

# Redetermination of the Second Dissociation Constant of Phosphoric Acid and Calculation of the pH Values of the pH Standards Based on Solutions of Dihydrogen and Hydrogen Phosphate Ions at 298.15 K

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Thermodynamic properties of aqueous mixtures of sodium or potassium hydrogen phosphate, dihydrogen phosphate and chloride at 298.15 K were studied by means of a recently developed method where a simple equation is used for ionic activity coefficients. The experimental data for these studies were taken from the literature. It is shown that almost all data used in the tests up to an ionic strength of  $0.6 \text{ mol kg}^{-1}$  can be interpreted within experimental error by the model used. The results of this model were compared to those of a model obtained recently on the basis of the Pitzer approach to mixed electrolyte solutions. A value of  $6.360 \times 10^{-8}$  was determined here for the thermodynamic value of the second dissociation constant of phosphoric acid. The pH values of the two standard reference solutions based on the mixtures of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ , i.e. the values of 6.865 and 7.413, can accurately be predicted by the equations determined in this study. The present results lead to the possibility of preparing a phosphate buffer whose pH can have any value between about 6.5 and 7.2; this value is probably known within  $\pm 0.005$  pH units.

Solutions of alkali-metal hydrogen and dihydrogen phosphates have for a long time been used as the standard solutions of pH measurements (see e.g., Refs. 1–3). The pH values assigned to the phosphate buffers in the early studies were based on electromotive force (EMF) measurements on cells containing a liquid junction. Because of the experimental and theoretical difficulties associated with the liquid junction in these cells, the National Institute of Standards and Technology (NIST) in United States [the National Bureau of Standards (NBS) at that time] preferred to define the pH scale by means of measurements on cells without a liquid junction. For this purpose, Bates and Acree<sup>4,5</sup> made a large number of measurements by Harned cells in solutions of  $\text{NaH}_2\text{PO}_4$  or  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  and  $\text{NaCl}$  at temperatures from 273.15 to 333.15 K. The revised pH scale of 1962<sup>6</sup> contained two phosphate buffer solutions. In one of those the molalities of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  were both  $0.025 \text{ mol kg}^{-1}$ , and in the other they were  $0.008695$  and  $0.03043 \text{ mol kg}^{-1}$ , respectively, and the pH values of these buffers at 298.15 K were 6.865 and 7.413. In

1985, Covington *et al.*<sup>7</sup> also recommended the pH values of the NBS scale in 1962 for the two phosphate buffer solutions as the primary pH standards.

In the present study, all reliable EMF data found in the literature from the second dissociation of phosphoric acid at 298.15 K are used in the tests of a recently developed model.<sup>8</sup> This model will be called below the Hückel model. In the Hückel model, a two-parameter equation is used for activity coefficients of the ionic species. In other previous communications the model was used, e.g. in acetic acid solutions<sup>9</sup> and in acidic solutions of aspartic acid.<sup>10</sup> In the present study by means of the Hückel model, the thermodynamic value of the second dissociation constant ( $K_{a,2}$ ) is revised. Also the recommended pH values of the primary standard solutions containing phosphate ions at 298.15 K (see above) and the experimentally obtainable values for the acidity function of  $p[a(\text{H}^+)\gamma(\text{Cl}^-)]$  (the symbols are given below) in equimolar solutions of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  at this temperature (these values are given by Bates and Gary<sup>11</sup>) are predicted by the new model. The results obtained by the Hückel model are compared to those

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obtained by a Pitzer model. A set of Pitzer equations for the phosphate solutions have been presented by Covington and Ferra.<sup>12</sup> The Hückel model is also compared to the model of Lito *et al.*<sup>13</sup> In the latter model, the equation of Bates and Guggenheim<sup>14</sup> is used for the activity coefficients.

