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# THERMODYNAMICS OF ELECTROLYTES. II. ACTIVITY AND OSMOTIC COEFFICIENTS FOR STRONG ELECTROLYTES WITH ONE OR BOTH IONS UNIVALENT

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# Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent.

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## (Abstract)

The system of equations developed in the first paper of this series is successfully applied to the available free energy data at room temperature for 227 pure aqueous electrolytes with one or both ions univalent. The experimental data are represented substantially within experimental error from dilute solutions up to an ionic strength varying from case to case but typically 6 M. Where the data extend to high concentration three parameters are evaluated for each solute, but one of these has negligible effect and is omitted if there are data only for the dilute range. This yields a very compact set of tables from which these important and useful properties can be reproduced. These parameters will also be of importance in treating mixed electrolytes. A simplified graphical presentation is given for activity coefficients of 1-1 electrolytes. In most cases the new equations are fitted to the osmotic coefficient data as recommended by Robinson and Stokes but for hydroxides, zinc halides, hydrogen halides, and a few other cases we have based our evaluation on the original data from several sources. The implications of our parameters are also discussed in terms of solvent structure and interionic forces.

(end of abstract)

It is the twofold purpose of this research to represent as compactly and as accurately as possible the very extensive array of experimental data on the thermodynamic properties of single aqueous electrolytes at room temperature and to interpret the resulting parameters in terms of interionic forces. In the first paper[1] of this series (cited hereafter as I) the theoretical aspects were considered in order to guide the selection of equations which reproduce the measured properties substantially within experimental accuracy, which are compact and convenient in that only a very few parameters need be tabulated for each substance and the mathematical calculations are simple, which have appropriate form for mixed electrolytes as well as for a single solute, and whose parameters have physical meaning as far as possible. Choices were made between several possible forms of equations on the basis of accuracy of representation of the experimental data for several solutes.

In this paper we present the results for single electrolytes which show no association. Also included are several solutes which are said, on the basis of some properties, usually conductance, to show some association but whose thermodynamic properties are fitted satisfactorily by the same equations used for non-associating electrolytes. In later papers we expect to treat single electrolytes showing moderate association as well as mixed electrolytes.

## Equations and General Parameters

The equations chosen in I differ from those generally used heretofore in several respects, but most important is the ionic strength dependence of the second virial coefficient. This was shown to be justified theoretically by a simple derivation in which the Debye-Hückel radial distribution is substituted into the osmotic pressure equation of statistical mechanics, although it was also noted that the more complex theory of Mayer[2] previously had indicated such a dependence. This same simple derivation also led to a different form for the long-range electrostatic term which was found to be empirically superior to the conventional Debye-Hückel form derived by a charging process (instead of the osmotic pressure equation).

The pertinent equations for single electrolytes for the excess Gibbs energy $G^{ex}$, the osmotic coefficient $\varphi$, and the activity coefficient $\gamma$ are as follows:

$$(G^{ex}/n_wRT) = f^{Gx} + m^2(2\upsilon_M\upsilon_X)B_{MX}{}^{Gx} + m^3[2(\upsilon_M\upsilon_X)^{3/2}]C_{MX}{}^{Gx} \tag{1}$$

$$\varphi - 1 = |z_Mz_X|f^{\varphi} + m\left(\frac{2\upsilon_M\upsilon_X}{\upsilon}\right)B_{MX}{}^{\varphi} + m^2\,\frac{2(\upsilon_M\upsilon_X)^{3/2}}{\upsilon}\,C_{MX}{}^{\varphi} \tag{2}$$

$$\ln\gamma = |z_Mz_X|f^{\gamma} + m\left(\frac{2\upsilon_M\upsilon_X}{\upsilon}\right)B_{MX}{}^{\gamma} + m^2\,\frac{2(\upsilon_M\upsilon_X)^{3/2}}{\upsilon}\,C_{MX}{}^{\gamma} \tag{3}$$

where $\upsilon_M$ and $\upsilon_X$ are the numbers of M and X ions in the formula and $z_M$ and $z_X$ give their respective charges in electronic units; also $\upsilon = \upsilon_M + \upsilon_X$, while $n_w$ is the number of kg of solvent and m is the conventional molality. The other quantities have the form

$$f^{Gx} = -A_{\varphi}\left(\frac{4I}{b}\right)\ln(1 + bI^{1/2}) \tag{4}$$

$$f^{\varphi} = -A_{\varphi}\,\frac{I^{1/2}}{1 + bI^{1/2}} \tag{5}$$

$$f^{\gamma} = -A_{\varphi}\left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right] \tag{6}$$

$$B_{MX}{}^{Gx} = \beta_{MX}{}^{(0)} + \frac{2\beta_{MX}{}^{(1)}}{\alpha^2 I}\,[1 - e^{-\alpha I^{1/2}}(1 + \alpha I^{1/2})] \tag{7}$$

$$\beta_{MX}{}^{\varphi} = \beta_{MX}{}^{(0)} + \beta_{MX}{}^{(1)}e^{-\alpha I^{1/2}} \tag{8}$$

