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Re-evaluation of the Second Stoichiometric Dissociation Constants of Phosphoric Acid at Temperatures from (0 to 60) °C in Aqueous Buffer Solutions with or without NaCl or KCl. 2. Tests and Use of the Resulting Hückel Model Equations

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Previously (in Part 1), equations were determined for the calculation of the second stoichiometric (molality scale) dissociation constant (K_{m2}) of phosphoric acid in buffer solutions containing sodium, or potassium, dihydrogen phosphate, hydrogen phosphate, and chloride from the determined thermodynamic values of this dissociation constant (K_{a2}) and the molalities of the components in the solutions. These equations were based on single-ion activity coefficient equations of the Hückel type. In the present study (Part 2), these equations were further tested with all reliable thermodynamic data found in the literature from this dissociation reaction in NaCl and KCl solutions. In these data were included a considerable amount of literature results from measurements on cells without liquid junction using hydrogen and silver−silver chloride or mercury−mercury(I) chloride electrodes at temperatures from (0 to 95) °C. Also literature data from hydrogen and glass electrode cells containing liquid junctions were included in the present tests. The new model usually applies well to these data. The new model equations were then used to calculate pH values of the two phosphate buffer solutions recommended by IUPAC (in 1985 and 2002) at temperatures from (0 to 70) °C. Values of p(m_H), giving the molality of hydrogen ions directly, calculated from these equations are also tabulated for these buffers as well as for the buffer solutions with NaCl or KCl as major component and with KH_2PO_4 and Na_2HPO_4 at an equal molality of 0.0025 mol·kg^{-1} as minor components.

Introduction

In the first part[1] (Part 1) of this study, activity coefficient equations of the Hückel type were presented for the calculation of the speciation of phosphate buffer solutions containing sodium or potassium dihydrogen phosphate with disodium hydrogen phosphate and sodium chloride at temperatures from (0 to 60) °C. The activity parameters describing interactions between sodium ions and dihydrogen and hydrogen phosphate ions were determined for these equations from the Harned cell data measured by Bates and Acree[2] in NaH_2PO_4, Na_2HPO_4, and NaCl solutions. Also the thermodynamic values of the second dissociation constant (K_{a2}) of phosphoric acid at various temperatures were determined from these data. The activity parameters describing interactions between potassium ions and dihydrogen and hydrogen phosphate ions were determined for these equations from the Harned cell data measured by Bates and Acree[3] in KH_2PO_4, Na_2HPO_4, and NaCl solutions. The resulting Hückel model was also tested with good results in Part 1 with the data used in the parameter estimations.

In the present part (Part 2), the tests of the new Hückel model have been made on all reliable thermodynamic data in the literature from the second dissociation reaction of phosphoric acid in NaCl and KCl solutions. Bates and Acree also gave in their first paper[2] Harned cell data for phosphoric acid in KH_2PO_4, Na_2HPO_4, and NaCl solutions at temperatures from (0 to 60) °C, and these data were included in the present tests as well as the studies discussed below. For the determination of pH values of the standard buffer solution for blood and other physiological media, Bower et al.[4] measured Harned cells using phosphate solutions with KCl containing a molality ratio of 1/3.5 of KH_2PO_4 and Na_2HPO_4, respectively, at temperatures from (0 to 50) °C. To set up standards for pH measurements in isotonic saline media of the ionic strength of 0.16 mol·kg^{-1}, Bates et al.[5] measured at (25 and 37) °C with Harned cells in the presence of NaCl the phosphate buffer solutions where $m(KH_2PO_4)/m(Na_2HPO_4)$ was also 1/3.5. To determine pH standards for higher temperatures from (60 to 95) °C, Bower and Bates[6] measured Harned cells in KH_2PO_4 and Na_2HPO_4 solutions at the same molality of 0.025 mol·kg^{-1} in both electrolytes, and the solutions also contained KCl. Vega et al.[7] measured Harned cells with equimolal KH_2PO_4 and Na_2HPO_4 solutions that also contained high molalities of NaCl at temperatures from (5 to 45) °C. Nims[8] measured cell potential differences (cpd) of Harned cells containing solutions of NaH_2PO_4 or KH_2PO_4, Na_2HPO_4, and NaCl at temperatures from (20 to 50) °C. Grzybowski[9] measured KH_2PO_4, $NaKHPO_4$, and NaCl solutions with cells containing a hydrogen electrode and a mercury−mercury(I) chloride electrode at temperatures from (5 to 50) °C. Using cells containing two liquid junctions and a hydrogen electrode and the saturated

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calomel electrode, Cohn[10] measured pH values for KH_2PO_4 and K_2HPO_4 solutions at 18 °C. Johansson and Wedborg[11] at (5, 15, and 25) °C, Hershey et al.[12] at 25 °C, and Atlas et al.[13] at 20 °C determined stoichiometric values for the second dissociation constant of phosphoric acid in NaCl and KCl solutions using potentiometric titration in glass electrode cells. Finally, the results from the general equations for stoichiometric dissociation constants of weak acids, determined by DeRobertis et al.[14] on the basis of the glass electrode data, were compared to those obtained by the presently recommended Hückel method.

The new calculation method recommended in Part 1 usually applies well to the data used in these tests. Therefore, it can be used for various purposes. On this basis, we present first the stoichiometric values (K_{m2}) for this dissociation constant at various temperatures in NaCl or KCl solutions where the salt effectively determines the ionic strength. Also equations are given for calculation of pH and $p(m_H)$ [$= -\log(m_H/m°)$ where $m°$ is 1 $mol \cdot kg^{-1}$] values for phosphate buffer solutions recommended by IUPAC, and the resulting pH values are compared to the recommended pH values. Calculated $p(m_H)$ values are also tabulated for buffer solutions containing NaCl or KCl as the major component and phosphate salts as minor components for calibration of glass electrode cells for direct measurements of hydrogen ion molality.

Theory

In the present study, the following equations are used for the molality scale activity coefficients (γ) of the ions in aqueous buffer solutions resulting from sodium or potassium salts of dihydrogen phosphate and hydrogen phosphate containing added chloride ions:

$$\ln \gamma_H = -\frac{\alpha\sqrt{I_m}}{1 + B_H\sqrt{I_m}} + b_{H,Cl}(m_{Cl}/m°) + \theta_{H,Na}(m_{Na}/m°) + \theta_{H,K}(m_K/m°) \quad (1)$$

$$\ln \gamma_{Cl} = -\frac{\alpha\sqrt{I_m}}{1 + B_{Cl}\sqrt{I_m}} + b_{H,Cl}(m_H/m°) + b_{Na,Cl}(m_{Na}/m°) + b_{K,Cl}(m_K/m°) \quad (2)$$

$$\ln \gamma_{HA} = -\frac{\alpha\sqrt{I_m}}{1 + B_{HA}\sqrt{I_m}} + b_{Na,HA}(m_{Na}/m°) + b_{K,HA}(m_K/m°) + \theta_{HA,A}(m_A/m°) \quad (3)$$

$$\ln \gamma_A = -\frac{4\alpha\sqrt{I_m}}{1 + B_A\sqrt{I_m}} + b_{Na,A}(m_{Na}/m°) + b_{K,A}(m_K/m°) + \theta_{HA,A}(m_{HA}/m°) \quad (4)$$

where $m° = 1\ mol \cdot kg^{-1}$ and where the following symbols are used: H = H^+, Cl = Cl^-, Na = Na^+, K = K^+, HA = $H_2PO_4^-$, and A = HPO_4^{2-}. I_m in these equations is the ionic strength on the molality scale, α is the Debye−Hückel parameter, and the values of this parameter at various temperatures were given in Tables 1−3 of Part 1.[1] B_i is a parameter that is dependent on ion i, and $b_{i,j}$ or $\theta_{i,j}$ are the ion−ion interaction parameters between ions i and j that have opposite or like charges, respectively. The following constant values were determined or already given for these equations in Part 1: $B_H = B_{Cl} = 1.4\ (mol \cdot kg^{-1})^{-1/2}$, $B_{HA} = B_A = 1.3\ (mol \cdot kg^{-1})^{-1/2}$, $\theta_{HA,A} = -1.00$, and $q_K = b_{K,A} + \theta_{H,K} - b_{K,HA} = 0.40$. Additionally, the following results are given in Part 1:

$$b_{H,Cl} = 0.30645 - 0.001006(t/°C) \quad (5)$$

$$b_{Na,Cl} + \theta_{H,Na} = 0.12175 + 0.001075(t/°C) - 0.0000104(t/°C)^2 \quad (6)$$

$$b_{K,Cl} + \theta_{H,K} = 0.00944 + 0.0009389(t/°C) - 0.0000094(t/°C)^2 \quad (7)$$

$$q_{Na} = b_{Na,A} + \theta_{Na,A} - b_{Na,HA} = -0.2172 + 0.005886(t/°C) - 0.000046(t/°C)^2 \quad (8)$$

