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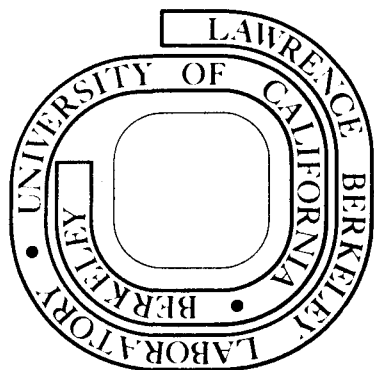
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THERMODYNAMICS OF ELECTROLYTES. VI.

WEAK ELECTROLYTES INCLUDING H_3PO_4

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(ABSTRACT)

Equations previously developed and widely applied to the thermodynamic properties of strong electrolytes are extended to solutions involving a dissociation equilibrium. Excellent agreement is obtained with the data for pure phosphoric acid to 6M and for phosphate buffer solutions. The parameters of the strong electrolyte components of the buffer solutions are taken from other work, and the remaining parameters for H^+ , H_2PO_4^- , and H_3PO_4 are evaluated including a pK of 2.146. The present method avoids ambiguities which formerly arose in treating weak acids with as small pK as this.

Key Words: Activity coefficient, osmotic coefficient, thermodynamics, solution theory, dissociation constants, phosphoric acid.

In much of the literature on weak electrolytes the entire focus is on the determination of the dissociation constant. While data for solutions of finite concentration are employed, the interpretation is directed entirely toward the limiting behavior at zero concentration which determines the dissociation constant. In contrast we seek to represent the thermodynamic properties of such solutions over a broad range from zero to rather high concentration. Appropriate sets of equations include, of course, the dissociation constant of a weak electrolyte, but also include terms for interaction of various solute species both neutral and charged.

In the earlier papers of this series¹⁻⁴ equations were developed which represent effectively the properties of mixed as well as pure strong electrolytes. In the case of 2-2 salts, where some association is indicated by other measurements, it was feasible to treat thermodynamic properties without explicitly considering association.³ We now consider cases where association is substantial and is explicitly recognized. The general equation adopted earlier is readily extended to include terms for the associated species.

In earlier work⁵⁻⁸ it was found that dissociation constants smaller than about 10^{-4} were determined without difficulty but that for stronger acids, pK 2 to 4, an ambiguity arises and becomes greater the larger the dissociation constant. This problem will be considered in some detail.

Phosphoric acid was chosen as an example in view of (1) the availability of excellent experimental data, (2) the fact

that its pK is in the range where ambiguities have arisen, and (3) its general importance.

General Equations

In paper I of this series¹ the statistical mechanical basis was given for the form of equation adopted. In brief the general framework is that of the McMillan-Mayer theory of solutions and the equation relating intermolecular forces and distributions to the osmotic pressure.⁹ Since we do not expect to make absolute calculations based upon detailed short-range intermolecular forces, we have ignored the differences between concentration and molality and between the McMillan-Mayer reference states and the standard states of chemical thermodynamics. The effects of these differences at finite concentration are absorbed in the virial coefficients for the interaction of solute species.

The basic equation is

$$\frac{G^{ex}}{RT} = n_w f(I) + \frac{1}{n_w} \sum_{ij} \lambda_{ij}(I) n_i n_j + \frac{1}{n_w^2} \sum_{ijk} \mu_{ijk} n_i n_j n_k \quad (1)$$

where G^{ex} is the excess Gibbs energy for a solution containing n_w kg of solvent and n_i , n_j , etc. moles of solute species i , j , etc. Also $f(I)$ is a function of ionic strength (also temperature and solvent properties) expressing the effect of long-range electrostatic forces between ions; $\lambda_{ij}(I)$ is a second virial coefficient giving the effect of short-range forces between species i and j (including indirect forces arising from the