## Results

*Equations for the activity coefficients.* In the Hückel model the following equation was used for the molal activity coefficient ( $\gamma$ ) of ion  $i$ :

$$\ln \gamma_i = -\alpha z_i^2 (I_m)^{1/2} / [1 + B_i (I_m)^{1/2}] + b_i I_m / m^\circ \quad (1)$$

where  $m^\circ = 1 \text{ mol kg}^{-1}$  (this symbol is generally used below as a symbol of the molality unit),  $z_i$  is the charge number of ion  $i$ ,  $I_m$  is the molal ionic strength,  $B_i$  and  $b_i$  are the ion parameters, and  $\alpha = 1.17444(m^\circ)^{-1/2}$  (see Ref. 15). For hydrogen and chloride ions, the following values<sup>8</sup> are generally used:  $B_H = B_{Cl} = 1.25(m^\circ)^{-1/2}$  and  $b_H = b_{Cl} = 0.238$ , where  $H = H^+$  and  $Cl = Cl^-$ . For the phosphate ions, it is assumed that  $B_{HA} = B_A = B$  where  $HA = H_2PO_4^-$  and  $A = HPO_4^{2-}$ , and this value is constant in all solutions considered. The characteristics of the ionic atmosphere were taken into account by the  $b$ -parameters of the hydrogen phosphate species, and these values are therefore assumed to be dependent also on the molality fractions of the salts in the solutions considered (see below).

Bates and Guggenheim<sup>14</sup> used eqn. (1) with  $B = 1.5(m^\circ)^{-1/2}$  and  $b = 0$  for the activity coefficients of  $Cl^-$  ions at molalities below  $0.1m^\circ$ . Lito *et al.*<sup>13</sup> applied this equation with the parameter values of Bates and Guggenheim for all ions.

Covington and Ferra<sup>12</sup> used the Pitzer formalism for the calculation of the values of the pH standards based on the phosphate solutions. The equations they used can be presented as follows:

$$\ln \gamma_H = f^\gamma + 2m_{Cl} B_{HCl} + 2m_K \Theta_{H,K} / (m^\circ) + 2m_{Na} \Theta_{H,Na} / (m^\circ) + f(B') \quad (2)$$

$$\ln \gamma_{Cl} = f^\gamma + 2m_{Na} B_{NaCl} + 2m_K B_{KCl} + 2m_{HA} \Theta_{Cl,HA} / (m^\circ) + 2m_A \Theta_{Cl,A} / (m^\circ) + f(B') \quad (3)$$

$$\ln \gamma_{HA} = f^\gamma + 2m_{Na} B_{NaHA} + 2m_K B_{KHA} + 2m_{Cl} \Theta_{Cl,HA} / (m^\circ) + 2m_A \Theta_{HA,A} / (m^\circ) + f(B') \quad (4)$$

$$\ln \gamma_A = 4f^\gamma + 2m_{Na} B_{NaA} + 2m_K B_{KA} + 2m_{Cl} \Theta_{Cl,A} / (m^\circ) + 2m_{HA} \Theta_{HA,A} / (m^\circ) + 4f(B') \quad (5)$$

where

$$f(B') = m_{Na} m_{Cl} B_{NaCl}' + m_K m_{Cl} B_{KCl}' + m_{Na} m_{HA} B_{NaHA}' + m_K m_{HA} B_{KHA}' + m_{Na} m_A B_{NaA}' + m_K m_A B_{KA}' \quad (6)$$

The new ion abbreviations in eqns. (2)–(6) are  $K = K^+$  and  $Na = Na^+$ , and the following symbols have been

used in these equations:

$$f^\gamma = -\alpha_p \{ I_m^{1/2} / [1 + 1.2(I_m/m^\circ)^{1/2}] + [2(m^\circ)^{1/2} / 1.2] \ln [1 + 1.2(I_m/m^\circ)^{1/2}] \} \quad (7)$$

$$B_{MX} = \beta_{MX}^\circ / (m^\circ) + \beta_{MX}^1 f_2 \quad (8)$$

$$\beta_{MX}' = \beta_{MX}^1 f_3 \quad (9)$$

$$f_2 = [1 / (2I_m)] \{ 1 - [1 + 2(I_m/m^\circ)^{1/2}] \times \exp[-2(I_m/m^\circ)^{1/2}] \} \quad (10)$$

$$f_3 = [1 / (2I_m^2)] \{ -1 + [1 + 2(I_m/m^\circ)^{1/2} + 2(I_m/m^\circ)] \times \exp[-2(I_m/m^\circ)^{1/2}] \} \quad (11)$$