The second thermodynamic dissociation constant (K_{a2}) of phosphoric acid is given by

$$K_{a2} = \frac{\gamma_H\gamma_A m_H m_A}{\gamma_{HA} m_{HA} m°} = \left(\frac{\gamma_H\gamma_A}{\gamma_{HA}}\right)K_{m2} \quad (9)$$

The stoichiometric dissociation constant K_{m2} in this equation is defined by equation $K_{m2} = m_H m_A/(m_{HA} m°)$. In Part 1, the following equation was determined for the temperature dependence of K_{a2}:

$$\ln K_{a2} = -16.82131 + 0.013846(t/°C) - 0.000163(t/°C)^2 \quad (10)$$

Results and Discussion

Results with the New Parameter Values from Data of Ref 2 on Cell 20 in Part 1. Bates and Acree[2] obtained precise data from Harned cells of the following type at temperatures from (0 to 60) °C:

$$Pt(s)|H_2(g, f = 101.325\ kPa)|MH_2PO_4(aq, m_a), Na_2HPO_4(aq, m_b), NCl(aq, m_s)|AgCl(s)|Ag(s) \quad (11)$$

where f is the fugacity and where N = Na^+. The data where M = Na^+ were used in Part 1 to estimate the K_{a2} values for phosphoric acid and the Hückel parameters for phosphate ions at various temperatures. In their first paper[2] at these temperatures, Bates and Acree also presented data sets where M is K^+ for the molality ratios of $m_a/m_b = 1.57$ and $m_a/m_s = 1.000$. The experimental K_{m2} values were obtained from these KH_2PO_4 data as described in Part 1 for the corresponding data of the second paper of Bates and Acree[3] (see Tables 6−8 in Part 1). The resulting K_{m2} values were then predicted with the Hückel model with the results shown here as pK_{m2} error plots in panels A [from (0 to 25) °C] and B [from (30 to 60) °C] of Figure 1. In these plots, the pK_{m2} error defined by

$$e(pK_{m2}) = pK_{m2}(\text{observed}) - pK_{m2}(\text{predicted}) \quad (12)$$

is presented at each temperature as a function of the ionic strength of the solution. These error plots correspond exactly to those presented in the four panels of Figures 1 and 2 in Part 1. The KH_2PO_4 data of Bates and Acree[2] support well the new Hückel model at the higher temperatures (panel B) but only satisfactorily at the lower temperatures (panel A).

Results with the New Parameter Values from Harned Cell Data of Refs 4 and 5 for Physiological Buffer Solutions. Bower et al.[4] reported precise data on Harned cells of type 11 where M = N = K^+, $m_a = 0.008695\ mol \cdot kg^{-1}$, $m_b = 0.03043\ mol \cdot kg^{-1}$, and where three molalities of (0.005, 0.010, and 0.015) $mol \cdot kg^{-1}$ were used for m_s at temperatures from (0 to 50) °C at intervals of 5 °C

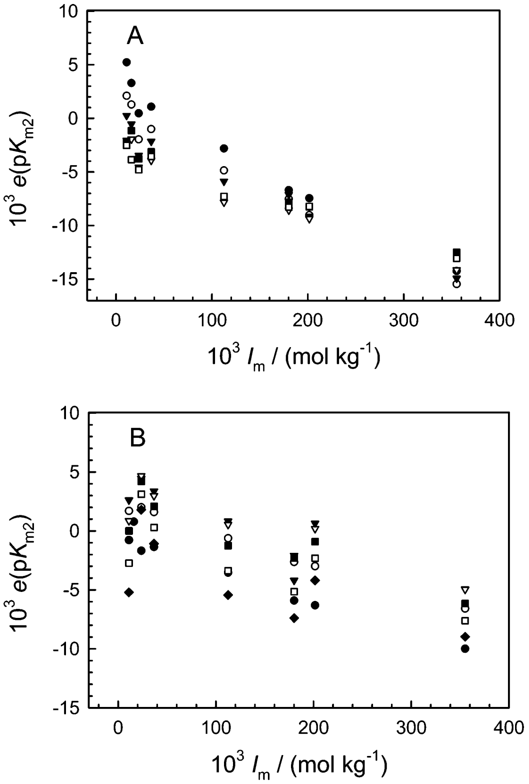

Figure 1. Differences, $e(\mathrm{p}K_{\mathrm{m2}})$ in eq 12, between the experimental $\mathrm{p}K_{\mathrm{m2}}$ values obtained for phosphoric acid from the cell potential data of Bates and Acree[2] on cell 11 where $\mathrm{M} = \mathrm{K}^+$ and $\mathrm{N} = \mathrm{Na}^+$ and those predicted by the Hückel method as a function of the ionic strength (I_{m}). The K_{m2} values were predicted by means of eqs 1, 3, 4, and 9 with the K_{a2} values calculated from eq 10 and with the suggested parameter values: ●, 0 °C (A), 30 °C (B); ○, 5 °C (A), 35 °C (B); ▼, 10 °C (A), 40 °C (B); ▽, 15 °C (A), 45 °C (B); ■, 20 °C (A), 50 °C (B); □, 25 °C (A), 55 °C (B); ◆, 60 °C (B).

including the temperature of 38 °C (that is close to the physiological temperature). At each KCl molality and at each temperature, several replicate determinations were reported, and these data were used by Bower et al. to determine the pH values for the chloride-free standard buffer solution, where $m_{\mathrm{a}} = 0.008695$ mol·kg^{-1} and $m_{\mathrm{b}} = 0.03043$ mol·kg^{-1} for blood and other physiological media at various temperatures. In the present Hückel model tests, these data were used as described above for the data of Bates and Acree.[2] The resulting error plots are shown in panels A (for salt molality $m_{\mathrm{s}} = 0.005$ mol·kg^{-1}), B ($m_{\mathrm{s}} = 0.01$ mol·kg^{-1}), and C ($m_{\mathrm{s}} = 0.015$ mol·kg^{-1}) of Figure 2. In the error plots of this figure, the $\mathrm{p}K_{\mathrm{m2}}$ errors defined by eq 12 are shown as a function of the temperature (*t*), and these plots support the applied model well. For the calculations at 38 °C, the parameter values shown in Table 1 of this part were used, obtained by linear interpolation of the reported $E°$ and α values in Tables 1−3 of Part 1.

Bates et al.[5] have measured on Harned cells of type 11 where $\mathrm{M} = \mathrm{K}^+$ and $\mathrm{N} = \mathrm{Na}^+$. To determine standards for pH measurements in isotonic saline media of ionic strength of 0.16 mol·kg^{-1}, they measured six solutions at (25 and 37) °C. In three of those, the ionic strength resulting from the phosphate species was 0.1 mol·kg^{-1}, the molalities of the phosphate components were $m_{\mathrm{a}} = 0.008695$ mol·kg^{-1} and $m_{\mathrm{b}} = 0.03043$ mol·kg^{-1} (i.e., $m_{\mathrm{a}}/m_{\mathrm{b}} = 1/3.5$), and the following three molalities of NaCl were used: 0.02, 0.04, and 0.06 mol·kg^{-1}. In the other three solutions, the molality ratio of $m_{\mathrm{a}}/m_{\mathrm{b}}$ was also 1/3.5 but the ionic strengths resulting from phosphate species [$= I_{\mathrm{m}}$(phosphate)] and salt molalities (m_{s}) in those were as follows: I_{m}(phosphate) = 0.08 and $m_{\mathrm{s}} = 0.08$, 0.06, and 0.10, and 0.04 and 0.12 mol·kg^{-1}.