solvent); and μ_{ijk} is a corresponding third virial coefficient for the interaction of three solute species i , j , and k . The second virial coefficients for ion-ion interactions are expected to depend on ionic strength for theoretical reasons given in I¹; this dependence has been amply justified empirically. While these effects which cause a first-order variation in λ with ionic strength for ion-ion interactions might cause indirect or second order variations in λ 's for ion-neutral or neutral-neutral interactions, these latter variations should be very small and will be ignored. Thus λ_{ij} is a function of ionic strength if both i and j are charged; otherwise it is a constant (for a particular solvent and temperature). The third virial coefficients are taken as constants even when all species are charged and are ignored if all species have the same sign of charge. It is assumed that the λ and μ matrices are symmetric, i.e., $\lambda_{ij} = \lambda_{ji}$, etc.

The appropriate derivatives yield the activity and osmotic coefficients

$$\ln \gamma_i = \frac{1}{RT} \frac{\partial G^{ex}}{\partial n_i} = z_i^2 f' + 2 \sum_j \lambda_{ij} m_j + \sum_{jk} m_j m_k \left(\frac{z_i^2}{2} \lambda_{jk}' + 3 \mu_{ijk} \right) \quad (2)$$

$$\phi^{-1} = - \frac{\partial G^{ex} / \partial n_w}{RT \sum_i m_i} = \left(\sum_i m_i \right)^{-1} \left[(If' - f) + \sum_{ij} m_i m_j (\lambda_{ij} + I \lambda_{ij}') + 2 \sum_{ijk} m_i m_j m_k \mu_{ijk} \right] \quad (3)$$

where $f' = \partial f / \partial I$, $\lambda'_{ij} = \partial \lambda_{ij} / \partial I$ and the various molalities $m_i = n_i / n_w$. Unless both species are ions, $\lambda'_{ij} = 0$. The general equations for the measureable combinations of ion activities such as γ_{\pm} are given in I¹ and III.³

In order to simplify these equations as far as possible without ignoring any important types of terms we now assume a solution comprising a weak acid HA and its ions H⁺ and A⁻ and another positive ion M⁺ and negative ion X⁻. The composition will be stated in terms of m_{HA} , m_H , m_A , m_M , and m_X . Neutrality requires that $m_H + m_M = m_A + m_X$. The resulting equations can readily be generalized for more complex solutions when desired.

The functions for long-range electrostatic forces x were determined in I and contain, of course, the Debye-Hückel limiting law. They are

$$f^{\phi} = \frac{1}{2} [f' - (f/I)] = -A_{\phi} [I^{1/2} / (1 + 1.2 I^{1/2})] \quad (4)$$

$$f^{\gamma} = \frac{1}{2} f' = -A_{\phi} [I^{1/2} / (1 + 1.2 I^{1/2}) + (2/1.2) \ln (1 + 1.2 I^{1/2})] \quad (5)$$

where A_{ϕ} is the Debye-Hückel constant for the osmotic coefficient and 1.2 is an empirical value discussed in I.

For the virial coefficients for ions it proved convenient to define the sums which appear in equations for the pure electrolyte MX. For a 1-1 electrolyte these are

$$B_{MX} = \lambda_{MX} + \frac{1}{2} \lambda_{MM} + \frac{1}{2} \lambda_{XX} \quad (6)$$

$$B'_{MX} = \lambda'_{MX} + \frac{1}{2} \lambda'_{MM} + \frac{1}{2} \lambda'_{XX} \quad (7)$$

$$C_{MX} = \frac{3}{2} (\mu_{MMX} + \mu_{MXX}). \quad (8)$$

The adopted empirical forms which include ionic strength dependence of B and B' are

$$B_{MX} = \beta_{MX}^{(0)} + (2\beta_{MX}^{(1)}/\alpha^2 I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (9)$$

$$B'_{MX} = (2\beta_{MX}^{(1)}/\alpha^2 I^2) [-1 + (1 + \alpha I^{1/2} + 1/2 \alpha^2 I) \exp(-\alpha I^{1/2})] \quad (10)$$

$$C_{MX}^{\phi} = 2C_{MX} = \frac{2}{3} C_{MX}^{\gamma} \quad (11)$$

where the general empirical constant α is 2.0 for all 1-1 and most other electrolytes and the specific constants $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, and C_{MX}^{ϕ} have been determined in II^2 for most aqueous electrolytes of interest.