In eqns. (8) and (9) MX refers to a general electrolyte where M is the cation and X the anion, and in eqns. (2)–(11) the following parameter values were used:  $\alpha_p = 0.392(m^\circ)^{-1/2}$ . KCl:  $\beta^\circ = 0.04835$ ,  $\beta^1 = 0.2122$ ; NaCl: 0.0765, 0.2664; HCl: 0.1775, 0.2945;  $KH_2PO_4$ :  $-0.0678$ ,  $-0.1042$ ;  $NaH_2PO_4$ :  $-0.0533$ ,  $0.0396$ ;  $K_2HPO_4$ : 0.0247, 1.247; and  $Na_2HPO_4$ :  $-0.05827$ , 1.465.  $\Theta_{Cl,HA} = 0.10$ ,  $\Theta_{Cl,A} = -0.07$ ,  $\Theta_{HA,A} = -0.53$ ,  $\Theta_{H,K} = 0.005$  and  $\Theta_{H,Na} = 0.036$ . The  $\beta$ -values were determined by Pitzer and Mayorga.<sup>16</sup> Covington and Ferra<sup>12</sup> present new  $\beta$ -values for  $NaH_2PO_4$  (i.e.  $\beta^\circ = -0.180$  and  $\beta^1 = 0.608$ ), too, and the calculations also were made by means of these values.

Guggenheim and Turgeon<sup>17</sup> (see also Lewis *et al.*<sup>18</sup>) have presented the following equations for the activity coefficients of a cation (M) and an anion (X) in aqueous mixtures of electrolytes:

$$\ln \gamma_M = -\alpha z_M^2 (I_m)^{1/2} / [1 + B_G (I_m)^{1/2}] + \sum_X \beta_{G,MX} m_X / m^\circ \quad (12)$$

and

$$\ln \gamma_X = -\alpha z_X^2 (I_m)^{1/2} / [1 + B_G (I_m)^{1/2}] + \sum_M \beta_{G,MX} m_M / m^\circ \quad (13)$$

where the sum in eqn. (12) goes over all anions (X) and that in eqn. (13) all cations (M) in the solution. In eqns. (12) and (13)  $B_G$  is  $1.0(m^\circ)^{-1/2}$  for all ions and  $\beta_G$  is the electrolyte parameter, and otherwise these equations have the same symbols as eqn. (1). These equations were not included in the present study because  $\beta_G$  values are not available for all electrolytes needed in these considerations. Ciavatta<sup>19</sup> has suggested for eqns. (12) and (13) a value of  $B_G = 1.5(m^\circ)^{-1/2}$  and presented a compilation of  $\beta_{G,MX}$  values corresponding to that value of  $B_G$ .

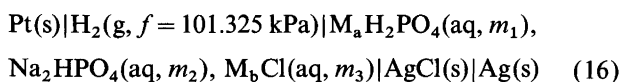
*Determination of  $K_{a,2}$ .* It was observed that only the second dissociation equilibrium needs to be taken into account when the second dissociation constant of phosphoric acid is determined from the existing EMF data (see below). The equilibrium constant for this reaction is given by

$$K_{a,2} = a_H a_A / a_{HA} = (\gamma_H \gamma_A / \gamma_{HA}) K_{m,2} \quad (14)$$

where

$$K_{m,2} = m_H m_A / (m_{HA} m^\circ) \quad (15)$$

and where  $a$  refers to the activity. Most of the EMF measurements considered in this study have been made on cells of the following type:



where  $M_a$  or  $M_b$  is either  $\text{Na}^+$  or  $\text{K}^+$  and where  $f$  is the fugacity of hydrogen. The electromotive force ( $E$ ) of this cell can be calculated by

$$E = E^\circ - (RT/F) \ln(\gamma_H \gamma_{Cl}) - (RT/F) \ln[m_H m_{Cl} / (m^\circ)^2] \quad (17)$$

where  $E^\circ$  is the standard electromotive force.