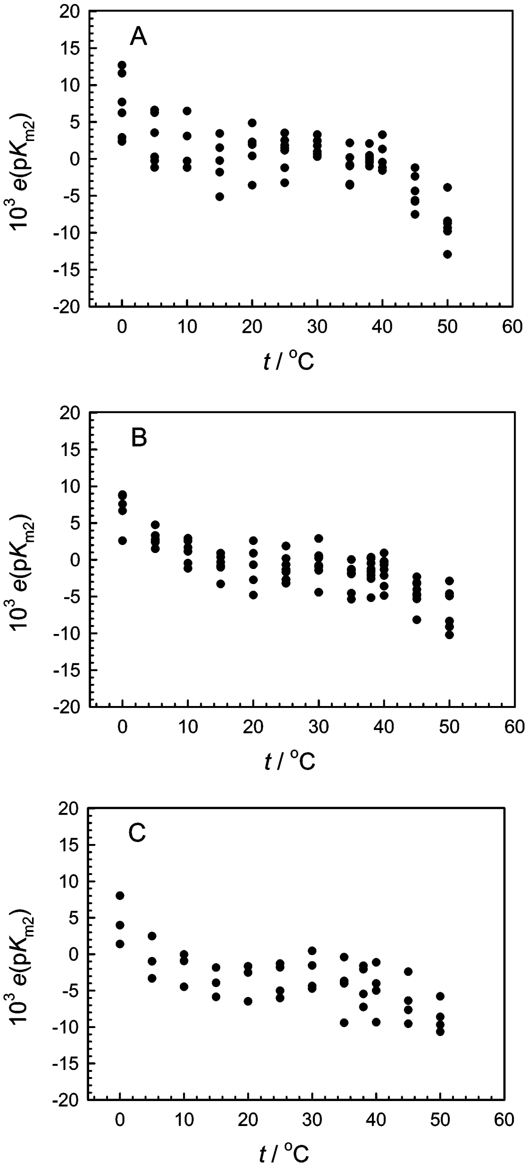

Figure 2. Differences, $e(\mathrm{p}K_{\mathrm{m2}})$ in eq 12, between the experimental $\mathrm{p}K_{\mathrm{m2}}$ values obtained for phosphoric acid from the cell potential data of Bower et al.[4] on cell 11 where $\mathrm{M} = \mathrm{N} = \mathrm{K}^+$, $m_{\mathrm{a}} = 0.008695$ mol·kg^{-1}, $m_{\mathrm{b}} = 0.03043$ mol·kg^{-1}, and $m_{\mathrm{s}} = 0.005$ mol·kg^{-1} (panel A), 0.010 mol·kg^{-1} (B), and 0.015 mol·kg^{-1} (C) and those predicted by the Hückel method as a function of the temperature (*t*). The K_{m2} values were predicted by means of eqs 1, 3, 4, and 9 with the K_{a2} values calculated from eq 10 and with the suggested parameter values.

Table 1. Debye−Hückel Parameter (α) and Standard Potential of Silver−Silver Chloride Electrode ($E°$) as a Function of Temperature at Higher Temperatures

t / °C	α / (mol·kg^{-1})$^{-1/2}$	$E°$ / mV	*t* / °C	α / (mol·kg^{-1})$^{-1/2}$	$E°$ / mV
37	1.2001[a]	214.30[a]	80	1.3143[b]	178.52[c]
38	1.2023[a]	213.57[a]	90	1.3460[b]	169.23[c]
60	1.2568[b]	196.19[c]	95	1.3626[b]	164.74[c]
70	1.2846[b]	187.56[c]			

[a] Estimated as described in the text. [b] Given by ref 15. [c] Estimated by Partanen and Covington[16] from the data of Bates and Bower.[17]

The data of Bates et al.[5] were used in the present Hückel model tests as the data of Bates and Acree[2] above, and the resulting error plots are given in Figure 3 where $\mathrm{p}K_{\mathrm{m2}}$

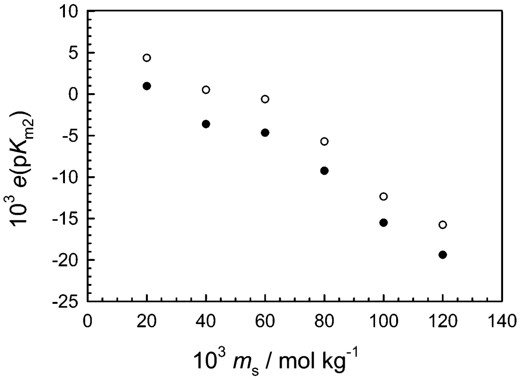

Figure 3. Differences, $e(\mathrm{p}K_{\mathrm{m2}})$ in eq 12, between the experimental $\mathrm{p}K_{\mathrm{m2}}$ values obtained for phosphoric acid from the cell potential data of Bates et al.[5] on cell 11 where $\mathrm{M} = \mathrm{K}^+$, $\mathrm{N} = \mathrm{Na}^+$ and $m_a/m_b = 1/3.5$ (see text) and those predicted by the Hückel method as a function of the salt molality (m_s). The K_{m2} values were predicted by means of eqs 1, 3, 4, and 9 with the K_{a2} values calculated from eq 10 and with the suggested parameter values. ●, 25 °C; ○, 37 °C.

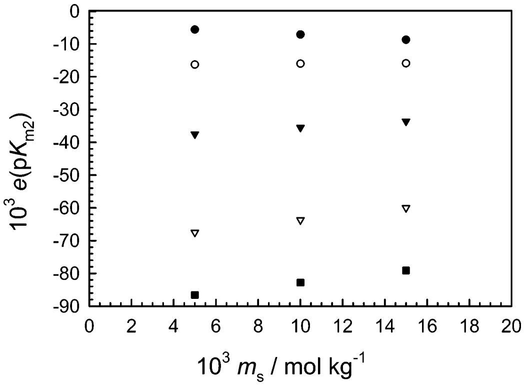

Figure 4. Differences, $e(\mathrm{p}K_{\mathrm{m2}})$ in eq 12, between the experimental $\mathrm{p}K_{\mathrm{m2}}$ values obtained for phosphoric acid from the cell potential data of Bower and Bates[6] on cell 11 where $\mathrm{M} = \mathrm{N} = \mathrm{K}^+$ and $m_a = m_b = 0.025\ \mathrm{mol{\cdot}kg^{-1}}$ and those predicted by the Hückel method as a function of salt molality (m_s). The K_{m2} values were predicted by means of eqs 1, 3, 4, and 9 with the K_{a2} values calculated from eq 10 and with the suggested values. ●, 60 °C; ○, 70 °C; ▼, 80 °C; ▽, 90 °C; ■, 95 °C.

errors, defined by eq 12, are shown as a function of the salt molality m_s. For the calculations at 37 °C, the $E°$ and α values shown in the present Table 1 were used, derived by linear interpolation from the reported values of these quantities in Tables 1−3 of Part 1. The error plots in Figure 3 support satisfactorily the chosen model because all absolute $\mathrm{p}K_{\mathrm{m2}}$ errors are smaller than 0.02.

Results with the New Parameter Values from Harned Cell Data of Ref 6 at Elevated Temperatures. Bower and Bates[6] obtained precise data on Harned cells of type 11 where $\mathrm{M} = \mathrm{N} = \mathrm{K}^+$, $m_a = m_b = 0.02500\ \mathrm{mol{\cdot}kg^{-1}}$, and three molalities of (0.005, 0.010, and 0.015) $\mathrm{mol{\cdot}kg^{-1}}$ were used for m_s at temperatures from (60 to 90) °C at intervals of 10 °C and also at 95 °C. Their purpose was to determine standard pH values for the phosphate buffer solution where $m_a = m_b = 0.02500\ \mathrm{mol{\cdot}kg^{-1}}$ at high temperatures. At each KCl molality and each temperature, replicate determinations were made. In the original paper,[6] cell potential data (E) were not reported, but the data were fit to the following linear representation:

$$\mathrm{p}w\mathrm{H} \equiv \frac{(E - E^\circ)F}{\ln(10)RT} + \log(m_{\mathrm{Cl}}/m^\circ) = \mathrm{p}w\mathrm{H}^\circ + a m_s \quad (13)$$

The results of the regression analysis were reported at each temperature (i.e., the values of parameters $\mathrm{p}w\mathrm{H}^\circ$ and a).