For mixed electrolytes additional terms appear involving differences in virial coefficients. These have been defined (for mixing singly charged ions A and X, or similarly for H and M)

$$\theta_{AX} = \lambda_{AX} - \frac{1}{2} \lambda_{AA} - \frac{1}{2} \lambda_{XX} \quad (12)$$

$$\psi_{MAX} = 6\mu_{MAX} - 3\mu_{MAA} - 3\mu_{MXX}. \quad (13)$$

Although the λ 's are presumed to vary with ionic strength, it was found to be a satisfactory approximation to take the θ 's to be constants.

We turn now to the new relationships arising from association and from the presence of neutral solute species. First is the dissociation equilibrium itself where standard chemical thermodynamics yields

$$\text{HA} = \text{H}^+ + \text{A}^-$$

$$-\Delta G^\circ / RT = \ln K = \ln(m_{\text{H}^+} m_{\text{A}^-} \gamma_{\text{H}^+} \gamma_{\text{A}^-} / m_{\text{HA}} \gamma_{\text{HA}}) \quad (14)$$

where K is the usual dissociation constant.

Once the HA association has been assumed, this reaction supercedes the second virial coefficient for $\text{H}^+ - \text{A}^-$ interaction. In practice one cannot determine the $\lambda_{\text{H},\text{H}}$ and $\lambda_{\text{A},\text{A}}$ terms separately, hence one assumes $B_{\text{H},\text{A}}$ to be zero. This point is discussed further below. For neutral-neutral interactions the second and third virial coefficients $\lambda_{\text{HA},\text{HA}}$ and $\mu_{\text{HA},\text{HA},\text{HA}}$ can be used directly. There are four second virial coefficients for ion-neutral interactions: $\lambda_{\text{H},\text{HA}}$, $\lambda_{\text{M},\text{HA}}$, $\lambda_{\text{A},\text{HA}}$; and $\lambda_{\text{X},\text{HA}}$. Only those sums or differences of these coefficients that correspond to electrical neutrality can be measured, i.e., $(\lambda_{\text{H},\text{HA}} + \lambda_{\text{A},\text{HA}})$ or $(\lambda_{\text{H},\text{HA}} - \lambda_{\text{M},\text{HA}})$, etc. There are six such sums or differences, but only three are independent. Hence, only three of these λ 's may be adjusted independently. We found it more convenient to set one λ at zero than to work with the various sum's and differences and chose to let $\lambda_{\text{X},\text{HA}} = 0$. Any desired sum or difference can, of course, be calculated from our results.

There are a large number of ion-neutral third virial coefficients - far more than could be determined from data now available or likely to be obtained. Such terms are included only when they are clearly required; none were required in the present example.

Phosphoric Acid

There are experimental data for certain buffer solutions as well as for pure phosphoric acid. For the pure acid the osmotic coefficient data based on solvent vapor pressure^{10,11} were used. Among various measurements on buffer solutions, the data of Bates⁵ on HCl - KH₂PO₄ mixtures are particularly extensive and of the highest accuracy. For the buffer solution calculations, the parameters are needed for the pure electrolytes HCl, KCl, and KH₂PO₄; these were obtained in paper II.² More recent data¹² on pure KH₂PO₄ were also considered, but they did not justify any change in the previously published parameters. Values are also needed for the parameters $\theta_{H,K}$ and $\theta_{Cl,A}$ (A⁻ is H₂PO₄⁻) from appropriate mixtures. The former is given in IV⁴; the latter was determined to be $\theta_{Cl,A} = 0.10$ from the isopiestic measurements of Childs, Downes, and Platford¹³ which also yield $\psi_{K,Cl,A} = -0.010_5$.