The thermodynamic value of the second dissociation constant of phosphoric acid was determined here from the data of set A measured by Bates and Acree<sup>5</sup> in 1945 on cells of type (16). Some details of this set are shown in Table 1, where the symbol of this set is BA45a. From each EMF value of this set, an "experimental" value of  $K_{m,2}$  was iteratively calculated by eqns. (1), (15) and (17). In eqn. (17) a value of  $E^\circ = 0.22250 \text{ V}$  was used.<sup>5,20,21</sup>  $m_H$  was obtained by eqn. (15), and  $\gamma_H$  and  $\gamma_{Cl}$  by eqn. (1). In this way, fifteen "experimental"  $K_{m,2}$  values were obtained. By means of these values,  $K_{a,2}$  was determined by linear regression analysis from the following equation:

$$\begin{aligned} \ln K_{m,2} - 3\alpha(I_m)^{1/2} / [1 + B(I_m)^{1/2}] \\ - \alpha(I_m)^{1/2} / [1 + B_H(I_m)^{1/2}] \\ = y = \ln K_{a,2} - [b_H + (b_A - b_{HA})]I_m / m^\circ \end{aligned} \quad (18)$$

where  $B = B_{HA} = B_A$ . The best straight line is obtained when  $B$  in this equation is  $1.35(m^\circ)^{-1/2}$ . From the slope

of this straight line and its intercept with the  $y$ -axis, the results  $K_{a,2} = 6.360 \times 10^{-8}$  and  $b_A - b_{HA} = \Delta b = 0.032$  can be determined.

*Tests for the validity of the model.* The new model was first tested by predicting all data of Bates and Acree<sup>4,5</sup> (Table 1). When the data of the sets in these papers were predicted,  $B (= B_{HA} = B_A)$  in eqn. (1) was assumed to be the same as that estimated above. On the other hand,  $\Delta b (= b_A - b_{HA})$  was determined for each set by minimizing the sum of squared prediction errors defined by