In the present Hückel model tests, the cell potential difference was back calculated from these reported $\mathrm{p}w\mathrm{H}^\circ$ and a values at each temperature and each molality of KCl, and the resulting E value was used in the tests. Otherwise, the calculations of these tests corresponded exactly to the calculations performed above for the data of Bates et al.[5] In the calculations for the higher temperatures, $E°$ and α values shown in Table 1 were used. The other parameters needed beyond 60 °C were calculated from eqs 5 to 10, and the resulting values were thus extrapolated ones. The error plots from these data are shown in Figure 4. The data for temperatures (60 and 70) °C support the model well, but the data for 80 °C only satisfactorily. The data at 90 and 95 °C cannot be explained by using the model, probably because of the long extrapolations needed.

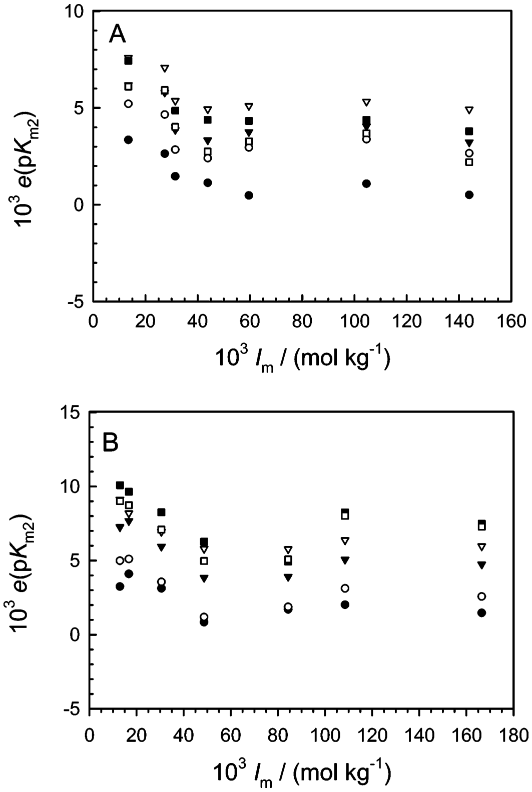

Figure 5. Differences, $e(\mathrm{p}K_{\mathrm{m2}})$ in eq 12, between the experimental $\mathrm{p}K_{\mathrm{m2}}$ values obtained for phosphoric acid from the cell potential data of Nims[8] on cell 11 where $\mathrm{N} = \mathrm{Na}^+$ and $\mathrm{M} = \mathrm{Na}^+$ (NimsA, panel A, see text) or $\mathrm{M} = \mathrm{K}^+$ (NimsB, panel B, see text) and those predicted by the Hückel method as a function of the ionic strength (I_m). The K_{m2} values were predicted by means of eqs 1, 3, 4, and 9 with the K_{a2} values calculated from eq 10 and with the suggested parameter values. ●, 25 °C (A), 20 °C (B); ○, 30 °C (A), 25 °C (B); ▼, 35 °C (A), 30 °C (B); ▽, 40 °C (A), 35 °C (B); ■, 45 °C (A), 40 °C (B); □, 50 °C (A), 45 °C (B).

Results with the New Parameter Values from Harned Cell Data of Ref 8. Nims[8] measured Harned cells of type 11 where $\mathrm{N} = \mathrm{Na}^+$ and where $\mathrm{M} = \mathrm{Na}^+$ or K^+. The data for seven solutions where $\mathrm{M} = \mathrm{Na}^+$ covered the temperature range from (25 to 50) °C and are denoted here by NimsA. The molality ratios of $m_a/m_b = 0.9969$ and $m_a/m_s = 1.0000$ were used in these sets and for the strongest solution $m_a = 0.28733\ \mathrm{mol{\cdot}kg^{-1}}$. The data for $\mathrm{M} = \mathrm{K}^+$ covered the temperature range from (20 to 45) °C, consisting of seven solutions, and these data are denoted as NimsB. Molality ratios of $m_a/m_b = m_a/m_s = 1.2803$ were used, and $m_a = 0.40367\ \mathrm{mol{\cdot}kg^{-1}}$ in the strongest solution in these sets.

Table 2. Standard Potential of Mercury−Mercury(I) Chloride Electrode ($E°$) as a Function of Temperature (t) According to Grzybowski[18]

	t/°C									
	5	10	15	20	25	30	35	40	45	50
$E°$/mV	273.21	272.18	270.99	269.64	268.13	266.47	264.67	262.73	260.66	258.46

In the present tests of the Hückel model, the data of NimsA and NimsB were analyzed similarly to those of Bates and Acree,[2] and the error plots are shown in panels A (NimsA) and B (NimsB) of Figure 5. In the error plots of these data, pK_{m2} errors are shown as a function of the ionic strength, and these plots support the proposed model well.

Results with the New Parameter Values from the Hydrogen−Mercury Mercury(I) Chloride Electrode Cell Data of Ref 9. Grzybowski[9] obtained very precise data on calomel electrode cells of the following type at temperatures from (5 to 50) °C:

$$\mathrm{Pt(s)|H_2(g,}\ f = 101.325\ \mathrm{kPa)|KH_2PO_4(aq,}\ m_a\mathrm{),\ KNaHPO_4(aq,}\ m_b\mathrm{),\ NaCl(aq,}\ m_s\mathrm{)|Hg_2Cl_2(s)|Hg(l)} \quad (14)$$

The molality ratios used were $m_a/m_b = 2.0527$ and $m_s/m_b = 3.3349$. Experimental K_{m2} values were obtained from these sets principally in the same way as from the data of Bates and Acree.[2] In the calculation of the experimental K_{m2} values, however, $E°$ values for mercury−mercury(I) chloride electrodes at various temperatures are needed. The values used are shown in Table 2, and those were determined by Grzybowski[18] from the hydrogen-calomel electrode cell containing hydrochloric acid at various temperatures.

The resultant experimental K_{m2} values were used to test the present Hückel model with the results shown as pK_{m2} error plots (see eq 12) in panels A [from (5 to 25) °C] and B [from (30 to 50) °C] of Figure 6. In these plots, the errors are presented as a function of the ionic strength, and the data support the applied model well.

Results with the New Activity Parameters from Harned Cell Data of Ref 7 at Higher Salt Molalities. Vega et al.[7] measured Harned cells of type 11 where M = K$^+$, N = Na$^+$, and $m_a = m_b$, and temperatures from (5 to 45) °C with intervals of 10 °C were used. Two series of buffer solutions were measured: in one series the ionic strength of the solutions was approximately 1.00 mol·kg^{-1} and in the other 3.00 mol·kg^{-1}, and the values of m_a varied in both series from (0.01 to 0.1) mol·kg^{-1}. The data set where $I_m = 1.00$ mol·kg^{-1} is here denoted by symbol VRBA, and the data set where $I_m = 3.00$ mol·kg^{-1} by VRBB.

In the tests of the Hückel model, the data sets VRBA and VRBB were used similarly to data of Bates and Acree,[2] and the resulting error plots are shown in panels A (VRBA) and B (VRBB) of Figure 7 where the pK_{m2} errors are shown as a function of KH$_2$PO$_4$ molality (m_a). These data seem to be in error and cannot be predicted even satisfactorily without using the following arbitrarily adjusted values for the standard cell potential difference of cell 11: $E°$ (5 °C) = 224 mV, $E°$ (15 °C) = 217 mV, $E°$ (25 °C) = 209 mV, $E°$ (35 °C) = 200 mV, and $E°$ (45 °C) = 190 mV (instead of the values shown in Tables 1−3 for this quantity in Part 1). The error plots shown in Figure 7 have been calculated with these adjusted $E°$ values, and they support quite satisfactorily the tested Hückel model because the same adjusted $E°$ value can be used at each temperature for both ionic strengths of (1.0 and 3.0) mol·kg^{-1}.

