefficient differences seem to be significant (see Figure 8). On the other hand, the activity and osmotic coefficients obtained from the new extended Hückel equations are clearly different, but also the differences are rather small. Only several galvanic cell errors (see Figure 7) for Pitzer and Hamer equations are larger than 0.5 mV (compare to experimental amalgam cell errors in Figures 1 and 2), and only a few absolute vapor pressure errors (see Figure 8) for these equations for NaCl solutions (see graph A) are larger than 1.3 Pa (i.e., 0.01 mmHg). These errors can be compared to experimental vapor pressure errors in Figure 5. For KCl solutions, all of these errors are smaller. The new extended Hückel equations have been tested with all reliable literature data, and thus the activity and osmotic coefficients from these equations are probably slightly more reliable than the literature values themselves.

The Hückel equations of Partanen and Minkkinen[35] (eqs 1 and 2 with $b_2 = 0$) have the parameter values of $B_{NaCl} = 1.41$ (mol·kg^{-1})$^{-1/2}$, $b_{1,NaCl} = 0.0724$, $B_{KCl} = 1.28$ (mol·kg^{-1})$^{-1/2}$, and $b_{1,KCl} = 0.0151$ (see equations for these calculations in the vicinity of eqs 1 and 2). These values are very close to the parameter values suggested in the present study for the Hückel equations for dilute solutions. Therefore, the former parameter values[35] give almost the same activity and osmotic coefficients as the new Hückel equations.

The errors that resulted from the use of the extended Hückel equations for NaCl and KCl at molalities less than or about 1 mol·kg^{-1} are also shown in Figures 7 and 8. These errors have been calculated by equations

$$e_{\mathrm{E,GC}} = -\frac{2RT}{F} \ln \frac{\gamma_{\mathrm{EH}}}{\gamma_{\mathrm{H}}} \tag{34}$$

$$e_{\mathrm{p,VPW}} = p_{\mathrm{EH}} - p_{\mathrm{H}} \tag{35}$$

where H and EH refer to the suggested Hückel equation (i.e., to eqs 1 or 2 with $b_2 = 0$) and the extended Hückel equation (i.e., to eqs 1 or 2), respectively. For activity coefficients, the absolute error is always smaller than 0.3 mV, and for the osmotic coefficients, it is always less than 0.4 Pa (= 0.003 mmHg). In these figures are also shown the errors of Robinson's activity and osmotic coefficients for dilute solutions when compared to those obtained by the Hückel equations (= H). These errors are always small.

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We are grateful for the opportunity to dedicate this work, to mark the occasion of this 90th birthday, to Robin Stokes, an inspiring, stalwart pioneer of latter-half 20th century electrolyte research, who with the late 'Robbie' Robinson did so much to raise the status of such work with their book Electrolyte Solutions, a book which inspired many students worldwide to research in the area, and which rightly took its place alongside other classic texts such as that of the late Roger Bates on Determination of pH.

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