$$S^2 = \sum_i e_i(E)^2 \quad (19)$$

where

$$e(E) = E(\text{observed}) - E(\text{predicted}) \quad (20)$$

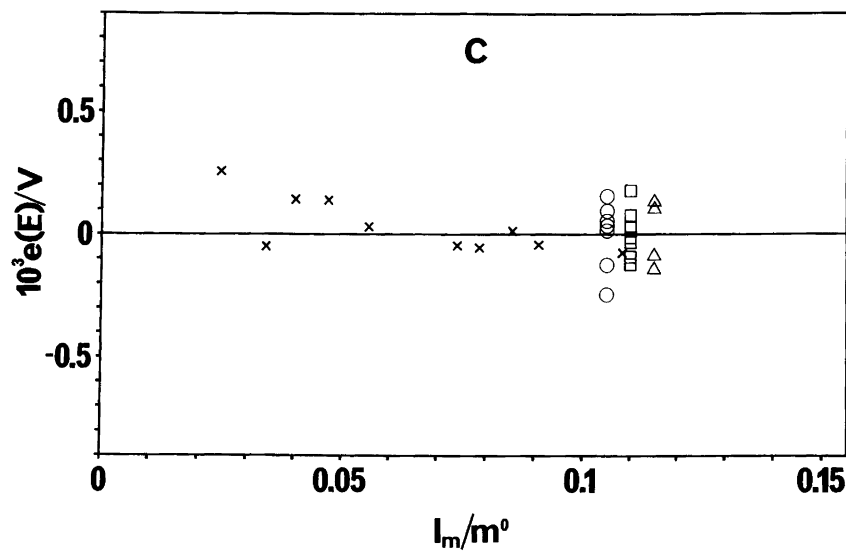
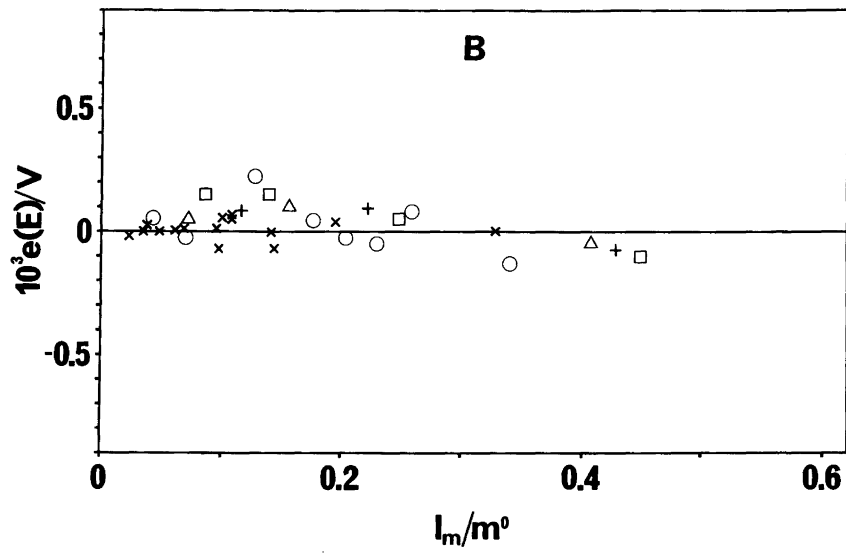
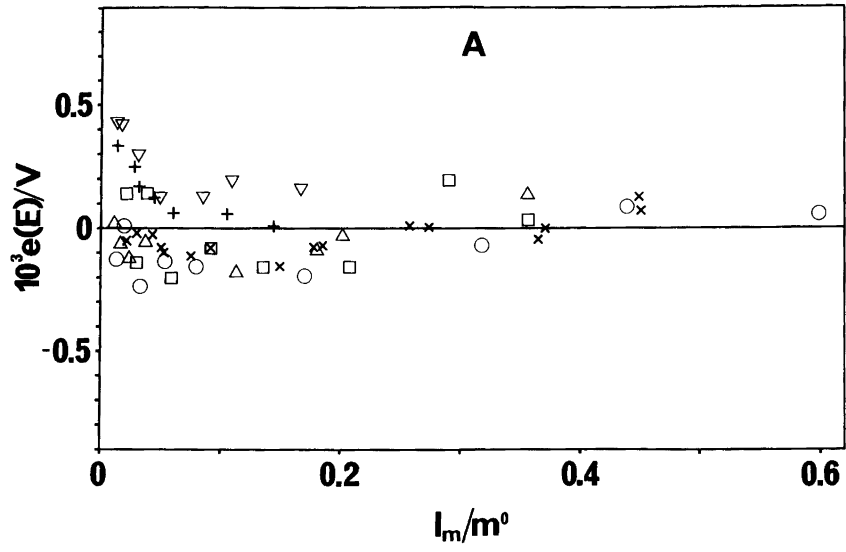
From each point in this set,  $E(\text{predicted})$  was calculated by eqns. (1), (14) and (17). The  $\Delta b$ -values obtained in this way are shown in Table 1. The error plots for these sets are shown in the graphs A and B of Fig. 1. In these plots, the errors defined by eqn. (20) are presented as a function of the ionic strength of the solution.

The model was also tested with the experimental data of Bower *et al.*,<sup>22</sup> Nims<sup>23</sup> and Grzybowski.<sup>24</sup> All these data have been measured on cells of type (16) and they are introduced in Table 1. In the measurements of Bower *et al.*,<sup>22</sup>  $M_b$  was  $\text{K}^+$ , the molalities  $m_1$  and  $m_2$  were  $0.008695 m^\circ$  and  $0.03043 m^\circ$ , respectively, and several replicate experiments were made at three different molalities of  $\text{KCl} (= m_3)$ . In cell (16), Grzybowski<sup>24</sup> used a mercury-mercurous chloride electrode instead of a silver-silver chloride electrode. A value of  $0.26804 \text{ V}$  was used here for  $E^\circ$  of this cell.<sup>21,25</sup> The test results obtained from the sets of Bower *et al.* and from that of Grzybowski are shown as error plots in graph C of Fig. 1 and those of Nims in graph A of this figure.

Table 1. List of the sets measured by cells of type (16) and used in the tests of the activity coefficient models