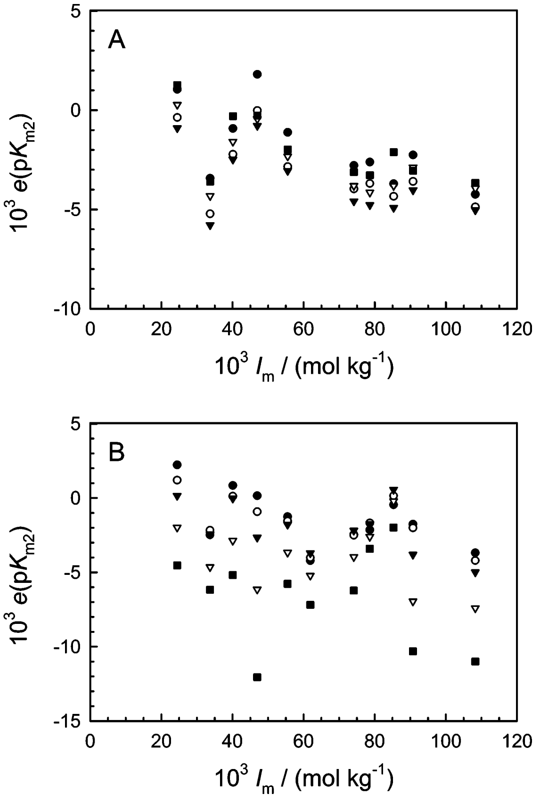

Figure 6. Differences, e(pK_{m2}) in eq 12, between the experimental pK_{m2} values obtained for phosphoric acid from the cell potential data of Grzybowski[9] on cell 14 and those predicted by the Hückel method as a function of the ionic strength (I_m). The K_{m2} values were predicted by means of eqs 1, 3, 4, and 9 with the K_{a2} values calculated from eq 10 and with the suggested parameter values (see text). ●, 5 °C (A), 30 °C (B); ○, 10 °C (A), 35 °C (B); ▼, 15 °C (A), 40 °C (B); ▽, 20 °C (A), 45 °C (B); ■, 25 °C (A), 50 °C (B).

Results with the New Parameter Values from pH Data of Ref 10 Measured on Cells Containing Liquid Junctions. Cohn[10] obtained extensive series of pH values at 18 °C using chloride-free cells of the following type containing a hydrogen electrode and a calomel electrode with double liquid junctions:

$$\mathrm{Pt(s)|H_2(g,}\ f = 101.3\ \mathrm{kPa)|KH_2PO_4(aq,}\ m_a\mathrm{),\ K_2HPO_4(aq,}\ m_b\mathrm{)||salt\ bridge(KCl)||KCl(aq,}\ c = 0.100\ \mathrm{mol{\cdot}dm^{-3})|Hg_2Cl_2(s)|Hg(l)} \quad (15)$$

In these series, the values of (0.0600, 0.1200, 0.3000, 0.6000, 0.9000, and 1.2000) mol·kg^{-1} were used for the total phosphate molality ($m_a + m_b$), and these series are denoted here as Ca, Cb, Cc, Cd, Ce, and Cf, respectively. In each series, the values for the molality ratio of m_a/m_b were 9, 5, 3, 2, 1, 0.5, and 0.125. These pH data were used previously[19] to evaluate activity coefficient equations for the calculation of pH values of phosphate buffer solutions at 25 °C.

In the present study, the experimental K_{m2} values were calculated from the reported pH values using eq 1 with values of $\theta_{H,K} = 0.012$ (see ref 20) and $\alpha = 1.1601$ (mol·kg^{-1})$^{-1/2}$ (obtained by linear interpolation for 18 °C from the reported α values in Table 2 of Part 1), and the resulting values were used in the Hückel model tests. The

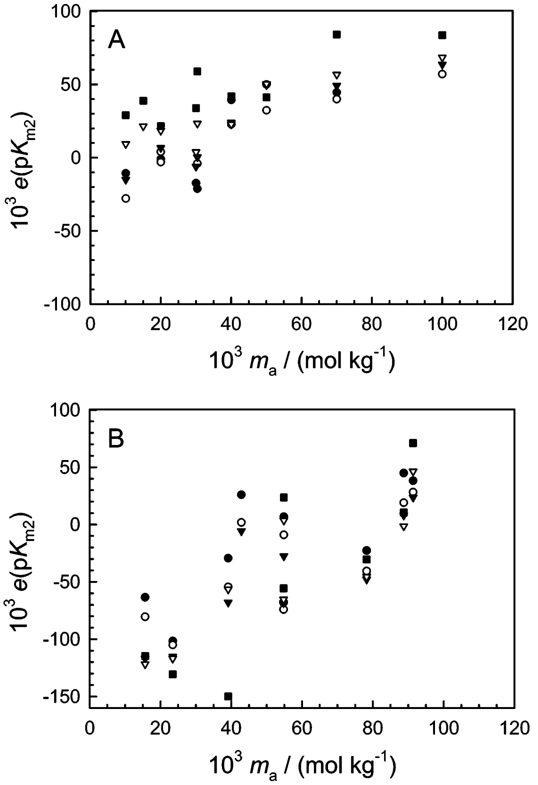

Figure 7. Differences, $e(\mathrm{p}K_{m2})$ in eq 12, between the experimental $\mathrm{p}K_{m2}$ values obtained for phosphoric acid from the cell potential data of Vega et al.[7] on cell 11 where M = K$^+$, N = Na$^+$, $m_a = m_b$, and $I_m = 1.0$ mol·kg^{-1} (VRBA, panel A, see text) or 3.0 mol·kg^{-1} (VRBB, panel B, see text) and those predicted by the Hückel method as a function of molality m_a. The K_{m2} values were predicted by means of eqs 1, 3, 4, and 9 with the K_{a2} values calculated from eq 10 and with the suggested parameter values (see text). ●, 5 °C; ○, 15 °C; ▼, 25 °C; ▽, 35 °C; ■, 45 °C.

reported pH values cannot be used in these tests before being appropriately corrected. The following equation was derived for the calculation of the corrected pH values from these data:

$$\mathrm{pH_{corrected}} = \mathrm{pH_{reported}} - \Delta\mathrm{pH} \qquad (16)$$

where

$$\Delta\mathrm{pH} = -0.0453 - 0.0766(I_m/m^\circ) \qquad (17)$$

and the empirical correction term ΔpH takes into account, for example, the calomel electrode and liquid junction potential corrections. The $\mathrm{p}K_{m2}$ error plots, see eq 12, for series Ca and Cb are shown in panel A and for the other series are shown in panel B of Figure 8. The small values of the errors in these two panels support the validity of the applied model.

Test Results with New Parameter Values from K_{m2} Data Measured on Cells Containing a Liquid Junction in NaCl and KCl Solutions That Are Very Dilute in Phosphate Ions. For aqueous mixtures of sodium or potassium dihydrogen phosphate and hydrogen phosphate, and MCl (where M is Na$^+$ or K$^+$) that are very dilute with respect to the phosphate ions, the following equation can be obtained on the basis of the present Hückel model:

$$\ln K_{m2} = \ln K_{a2} + \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{3}{1 + B_A\sqrt{I_m}}\right) - (b_{H,Cl} + q_M)(I_m/m^\circ) \qquad (18)$$

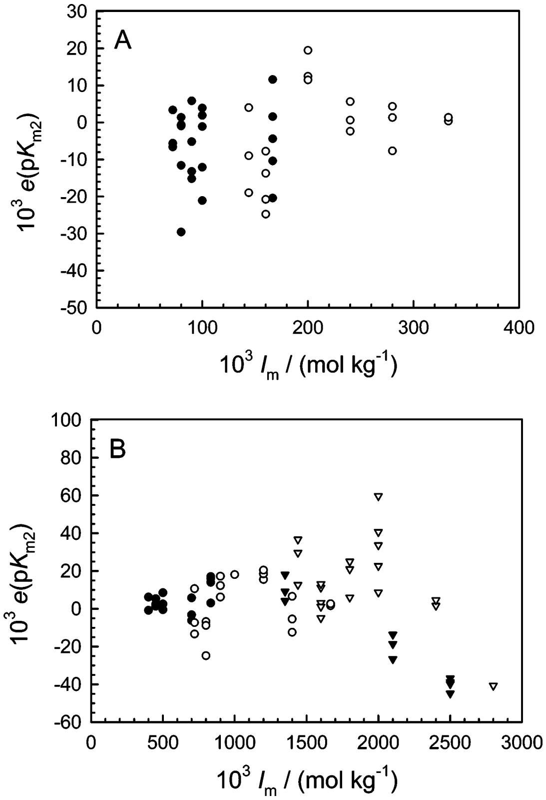

Figure 8. Differences, $e(\mathrm{p}K_{m2})$ in eq 12, between the experimental $\mathrm{p}K_{m2}$ values obtained for phosphoric acid from the pH data of Cohn[10] at 18 °C on cell 15 (from the pH data sets of Ca − Cf, see text) and those predicted by the Hückel method as a function of the ionic strength (I_m). K_{m2} values were predicted by means of eqs 1, 3, 4, and 9 with the K_{a2} values calculated from eq 10 and with the suggested parameter values. ●, Ca (A), Cc (B); ○, Cb (A), Cd (B); ▼, Ce (B); ▽, Cf(B).