For pure H₃PO₄ the pertinent equations are as follows, where ϕ is an osmotic coefficient calculated from the water activity on the basis of dissociation into two ions, $\nu = 2$ (note that Platford reports his data on the basis $\nu = 4$). If the actual dissociation of acid of molality m yields molality m_H of H⁺ and A⁻, the osmotic coefficient on that basis ϕ' is obtained from equation (3).

$$\begin{aligned}
 (\phi' - 1)(m + m_H) &= 2m_H f^\phi + 2m_H(m - m_H)(\lambda_{H,HA} + \lambda_{A,HA}) \\
 &+ (m - m_H)^2 \lambda_{HA,HA} + 2(m - m_H)^3 \mu_{HA,HA,HA}
 \end{aligned}
 \tag{15}$$

$$\phi'(m+m_H) = 2m\phi. \quad (16)$$

In addition we have the dissociation equilibrium determined from equation (14) and the expressions for $\frac{1}{2} \ln(\gamma_H \gamma_A) = \ln \gamma_{\pm}$ and $\ln \gamma_{HA}$ which may be obtained from equation (2) and several that follow it.

$$\frac{1}{2} \ln(\gamma_H \gamma_A) = f^Y + (m-m_H)(\lambda_{H,HA} + \lambda_{A,HA}) \quad (17)$$

$$\begin{aligned} \ln \gamma_{HA} = & 2m_H(\lambda_{H,HA} + \lambda_{A,HA}) + 2(m-m_H) \lambda_{HA,HA} \\ & + 3(m-m_H)^2 \mu_{HA,HA,HA}. \end{aligned} \quad (18)$$

In view of the high concentrations of pure phosphoric acid to be considered, the third virial coefficient $\mu_{HA,HA,HA}$ was included in equation (18). Third virial coefficients for ion-neutral interaction were tentatively omitted and later results justify that decision.

For the buffer solutions with $HCl(m_1)$ and $KH_2PO_4(m_2)$ the measured quantity is the potential E of a cell with hydrogen and silver-silver chloride electrodes. If the hydrogen ion molality is m_H and the standard potential is E° , we obtain

$$E - E^\circ = -(RT/F) \ln(m_H m_1 \gamma_H \gamma_{Cl}). \quad (19)$$

Other symbols have their usual meaning and we take $E^\circ = 0.2224$ v. Since the buffer solution measurements extend only to a maximum concentration of 0.4 M, third virial coefficients are omitted throughout.

We obtain for the ionic strength $I = m_2 + m_H$, also $m_{HA} = m_1 - m_H$, $m_{Cl} = m_1$, $m_K = m_2$, $m_A = m_2 - m_1 + m_H$. For these buffer solutions equation (2) and subsequent equations yield

$$\begin{aligned} \ln \gamma_{HCl} &= \frac{1}{2} \ln(\gamma_H \gamma_{Cl}) \\ &= f^Y + (m_1 + m_H) B_{HCl} + m_2 (B_{KCl} + \theta_{HK}) \\ &+ m_H m_1 B'_{HCl} + m_1 m_2 B'_{KCl} + m_2 (m_2 - m_1 + m_H) B'_{KA} \\ &+ (m_2 - m_1 + m_H) \theta_{Cl,A} + (m_1 - m_H) (\lambda_{H,HA} + \lambda_{Cl,HA}) \end{aligned} \quad (20)$$

$$\begin{aligned} \frac{1}{2} \ln(\gamma_H \gamma_A) &= f^Y + m_1 (B_{HCl} + \theta_{Cl,A}) + m_2 B_{KA} \\ &+ m_H m_1 B'_{HCl} + m_1 m_2 B'_{KCl} + m_2 (m_2 - m_1 + m_H) B'_{KA} \\ &+ m_2 \theta_{H,K} + (m_1 - m_H) (\lambda_{H,HA} + \lambda_{A,HA}) \end{aligned} \quad (21)$$

$$\begin{aligned} \ln \gamma_{HA} &= 2 [m_H \lambda_{H,HA} + m_1 \lambda_{Cl,HA} + m_2 \lambda_{K,HA} \\ &+ (m_2 - m_1 + m_H) \lambda_{A,HA} + (m_1 - m_H) \lambda_{HA,HA}] \end{aligned} \quad (22)$$

For either the pure acid or the buffer solutions it was necessary to eliminate the hydrogen ion molality m_H by an iterative solution of the appropriate set of equations.