Symbol	$M_a$	$M_b$	$N^a$	$m_2/m_1$	$m_3/m_1$	$\Delta b^b$	$\Delta \text{pH}^c$	Ref.
BA43a	$\text{Na}^+$	$\text{Na}^+$	16	0.987	1.000	-0.054	6.6-7.0	4
BA43b	$\text{Na}^+$	$\text{Na}^+$	9	0.638	1.000	-0.187	6.5-6.8	4
BA43b*	$\text{K}^+$	$\text{Na}^+$	8	0.638	1.000	-0.088		4
BA43c	$\text{Na}^+$	$\text{Na}^+$	9	1.529	1.000	+0.049	6.8-7.2	4
BA45a	$\text{K}^+$	$\text{Na}^+$	15	1.000	1.000	+0.032		5
BA45b	$\text{K}^+$	$\text{Na}^+$	4	1.000	0.521	+0.100		5
BA45c	$\text{K}^+$	$\text{Na}^+$	3	1.000	0.312	+0.109		5
BA45d	$\text{K}^+$	$\text{Na}^+$	8	1.000	0.123	+0.148		5
BA45e	$\text{K}^+$	$\text{Na}^+$	3	1.000	0.101	+0.142		5
BPBa	$\text{K}^+$	$\text{K}^+$	8	3.500	0.575	+0.272		22
BPBb	$\text{K}^+$	$\text{K}^+$	8	3.500	1.150	+0.240		22
BPBc	$\text{K}^+$	$\text{K}^+$	4	3.500	1.725	+0.203		22
Na <sup>d</sup>	$\text{Na}^+$	$\text{Na}^+$	7	1.003	1.000	-0.054		23
Nb <sup>e</sup>	$\text{K}^+$	$\text{Na}^+$	7	1.280	1.000	+0.032		23
G <sup>f</sup>	$\text{K}^+$	$\text{Na}^+$	10	0.487	1.625	-0.007		24

<sup>a</sup> The number of points in the set. <sup>b</sup> An estimated parameter ( $\Delta b = b_A - b_{HA}$ ) required for calculations, see text. <sup>c</sup> pH ranges suitable for buffer solutions. <sup>d</sup> The same  $\Delta b$ -value was used as in the set BA43a. <sup>e</sup> The same  $\Delta b$ -value was used as in the set BA45a. <sup>f</sup> In cell (16) a mercury-mercurous chloride electrode was used instead of a silver-silver chloride electrode and  $\text{NaKHPO}_4$  instead of  $\text{Na}_2\text{HPO}_4$ .



## Discussion

According to Fig. 1, the experimental data presented in this figure support strongly the calculation method used in this study. As graphs A–C show, the measured results can be probably predicted within their precision by the Hückel model. The errors of the replicate experiments of Bower *et al.*<sup>22</sup> (see graph C) illustrate this precision.

In the present study, a value of  $6.360 \times 10^{-8}$  was obtained for  $K_{a,2}$  of phosphoric acid. This value is very close to that of Bates and Acree,<sup>5</sup> i.e. the value of  $6.345 \times 10^{-8}$ . The literature value was based on a value of 0.22246 V for  $E^\circ$  determined by Harned and Ehlers<sup>20</sup> for hydrogen–silver chloride cells. Later Bates and Bower<sup>26</sup> studied these cells very extensively and suggested a value of 0.22234 V for  $E^\circ$  at 298.15 K. The recalculation of the data of Bates and Acree with the value of Bates and Bower for  $E^\circ$  leads to a value of  $6.31 \times 10^{-8}$  for  $K_{a,2}$  of phosphoric acid (see, e.g., Bates and Gary<sup>11</sup>). Covington and Ferra<sup>12</sup> also determined by the Pitzer method the value of  $6.31 \times 10^{-8}$  for  $K_{a,2}$ . It is, however, well known that the standard potential of a silver–silver chloride electrode can vary as much as 0.2 mV at different laboratories (see, e.g., Bates and Macaskill<sup>27</sup>). If this variation is not eliminated by adjusting  $E^\circ$ , it also reflects on the values of the dissociation constants determined by the Harned cells. We therefore still have a good reason to recommend the value of  $K_{a,2} = 6.36 \times 10^{-8}$  for phosphoric acid, owing to the experimental evidence presented in Fig. 1.

The Pitzer equations for the ionic activity coefficients can also be tested with the data of Bates and Acree.<sup>4,5</sup> For these tests, sets BA43a and BA45a were chosen in Table 1. The data in these sets were predicted with eqns. (2)–(6) and with the values of  $E^\circ = 0.22234$  V and  $K_{a,2} = 6.31 \times 10^{-8}$ . In these calculations, both the values of Pitzer and Mayorga<sup>16</sup> and those of Covington and Ferra<sup>12</sup> were used for the  $\beta$ -parameters of  $\text{NaH}_2\text{PO}_4$  (see above). The results are shown as error plots in Fig. 2. According to this figure, the parameter values of Covington and Ferra for  $\text{NaH}_2\text{PO}_4$  apply better to these experimental data. In this figure, the errors obtained by the better Pitzer parameters form a random pattern when the results of set BA43a are predicted. In other cases, however, the EMF data of this figure do not fully support the Pitzer equations used in the calculations.