Table 3. Recommended Values of the Second Stoichiometric Dissociation Constant ($10^8\ K_{m2}$) for Phosphoric Acid from Equation 18 at Various Temperatures as a Function of the Ionic Strength (I_m) in Aqueous NaCl Solution When the NaCl Molality Effectively Determines the Ionic Strength

	$10^8\ K_{m2}$ at I_m/mol·kg^{-1}								
t/°C	0	0.05	0.1	0.2	0.3	0.5	1.0	1.5	2.0
0	4.95	10.7	13.4	17.3	20.2	24.6	31.6	35.7	38.3
5	5.28	11.5	14.4	18.5	21.7	26.3	33.4	37.4	39.6
10	5.59	12.3	15.3	19.7	23.0	27.9	35.2	39.0	40.9
15	5.87	12.9	16.2	20.9	24.3	29.4	36.8	40.5	42.1
20	6.12	13.5	17.0	21.9	25.5	30.8	38.4	41.9	43.3
25	6.32	14.1	17.7	22.8	26.6	32.1	39.7	43.1	44.3
30	6.48	14.5	18.3	23.6	27.5	33.2	41.0	44.3	45.3
35	6.58	14.9	18.7	24.2	28.3	34.1	42.0	45.3	46.1
37	6.61	15.0	18.9	24.4	28.5	34.4	42.4	45.6	46.4
40	6.64	15.1	19.1	24.7	28.8	34.8	42.9	46.1	46.9
45	6.63	15.2	19.2	25.0	29.2	35.3	43.6	46.8	47.5
50	6.58	15.2	19.3	25.1	29.4	35.6	44.0	47.3	48.0
55	6.47	15.1	19.2	25.1	29.4	35.7	44.2	47.7	48.4
60	6.32	14.9	19.0	24.8	29.2	35.5	44.3	47.8	48.7
70	5.87	14.1	18.1	23.9	28.2	34.6	43.6	47.5	48.8
80	5.3	13	17	22	27	33	42	47	49

For NaCl solutions (M = Na$^+$), parameter q_{Na} is given by eq 8. For KCl solutions (M = K$^+$), parameter q_K is 0.40 at all temperatures. The K_{m2} values predicted by eq 18 are given at rounded ionic strengths and various temperatures in Tables 3 (NaCl) and 4 (KCl). The values calculated from eq 18 can be compared to K_{m2} values of phosphoric acid given in the literature for the NaCl and KCl solutions of this kind.

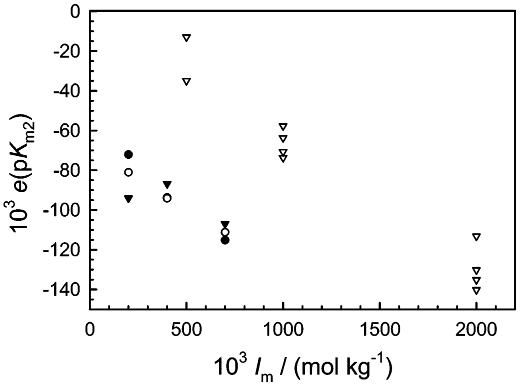

Figure 9. Differences, $e(\mathrm{p}K_{m2})$ in eq 12, between the experimental $\mathrm{p}K_{m2}$ values obtained for phosphoric acid from the glass electrode data of Johansson and Wedberg[11] (JoWe) and Hershey et al.[12] (HFM) for NaCl solutions and those predicted by the Hückel method as a function of the ionic strength (I_m). The K_{m2} values were predicted by means of eq 18 with the K_{a2} values calculated from eq 10 and with the suggested parameter values. ●, JoWe, 5 °C; ○, JoWe, 15 °C; ▼, JoWe, 25 °C; ▽, HFM, 25 °C.

Table 4. Recommended Values of the Second Stoichiometric Dissociation Constant ($10^8\ K_{m2}$) for Phosphoric Acid from Equation 18 at Various Temperatures as a Function of the Ionic Strength (I_m) in Aqueous KCl Solution When the KCl Molality Effectively Determines the Ionic Strength

	$10^8\ K_{m2}$ at I_m/mol·kg^{-1}								
t/°C	0	0.05	0.1	0.2	0.3	0.5	1.0	1.5	2.0
0	4.95	10.4	12.6	15.3	16.8	18.1	17.1	14.2	11.1
5	5.28	11.2	13.6	16.5	18.1	19.6	18.6	15.5	12.2
10	5.59	11.9	14.5	17.6	19.5	21.1	20.0	16.8	13.3
15	5.87	12.6	15.3	18.7	20.7	22.5	21.5	18.0	14.3
20	6.12	13.2	16.1	19.7	21.8	23.8	22.9	19.3	15.4
25	6.32	13.7	16.8	20.6	22.9	25.0	24.1	20.4	16.3
30	6.48	14.2	17.4	21.4	23.8	26.1	25.3	21.5	17.3
35	6.58	14.5	17.9	22.0	24.6	27.0	26.3	22.5	18.1
40	6.64	14.8	18.2	22.5	25.2	27.7	27.2	23.3	18.8
45	6.63	14.9	18.4	22.9	25.6	28.3	27.9	24.0	19.5
50	6.58	14.9	18.5	23.0	25.8	28.6	28.4	24.5	20.0
55	6.47	14.8	18.4	23.0	25.8	28.8	28.7	24.9	20.4
60	6.32	14.6	18.2	22.8	25.7	28.7	28.8	25.1	20.6
70	5.87	13.8	17.3	21.9	24.8	27.9	28.4	24.9	20.6
80	5.3	13	16	20	23	26	27	24	20

Johansson and Wedborg[11] measured using glass electrodes $\mathrm{p}K_{c2}$ values (c refers to the molarity scale) for phosphoric acid in NaCl solutions at molarities of (0.2, 0.4, and 0.7) mol dm^{-3} and at temperatures of (5, 15, and 25) °C. Despite the problems associated with the calibration of a glass electrode cell and the different concentration scales, the $\mathrm{p}K_{c2}$ values are used here in the Hückel model tests as experimental $\mathrm{p}K_{m2}$ values at molalities of (0.2, 0.4, and 0.7) mol·kg^{-1}, respectively, without correction. The results are shown in Figure 9 where $\mathrm{p}K_{m2}$ errors (see eq 12) are presented as a function of the ionic strength. If the calibration problems and an acceptable glass electrode error of 0.06 in pH (see ref 21) are taken into account, these data support the applied model satisfactorily.

Hershey et al.[12] have measured with glass electrodes $\mathrm{p}K_{m2}$ values for phosphoric acid in NaCl solutions at 25 °C at rounded molalities from 0.05 mol·kg^{-1}. Also these data up to I_m of 2.0 mol·kg^{-1} are used here to test the Hückel model without any correction. The results are shown in Figure 9. For the reasons mentioned in the previous paragraph, these data support the applied model satisfactorily.