In equations (20) and (21) all of the B and θ parameters are independently known. Thus in the full array of equations (14) to (21) there are six parameters to be evaluated. While all might be simultaneously evaluated from the full array of data for both pure acid and buffer solutions, that calculation

would be very complex and the assignment of appropriate weights would be difficult. Instead we chose to evaluate three parameters from each set of data. From the pure acid data the sum $(\lambda_{H,HA} + \lambda_{A,HA})$ and the second and third virial coefficients for neutral-neutral interaction were determined by appropriate least-squares methods, while K and the individual second virial coefficients for ion-neutral interaction were determined from data on buffer solutions. This process was iterated until all results were consistent. The resulting parameters are given in Table I. The standard deviation of fit for the buffer solutions was 0.0002 v. in the cell potential while for the pure acid to 6M it was 0.005 in the osmotic coefficient. In each case the fit is essentially within the experimental uncertainty. Figure 1 shows in the lower section the deviations in osmotic coefficient as a function of total molality for each set of experimental measurements. In the upper portion of Figure 1 the fraction dissociated m_H/m is shown. The increase in dissociation at very low concentration is expected; the minimum near 2M and increase at higher concentration are surprising and are caused primarily by the large, negative value of the sum of ion-neutral second virial coefficients $(\lambda_{H,HA} + \lambda_{A,HA})$.

Table I. Parameters for Phosphoric
Acid Solutions at 25°C. (A^- is $H_2PO_4^-$)

$$K = 7.142_5 \times 10^{-3} \quad (pK = 2.1461_5)$$

$$\lambda_{HA,HA} = 0.0503_1 \quad \mu_{HA,HA,HA} = 0.0109_5$$

$$\lambda_{A,HA} = -0.400 \quad \lambda_{H,HA} = 0.290$$

$$\lambda_{K,HA} = -0.070 \quad (\lambda_{Cl,HA} = 0)$$

Also determined from $KCl - KH_2PO_4$ mixtures

$$\theta_{Cl,A} = 0.10 \quad \psi_{K,Cl,A} = -0.010_5$$

Discussion

First we recall the ambiguities noted by Bates⁵ and others⁶⁻⁸ in determining the dissociation constant of phosphoric acid. Bates used the conventional Debye-Hückel expression for an activity coefficient, including the term involving a distance of closest approach a , and found that the value of pK obtained by linear extrapolation to zero ionic strength varied not only with the value of a but also with the buffer ratio. Also the slopes of the lines for different buffer ratios differed greatly.

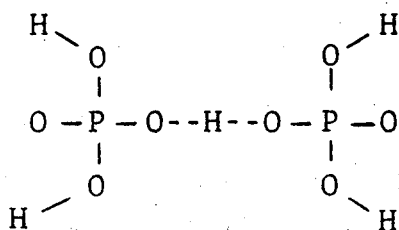
The primary effect of buffer ratio can be seen in equations (20) and (21) where the second virial terms in B 's and θ 's have different coefficients involving m_1 or m_2 . Since these second virial coefficients can be measured independently, it is desirable to include them explicitly. Also it is important to note the appearance of m_H in some of the coefficients of B and θ terms. As solutions of constant buffer ratio, i.e., constant m_2/m_1 , are diluted the ratio of m_H to m_2 or m_1 increases. Hence the ratios of these various coefficients of B 's and θ 's are not constant for a fixed buffer ratio. This explains the failure of Bates' linear extrapolations to give the same pK even for a given value of a .