The activity coefficient equation of Lito *et al.*,<sup>13</sup> see above, was also tested with the results of set BA45a (Table 1). The results of the calculations are shown as an error plot in Fig. 2. According to this plot, the experimental data do not support this equation.

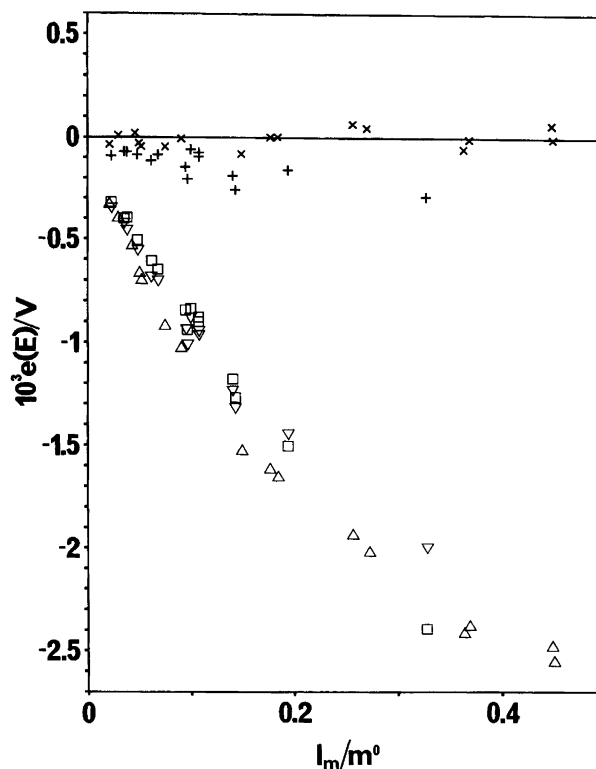


Fig. 2. The difference between the observed and predicted EMF values as a function of the ionic strength in the sets measured by Bates *et al.*<sup>4,5</sup> on galvanic cells without a liquid junction [cell (16)]. The differences,  $e(E)$ , were calculated by eqn. (20). The predicted values for that equation were calculated by means of eqn. (17) with eqns. (14) and (15) and with the Bates–Guggenheim equation [i.e. with eqn. (1) with the parameter values given by Lito *et al.*<sup>13</sup>] or with the Pitzer equation [i.e. with eqns. (2)–(6) with the parameter values given by Covington *et al.*<sup>12</sup>]. Symbols for the sets and equations (see text and Table 1). Pitzer equation with  $\beta^\circ(\text{NaH}_2\text{PO}_4) = -0.0533$ ,  $\beta^1(\text{NaH}_2\text{PO}_4) = 0.0396$ : BA43a,  $\Delta$  and BA45a,  $\nabla$ . Pitzer equation with  $\beta^\circ(\text{NaH}_2\text{PO}_4) = -0.180$  and  $\beta^1(\text{NaH}_2\text{PO}_4) = 0.608$ : BA43a,  $\times$  and BA45a,  $+$ . Bates–Guggenheim equation: BA45a,  $\square$ .

Two of the pH standards recommended by NIST have been based on phosphate buffers (see above). At 298.15 K, the recommended pH values of these buffers are 6.865 and 7.413. The “experimental values” for the buffers are 6.864 and 7.414.<sup>6</sup> In the new model,  $\Delta b$ -values for the chloride-free buffers can be determined by extrapolations from the results of Table 1. By using a function of  $\Delta b = f(m_3/I_m)$  in the extrapolations, a value of 0.170 for  $\Delta b$  was obtained from the results of the sets BA45a–BA45e for the equimolar aqueous mixture of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ , and a value of 0.310 from the