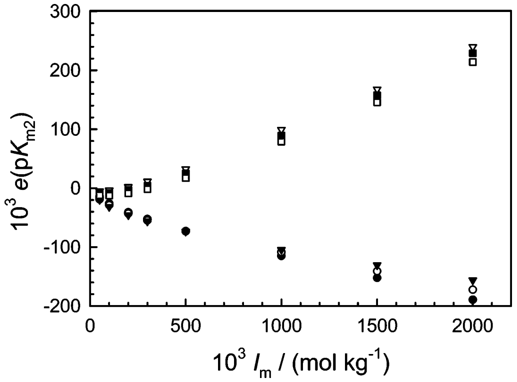

Figure 10. Differences between the recommended $\mathrm{p}K_{m2}$ values (Tables 3 and 4) and predicted $\mathrm{p}K_{m2}$ values, $e(\mathrm{p}K_{m2}) = \mathrm{p}K_{m2}$(recommended) − $\mathrm{p}K_{m2}$(predicted), for phosphoric acid in NaCl and KCl solutions as a function of the ionic strength (I_m). K_{m2} values were predicted from the equations of DeRobertis et al.,[14] see eq 19. ●, 20 °C, NaCl; ○, 25 °C, NaCl; ▼, 30 °C, NaCl; ▽, 20 °C, KCl; ■, 25 °C, KCl; □, 30 °C KCl.

Atlas et al.[13] have measured at 20 °C with glass electrodes a K_{c2} value of 4.0×10^{-7} for phosphoric acid at a 0.68 mol·dm^{-3} NaCl solution and a value of 2.8×10^{-7} at a 0.68 mol·dm^{-3} KCl solution. Also in the calculation of these values, the activity of hydrogen ions was used instead of the molarity. These values are used here as experimental K_{m2} values without any correction, and they are predicted by using the present Hückel model for phosphoric acid in NaCl and KCl solutions. The results are 3.4×10^{-7} and 2.4×10^{-7}, respectively. Thus, both $\mathrm{p}K_{m2}$ errors are approximately −0.07 and support the applied models satisfactorily.

The recommended K_{m2} values in Tables 3 and 4 can be compared to the values calculated from the general equations suggested by DeRobertis et al.[14] for K_m of various weak acids in NaCl and KCl solutions. For the second dissociation constant of phosphoric acid, this equation has the form:

$$\log K_{m2} = \log K_{a2} + \frac{4\sqrt{I_m/m^\circ}}{2 + 3\sqrt{I_m/m^\circ}} - C(I_m/m^\circ) - E(I_m/m^\circ)^2 \quad (19)$$

where parameters C and D depend on the salt (NaCl or KCl). In the present study, the equations for NaCl and KCl solutions were tested at the temperatures of (20, 25, and 30) °C. In NaCl solutions, the values of parameter C in eq 19 are (0.112, 0.105, and 0.098) at these temperatures, respectively.[14] Parameter E for NaCl does not depend on the temperature, and the value of 0.00548 was suggested. For KCl solutions, parameters C and E do not depend on the temperature and have the values of $C = 0.1264$ and $E = 0.00324$.

In the present tests, the NaCl and KCl forms from eq 19 were tested with the K_{m2} values calculated by the Hückel method and given in Tables 3 and 4. In the calculations, the K_{a2} values suggested in this study were used at the three temperatures considered (also shown in Tables 3 and 4). The results are shown as error plots in Figure 10 and show that values obtained using eq 19 agree satisfactorily with the recommended values for both NaCl and KCl solutions up to I_m of about 0.5 mol·kg^{-1}.

Suggested pH and p(m_H) Values for Phosphate Buffers. IUPAC[22,23] suggested pH values for the following two phosphate buffer solutions: 0.025 mol·kg^{-1} KH_2PO_4 + 0.025 mol·kg^{-1} Na_2HPO_4 (buffer I1) and 0.008695 mol·kg^{-1} KH_2PO_4 + 0.03043 mol·kg^{-1} Na_2HPO_4 (buffer I2).

Table 5. pH Values and p($m_{\rm H}$) Values for Phosphate Buffer Solutions, KH_2PO_4(aq, m_a) + Na_2HPO_4(aq, m_b) with $m_a = m_b = 0.025$ mol·kg^{-1} (Buffer I1) and KH_2PO_4(aq, m_a) + Na_2HPO_4(aq, m_b) with $m_a = 0.008695$ mol·kg^{-1} and $m_b = 0.03043$ mol·kg^{-1} (Buffer I2)

t/°C	pH (I1,re)[a]	pH (I1,pr)[b]	p[$m_{\rm H}$ (I1)][b]	pH (I2,re)[a]	pH (I2,pr)[b]	p[$m_{\rm H}$ (I2)][b]
0	6.984	6.974	6.868	7.534	7.523	7.417
5	6.951	6.944	6.837	7.500	7.493	7.387
10	6.923	6.917	6.809	7.472	7.466	7.359
15	6.900	6.894	6.785	7.448	7.443	7.335
20	6.881	6.874	6.764	7.429	7.423	7.314
25	6.865	6.857	6.747	7.413	7.407	7.297
30	6.853	6.844	6.733	7.400	7.394	7.283
35	6.844	6.834	6.722	7.389	7.384	7.272
37	6.841	6.831	6.718	7.386	7.381	7.269
40	6.838	6.827	6.714	7.380	7.377	7.264
45		6.824	6.710		7.374	7.260
50	6.833	6.824	6.709	7.367	7.374	7.259
55		6.828	6.711		7.378	7.261
60	6.836	6.835	6.717		7.385	7.267
70	6.845	6.858	6.738			
80	6.859	6.90	6.77			

[a] Recommended by Covington et al.[22] [b] Predicted in the present study.

Table 6. pH Values and p($m_{\rm H}$) Values for Phosphate Buffer Solutions, KH_2PO_4(aq, m_a) + Na_2HPO_4(aq, m_b) + NaCl(aq, m_s), with $m_a = 0.005217$ mol·kg^{-1}, $m_b = 0.018258$ mol·kg^{-1}, and $m_b = 0.10000$ mol·kg^{-1}

t/°C	pH(BVW)[a]	pH[b]	p($m_{\rm H}$)[b]
0		7.452	7.343
5	7.406	7.422	7.313
10	7.379	7.396	7.286
15	7.356	7.373	7.261
20	7.337	7.354	7.241
25	7.323	7.337	7.223
30	7.309	7.324	7.208
35	7.298	7.314	7.197
37	7.297	7.311	7.193
40	7.291	7.308	7.189
45	7.289	7.304	7.184
50	7.287	7.304	7.182
55		7.307	7.184
60		7.313	7.188

[a] Reported by Bates et al.[5] [b] Predicted in the present study.

Table 7. p($m_{\rm H}$) Values at Various Temperatures for the Phosphate Buffer Solutions, KH_2PO_4(aq, m_a) + Na_2HPO_4(aq, m_b) + MCl(aq, m_s), with $m_a = m_b = 0.0025$ mol·kg^{-1} and $m_s = 0.2$ mol·kg^{-1}, with $m_a = m_b = 0.0025$ mol·kg^{-1} and $m_s = 0.5$ mol·kg^{-1}, and with $m_a = m_b = 0.0025$ mol·kg^{-1} and $m_s = 1.0$ mol·kg^{-1} Where M Is Na^+ or K^+

	p($m_{\rm H}$) at m_s/mol·kg^{-1}					
t/°C	0.2[a]	0.5[a]	1.0[a]	0.2[b]	0.5[b]	1.0[b]
0	6.754	6.605	6.498	6.807	6.739	6.766
5	6.723	6.576	6.474	6.774	6.704	6.730
10	6.696	6.551	6.452	6.745	6.673	6.696
15	6.672	6.528	6.432	6.719	6.645	6.666
20	6.651	6.508	6.414	6.696	6.620	6.639
25	6.634	6.490	6.399	6.677	6.599	6.616
30	6.619	6.476	6.386	6.661	6.580	6.595
35	6.607	6.464	6.375	6.648	6.565	6.578
37	6.604	6.460	6.371			
40	6.599	6.455	6.366	6.638	6.554	6.564
45	6.594	6.448	6.359	6.632	6.545	6.553
50	6.591	6.445	6.355	6.629	6.540	6.545
55	6.592	6.444	6.353	6.630	6.538	6.540
60	6.596	6.446	6.352	6.633	6.539	6.539
70	6.613	6.457	6.359	6.651	6.551	6.546

[a] MCl is NaCl. [b] MCl is KCl.