One might think that the effect of change of a in the Debye-Hückel expression could be obtained in our equations by a change in the empirical parameter $l.2$ in equations (4) and (5). But the various B and θ parameters were determined with the expressions of f^ϕ and f^γ in equations (4) and (5) including

the parameter 1.2. Hence we cannot now vary that parameter without redetermining all of the B and θ values. This situation helps one to understand the problems in Bates treatment. The needed products of activity coefficients $(\gamma_H \gamma_{Cl})$ and $(\gamma_H \gamma_A)$ are related to the real properties of the electrolyte-components present such as HCl , KCl , and KH_2PO_4 , and one cannot properly vary these arbitrarily. Thus the Bates treatment would be most nearly correct for an \underline{a} -value which yields activity coefficients that approximate those of the various component electrolytes. Bates' final choice of pK as an average of extrapolated values for $\underline{a} = 4 \text{ \AA}$ and $\underline{a} = 6 \text{ \AA}$ is appropriate on this basis, and his result $pK = 2.148$ differs only slightly from our value of 2.146.

In our treatment we omitted the second virial coefficient $B_{H,A}$ for H^+ interaction with A^- on the basis that it was redundant once the association equilibrium was introduced. It can be shown that the introduction of a small value of $B_{H,A}$ should change the dissociation constant by an amount $\Delta(1/K) = 2B_{H,A}$. This was verified in a calculation for the buffer solutions with $B_{H,A} = -0.05$ in which the value of K changed by the expected amount and the agreement with the experimental data was unchanged. Not only was the standard deviation unchanged, but the individual differences between calculated and experimental cell potentials were the same to 0.00001 v. Thus the redundancy of this parameter was confirmed and its omission justified.

With respect to intermolecular phenomena the most interesting result is the large negative value ($\lambda_{A,HA} = -0.4$) for the interaction of $H_2PO_4^-$ with H_3PO_4 . This indicates a tendency toward association to form $H_5P_2O_8^-$. Presumably this species would be hydrogen bonded in a manner:



Evidence for this species has been presented by Elmore, et al¹⁴ from thermodynamic data and by Selvaratnam and Spiro¹⁵ from conductance and transference data, also by Childs¹⁶ and by Ivakin and Voronova.¹⁷ It has also been suggested by some of these authors and by Wood and Platford¹⁸ that the ion $H_2PO_4^-$ has a tendency to dimerize to $H_4P_2O_8^{-2}$. This is consistent with the abnormally low $\beta^{(0)}$ and $\beta^{(1)}$ for sodium and potassium salts of $H_2PO_4^-$ and the relatively large, positive $\theta_{Cl,A} = 0.1$ for the $Cl^- - H_2PO_4^-$ mixtures. Since $\theta_{Cl,A} = (\lambda_{Cl,A} - 1/2 \lambda_{Cl,Cl} - 1/2 \lambda_{A,A})$, if the other λ 's are small, $\lambda_{AA} \approx -0.2$. Thus the tendency of $H_2PO_4^-$ to dimerize is about half as great as the tendency of H_3PO_4 and $H_2PO_4^-$ to associate. Each of these associations is mild enough that the virial coefficient treatment is satisfactory as verified by the excellent agreement we obtained.

Elmore, et al¹⁴ calculated values for the molality of H^+ in phosphoric acid over a wide range of concentration using their model which included the $H_5P_2O_8^-$ species. Their values

for m_H are somewhat larger than ours, but the general trend is similar. Since m_H is not directly measured, it is quite possible for treatments to differ with respect to this quantity while agreeing on measured quantities such as the solvent vapor pressure.

Finally, the excellent fit with experimental data demonstrates that our equations treating most solute interactions by virial coefficients can be combined with an association equilibrium. Also it seems clear that presently well-established dissociation constants (below the range of ambiguity discussed above) can be used in such treatments if desired.