$$B_{MX}^{\gamma} = 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{\alpha^2 I} \; [1 - e^{-\alpha I^{1/2}} \; (1 + \alpha I^{1/2} - \tfrac{1}{2}\alpha^2 I] \qquad (9)$$

$$C_{MX}^{Gx} = \tfrac{1}{2} C_{MX}^{\varphi} \qquad (10)$$

$$C_{MX}^{\gamma} = \tfrac{3}{2} C_{MX}^{\varphi} \qquad (11)$$

Here I is the ionic strength, $\frac{1}{2}\sum m_i z_i^2$, and $A_\varphi$ is the Debye-Hückel coefficient for the osmotic function, $[\frac{1}{3}(2\pi N_o d_w/1000)^{1/2}(e^2/DkT)^{3/2}]$, which has the value 0.392 at 25°C for water. In order to maintain simple equations for mixed electrolytes b and α must remain the same for all solutes and in I the values b = 1.2 and α = 2.0 were selected. For each substance the two parameters $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ define the second virial coefficient and $C_{MX}^{\varphi}$ defines the third virial coefficient which is usually very small and sometimes completely negligible. If necessary to fit unusual behavior one could add to the second virial coefficient further terms of the same form but with different values of α and β but this was not required for the present work.

The numerical factors, such as $(2\nu_M\nu_X)$, multiplying the second and third virial coefficients in equations (1) to (3) are needed in order to retain the simple meaning that the virial coefficients represent the short-range interaction of pairs and triplets of ions, respectively. In equations (2) and (3) the quantities $(2\nu_M\nu_X/\nu)$ and $2(\nu_M\nu_X)^{3/2}/\nu$ are both unity for a symmetrical MX electrolyte. For convenience in working with single electrolytes we shall tabulate $\frac{4}{3}\beta^{(0)}$, $\frac{4}{3}\beta^{(1)}$, and $(2^{5/2}/3)C^{\varphi}$ for 2-1 electrolytes and the corresponding quantities for other types, but these numerical factors must be removed before the virial coefficients are used in work with mixed electrolytes.

While equations (1) to (11) are quite simple and should be used by anyone desiring accurate values of the thermodynamic properties, we recognize that for many purposes a rough estimate of the activity coefficient will suffice. Since we shall see that there is a close relationship between $\beta^{(1)}$ and $\beta^{(0)}$ and that $C^{\varphi}$ is usually very small, one can make a reasonably good estimate of the activity coefficient from $\beta^{(0)}$ alone. For this purpose we present a large graph with curves of $\gamma$ for various values of $\beta^{(0)}$ from which one can visually interpolate values of the activity coefficient directly for 1-1 electrolytes.

## 1-1 Electrolytes

### Inorganic salts and acids.

Most of the data for inorganic salts and acids were critically reviewed by Robinson and Stokes in their classic papers and in the various editions of their book. Unless noted otherwise we have accepted the tables of osmotic coefficients in the second (revised) edition of their book[3] and evaluated by least squares the best values of $\beta^{(0)}$, $\beta^{(1)}$, and $C^{\varphi}$ which are listed in Table I. Also listed are the maximum molality for which agreement is attained to 0.01 in $\varphi$ or for which data are available, the standard deviation of fit, and the reference (3 to Robinson and Stokes or as is appropriate in other cases).

In evaluating parameters we sought to fit the experimental points within their estimated uncertainty to as high a concentration as possible. Various weighting schemes were used in the least-squares calculations. For most 1-1 electrolytes (and many with higher-charged ions) satisfactory results were obtained with the system of equal weights up to I = 4 and weights proportional to $(4/I)^2$ thereafter. In a few cases this was changed to reduce the weights at high concentration more sharply (for example as $(4/I)^8$) or to begin the reduction at a lower ionic strength.

Unless the data extend to rather high concentration it is not possible to obtain a reliable third virial coefficient. For inorganic salts of 1-1 type the third virial was included when the data extended to 2 M or above but not otherwise. Among the two cases where the maximum concentration is 2 M, one, KF, yielded reasonable results with the third virial but $NH_4ClO_4$ gave a peculiar set of constants. Hence, we report the alternate results for $NH_4ClO_4$ without the third virial coefficient.

The resulting values of $\beta^{(0)}$ and $\beta^{(1)}$ are plotted on figure 1. While the general discussion of this figure will be postponed until a later section, we note now that the values for most inorganic salts, acids, and bases fall in a rather narrow band. This is not unexpected since $\beta^{(0)}$ $\beta^{(1)}$ depend upon the same properties of the ions and the solvent although we shall see that these properties are weighted somewhat differently for the two parameters. In a few cases the data were sufficiently scattered that the parameters were sensitive to the choice of weight given to different series of data or to points at high concentration; in these cases a choice which yielded parameters within the principal band of figure 1 was accepted.

For the hydrogen halides, where most of the data come from galvanic cells, we reviewed the original literature which includes work subsequent to Robinson and Stokes last edition. In each case, the data are concordant to rather high accuracy.