Fig. 1. The difference between the observed and predicted EMF values as a function of the ionic strength in the sets measured by Bates *et al.*,<sup>4,5</sup> Bower *et al.*,<sup>22</sup> Nims<sup>23</sup> and Grzybowski<sup>24</sup> on galvanic cells without a liquid junction, see cell (16). The differences,  $e(E)$ , were calculated by eqn. (20) and the predicted values for that equation were calculated by means of eqn. (17) with eqns. (1), (14) and (15). In eqn. (1) the parameter values given in the text were used for ions. Symbols for the sets (Table 1): BA43a,  $\times$ , graph A; BA43b,  $\square$ , A; BA43b\*,  $\Delta$ , A; BA43c,  $\circ$ , A; BA45a,  $\times$ , B; BA45b,  $\square$ , B; BA45c,  $+$ , B; BA45d,  $\circ$ , B; BA45e,  $\Delta$ , B; BPBa,  $\circ$ , C; BPBb,  $\square$ , C; BPBc,  $\Delta$ , C; Na,  $+$ , A; Nb,  $\nabla$ , A; G,  $\times$ , C.

results of the sets BPBa–BPBc for the mixture where  $m_2/m_1 = 3.5$ . With these values by the method used here, it can be calculated that the pH of the first buffer solution is 6.8648 and the second is 7.4149. Therefore the pH values of the two standard solutions can be predicted accurately by the Hückel model.

Bates and Gary<sup>11</sup> has suggested that a function of  $p(a_{\text{H}^+}\gamma_{\text{Cl}})$  ( $=af$ ) can be used as a useful acidity function for measuring the acidic and basic character of electrolyte solutions. It is possible to evaluate experimentally the values of this function from electromotive forces measured by cells of type (16). Based on measurements in aqueous equimolar mixtures of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  at 298.15 K, these researchers suggest the following values for the acidity function in the phosphate solutions:

$I_m/m^\circ$	$af$	$af_1$	$af_2$
0.01	7.111	7.110	7.110
0.03	7.058	7.057	7.056
0.05	7.026	7.025	7.023
0.08	6.992	6.991	6.989
0.10	6.974	6.974	6.971
0.15	6.940	6.939	6.936
0.20	6.912	6.914	6.910

In this short table, the  $af_1$  values for the acidity function have been calculated by the Hückel model with  $\Delta b = 0.170$  and with  $K_{a,2} = 6.31 \times 10^{-8}$  [this  $K_{a,2}$  was used because Bates and Gary used the value of 0.22234 V for the standard potential of the silver–silver chloride electrode when they determined the experimental  $p(a_{\text{H}^+}\gamma_{\text{Cl}})$  values ( $=af$ ), see above]. The  $af_2$  values in this table have been obtained by the Pitzer model in which  $\beta^\circ = -0.180$  and  $\beta^1 = 0.608$  for  $\text{NaH}_2\text{PO}_4$ . As shown in this table the agreement between experimental values of the acidity function and those obtained by the Hückel model is very good. This model also predicts the experimental values slightly better than the Pitzer one.

The model used in the present study predicts almost perfectly the experimental data that have been measured from phosphate buffers at 298.15 K. The Hückel model also predicts correctly the standard values assigned to these buffers. Therefore it seems natural to suggest that any phosphate buffer (the solution may also contain NaCl) for which  $\Delta b [= (b_A - b_{\text{HA}})]$ , where  $A = \text{HPO}_4^{2-}$ ,  $\text{HA} = \text{H}_2\text{PO}_4^-$  and  $b$  is an ion parameter in eqn. (1)] has reliably been determined can be used as a pH standard. Several possibilities for such solutions are suggested in Table 1. For each recommended set in this table are also included the pH ranges within which the solutions of this set can be used. The pH for the solutions can be calculated by means of the activity coefficient equations presented here and by using the value of  $K_{a,2} = 6.36 \times 10^{-8}$ . The accuracy of the pH values calculated in this way can be evaluated by using different ionic activity coefficient models (also others than those used in this study) to predict the EMF data presented in

Table 1. By comparing the pH predictions of the good models, it can be concluded that the errors of the pH values calculated by the method suggested above for the sets recommended in Table 1 are probably less than 0.005 pH-units at ionic strengths smaller than  $0.2 \text{ mol kg}^{-1}$ .

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