Acknowledgement

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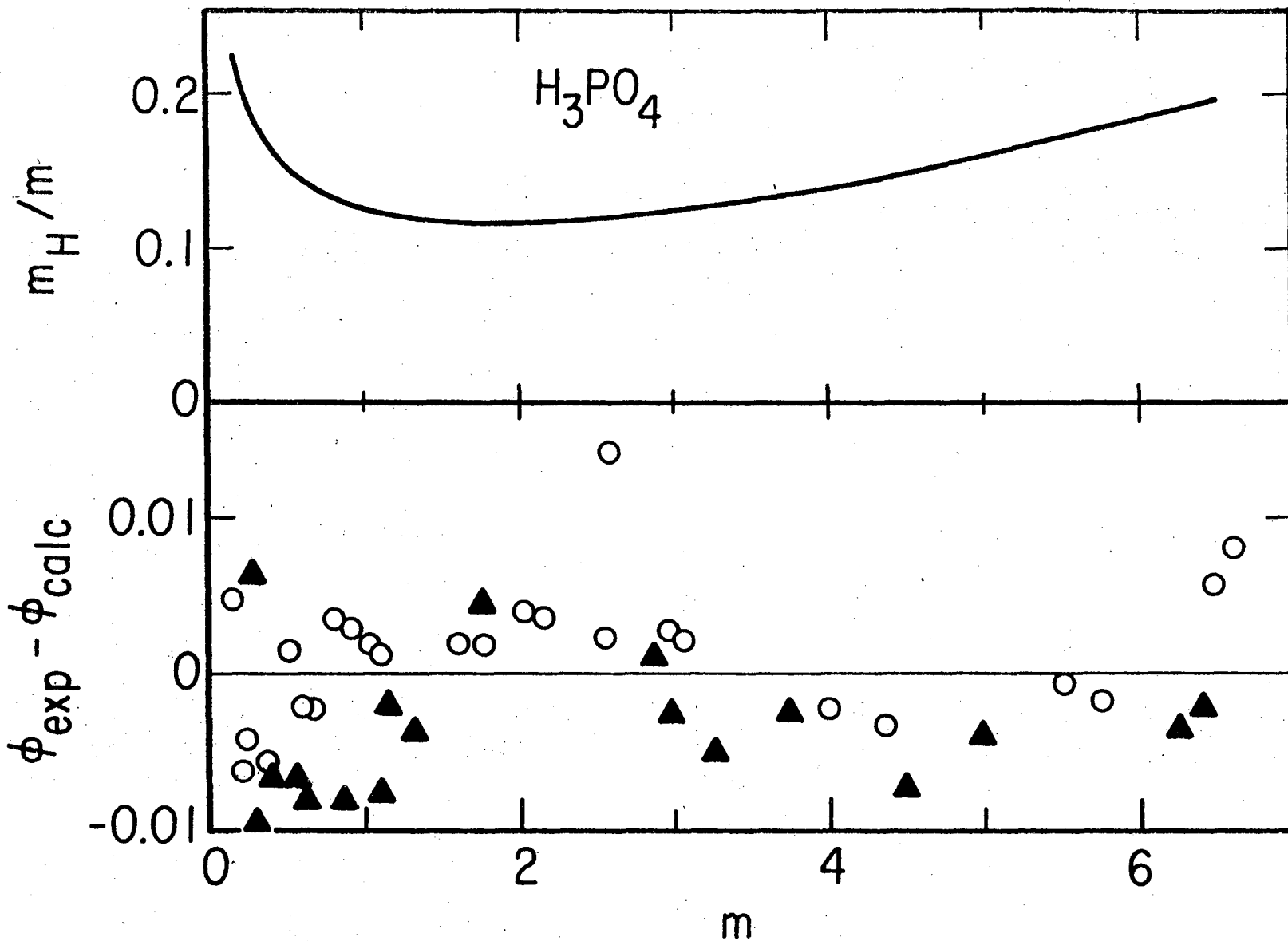


Figure 1. Fraction dissociation of H_3PO_4 in upper section; deviation of calculated from experimental osmotic coefficients in lower section (circles, Elmore, et al¹⁰; triangles, Platford¹¹).

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