In ref 23, pH values for these buffers are reported at temperatures from (0 to 50) °C. In ref 22, additional pH values for buffer I1 are reported from (60 to 95) °C. Bates et al.[5] reported the pH values for the following buffer solution from (5 to 50) °C: 0.005217 mol·kg^{-1} KH_2PO_4 + 0.018258 mol·kg^{-1} Na_2HPO_4 + 0.10000 mol·kg^{-1} NaCl (denoted here as buffer BVW).

Use of the Hückel method permits the calculation of the values of p($m_{\rm H}$) [= $-\log(m_{\rm H}/m°)$] for these phosphate buffer solutions, and, additionally with some extra assumptions concerning the values of parameters $\theta_{\rm H,Na}$ and $\theta_{\rm H,K}$, the calculation of pH values of these buffers and the comparison of the resulting pH values with the IUPAC values. In the calculation of the pH values, the assumptions that $\theta_{\rm H,Na} = 0.070$ (see ref 24) and $\theta_{\rm H,K} = 0.012$ (see ref 20) at all temperatures considered are made here. The latter assumption is also supported above by the pH data measured by Cohn at 18 °C in phosphate buffer solutions. In the calculation of p($m_{\rm H}$) values, these assumptions are not needed; therefore, p($m_{\rm H}$) values can be predicted more reliably than pH values. For the buffers I1 and I2, the results of the comparison of the pH values recommended by IUPAC with the values predicted by the Hückel model are shown in Table 5. For the buffer BVW, this comparison is made in Table 6. In this comparison, the agreement is usually within 0.01 in Table 5 and within 0.02 in Table 6.

The p($m_{\rm H}$) values in salt solutions dilute with respect to the weak acid species can be used to calibrate glass electrode cells, particularly for titrimetry, so that the cells should measure directly the molality of hydrogen ions.[24] Such p($m_{\rm H}$) values are shown in Table 7 for the following six phosphate buffers in NaCl and KCl solutions at temperatures from (0 to 70) °C. The buffer solutions contain 0.0025 mol·kg^{-1} KH_2PO_4, 0.0025 mol·kg^{-1} Na_2HPO_4, and NaCl or KCl with the molalities of (0.2, 0.5, or 1.0) mol·kg^{-1}. The results in Table 7 are analogous to the results in Table 14 of the previous acetic acid paper[24] and can be used similarly.

Literature Cited

(1) Partanen, J. I.; Covington, A. K. Re-evaluation of second stoichiometric dissociation constants of phosphoric acid at temperatures from (0 to 60) °C in aqueous buffer solutions with or without NaCl or KCl. 1. Estimation of the parameters for the Hückel model activity coefficient equations. *J. Chem. Eng. Data* **2005**, *50*, 1502−1509.

(2) Bates, R. G.; Acree, S. F. H Values of certain phosphate−chloride mixtures, and the second dissociation constant of phosphoric acid from 0° to 60 °C. *J. Res. Natl. Bur. Stand.* **1943**, *30*, 129−155.

(3) Bates, R. G.; Acree S. F. pH values of aqueous mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate at 0° to 60 °C. *J. Res. Natl. Bur. Stand.* **1945**, *34*, 373−394.

(4) Bower, V. E.; Paabo, M.; Bates, R. G. A standard for the measurement of the pH of blood and other physiological media. *J. Res. Natl. Bur. Stand. Sect. A* **1961**, *65*, 267−270.

(5) Bates, R. G.; Vega, C. A.; White, D. R. Standards for pH measurements in isotonic saline media of ionic strength $I = 0.16$. *Anal. Chem.* **1978**, *50*, 1295−1300.

(6) Bower, V. E.; Bates, R. G. Standards for pH measurements from 60° to 95 °C. *J. Res. Natl. Bur. Stand.* **1957**, *59*, 261−264.

(7) Vega, C. A.; Romero, M.; Bates, R. G. First and second dissociation constants of phosphoric acid in 1 and 3 *m* sodium chloride solutions from 268.15 to 318.15 K. *J. Chem. Eng. Data* **1994,** *39*, 294−297.

(8) Nims, L. F. The second dissociation constant of phosphoric acid from 20 to 50°. *J. Am. Chem. Soc.* **1933**, *55*, 1946−1951.

(9) Grzybowski, A. K. The standard potential of the calomel electrode and its application in accurate physicochemical measurements. II. Thermodynamics of the second ionization of orthophosphoric acid. *J. Phys. Chem.* **1958**, *62*, 555−559.

(10) Cohn, E. J. The activity coefficients of the ions in certain phosphate solutions. A contribution to the theory of buffer action. *J. Am. Chem. Soc.* **1927**, *49*, 173−193.

(11) Johansson, O.; Wedborg, M. Stability constants of phosphoric acid in seawater of 5−40 ‰ salinity and temperatures of 5−25 °C. *Mar. Chem.* **1979**, *8*, 57−69.

(12) Hershey, J. P.; Fernandez, M.; Millero, F. J. The dissociation of phosphoric acid in NaCl and NaMgCl solutions at 25 °C. *J. Solution Chem.* **1989**, *18*, 875−891.

(13) Atlas, E.; Culberson, C.; Pytkowics, R. M. Phosphate association with Na^+, Ca^{2+} and Mg^{2+} in seawater. *Mar. Chem.* **1976**, *4*, 243−254.

(14) DeRobertis, A.; DeStefano, C.; Foti, C. Medium effects on protonation of carboxylic acids at different temperatures. *J. Chem. Eng. Data* **1999**, *44*, 262−270.

(15) Archer, D. G.; Wang, P. The dielectric constant of water and Debye−Hückel limiting law slopes. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371−411.

(16) Partanen, J. I.; Covington, A. K. Re-evaluation of the activity coefficients of aqueous hydrochloric acid solutions up to a molality of 2.0 $mol \cdot kg^{-1}$ Using two-parameter Hückel and Pitzer equations. Part II. Results from 0 to 95 °C. *J. Solution Chem.* **2002**, *31*, 197−210.

(17) Bates, R, G.; Bower, V. E. Standard potential of the silver−silver-chloride electrode from 0° to 95 °C and the thermodynamic properties of dilute hydrochloric acid solutions. *J. Res. Natl. Bur. Stand.* **1954**, *53*, 283−290.

(18) Grzybowski, A. K. The standard potential of the calomel electrode and its application in accurate physicochemical measurements. I. The standard potential. *J. Phys. Chem.* **1958**, *62*, 550−555.

(19) Partanen, J. I.; Minkkinen, P. O. Equations for calculation of the pH of buffer solutions containing sodium or potassium dihydrogen phosphate, sodium hydrogen phosphate, and sodium chloride at 25 °C. *J. Solution Chem.* **1997**, *26*, 709−727.

(20) Partanen, J. I.; Covington, A. K. Re-evaluation of stoichiometric dissociation constants from electrochemical cell data for formic acid at temperatures from (0 to 60) °C and for some other aliphatic carboxylic acids at (18 or 25) °C in aqueous potassium chloride solutions. *J. Chem. Eng. Data* **2005** *50* 497−507.

(21) Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants. A Laboratory Manual*, 3rd ed.; Chapman and Hall: London, 1984.

(22) Covington, A. K.; Bates, R. G.; Durst, R. A. Definition of pH scales, standard reference values, measurements of pH and related terminology. *Pure Appl. Chem.* **1985**, *57*, 531−542.

(23) Buck, R. P.; Rondinini, S.; Covington, A. K.; Baucke, F. G. K.; Brett, C. M. A.; Camoes, M. F.; Milton, M. J. T.; Mussini, T.; Naumann, R.; Pratt, K. W.; Spitzer, P.; Wilson, G. S. The measurement of pH. Definition, standards, and procedures. *Pure Appl. Chem.* **2002**, *74*, 2169−2200.

(24) Partanen, J. I.; Covington, A. K. Determination of stoichiometric dissociation constants of acetic acid in aqueous solutions containing acetic acid, sodium acetate, and sodium chloride at (0 to 60) °C. *J. Chem. Eng. Data* **2003**, *48*, 797−807.

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