The final values for HCl are based on the combined data of Harned and Ehlers[12] and of Akerlof and Teare[13] (from 3 to 6 M) on the cell $H_2|HCl(m)|AgCl,Ag$ and that of Gupta, Hills, and Ives[14] on the cell $H_2|HCl(m)|Hg_2Cl_2,Hg$. The $E_o$ values were adjusted independently for each set of data with the result 0.2224 v for Harned and Ehlers, 0.2232 for Akerlof and Teare, and 0.26815 for Gupta, et al. The difference of 0.0008 v between the two values for the silver electrode cells seems large but it is clearly indicated by the data in the range where both studies overlap (3 to 4 M).

The constants for HBr are based on the combined data of Gupta, Hills and Ives[15] on the cell $H_2|HBr(m)|Hg_2Br_2,Hg$ and that of Harned, Keston, and Donaldson[16]; of Biermann and Yamasaki[17]; and of Hetzer, Robinson, and Bates on the cell $H_2|HBr(m)|AgBr,Ag$. The $E_o$ for the mercury cell was found to be 0.1392 v while the values for the silver cell are 0.0710 for the combined data of Harned, et al, and of Biermann and Yamasaki and 0.0709 for Hetzer, et al. In this case the difference in $E_o$ values for the silver cell is negligible.

For HI the isopiestic data of Harned and Robinson[19] and the results of Hetzer, Robinson, and Bates for the cell $H_2|HI(m)|AgI,Ag$ were combined with appropriate weights to yield the constants in Table I and the value $E_o = -0.1522$ v for the cell.

In view of its extensive use as a reference solute in isopiestic measurements we gave particular attention to KCl. The osmotic coefficient as recommended by Robinson and Stokes is highly concordant with the measurements of Harned and Cook[21] on the cell with flowing amalgam electrode $Ag,AgCl|KCl(m_1)|K_xHg_{1-x}|KCl(m_2)|AgCl,Ag$ and those of Shedlovsky and MacInnes[22] on the cell with transference $Ag,AgCl|KCl(m_1)|KCl(m_2)|AgCl,Ag$. The transference number must be known as a function of concentration in order to interpret the results of the second type of cell. Our final values were obtained by least squares treatment of the combined data on the osmotic coefficient and on the cell measurements of Harned and Cook, but the resulting thermodynamic properties would be substantially the same if any combination of these measurements had been used.

The original data on several other alkali halides (including NaCl) were also examined in detail and in all cases except CsCl it was decided to accept the constants based upon Robinson and Stokes tables. Special attention was given to CsCl because its parameters (and those of CsBr and CsI) appeared to depart from the general trend shown in figure 1 and in view of the recent measurements of Mussini, Longhi, and Riva[23a] on the amalgam electrode cells

$$\mathrm{Pt}|\mathrm{Cs}_x\mathrm{Hg}_{1-x}|\mathrm{CsCl}(m)|\mathrm{AgCl},\mathrm{Ag}$$

After examining the various series of cell measurements we decided to accept as input data for our analysis the ratios of activity coefficients determined by the cell data in the range of measured concentrations and the original isopiestic measurements of Robinson and Sinclair[23b]. All data are reasonably concordant and the resulting parameters confirm the significant difference between the cesium halides and such salts as $NaNO_3$, $NaClO_3$, and $NH_4NO_3$ which have similar or smaller values of $\beta^{(0)}$ but much larger values of $\beta^{(1)}$. Subsequently we shall consider the possible meaning of this difference in terms of interionic forces.

Recently published data for other salts were treated in a corresponding manner and the results and sources are entered in Table I.

Hydroxides

The activity coefficients of alkali metal hydroxides can be obtained from two types of galvanic cell.

A: $\mathrm{Pt,H_2}\,|\mathrm{MOH}(m')|\mathrm{M_xHg}|\mathrm{MOH}(m'')|\,\mathrm{H_2,Pt}$

B: $\mathrm{Pt,H_2}\,|\mathrm{MOH}(m_a)\mathrm{MX}(m_b)|\,\mathrm{AgX,Ag}$

where $\mathrm{M_xHg}$ indicates an amalgam electrode in cell A and X indicates either Cl or Br in cell B.

Amalgam electrode cells were employed by both Harned and Akerlof and their respective collaborators. Although the amalgam electrodes are troublesome, these investigators have used them successfully in other types of cells where the results can be checked from independent sources. The reaction for cell A involves transfer of solvent as well as solute, hence the equation for the potential includes both the activity and osmotic coefficients

$$E = \frac{RT}{F}\left[2\ln\frac{\gamma''m''}{\gamma'm'} + 0.036\,(m''\varphi'' - m'\varphi')\right] \qquad (12)$$

Since both activity and osmotic coefficients can be expressed in terms of $\beta^{(0)},\beta^{(1)}$, etc., we have evaluated these quantities directly by least squares from the original cell potentials. The values for Li, Na, K and Cs hydroxides presented in Table I come from measurements of amalgam cells but with weighting of data influenced by the measurements of type B cells as discussed below. In the case of sodium hydroxide the isopiestic measurements of Stokes[24] were used along with cell potentials.

In 1954 Guggenheim and Turgeon[25] showed that, with certain assumptions, the activity coefficients of these hydroxides could also be evaluated from the existing measurements of cells of type B. Since the solutions in these cells are mixed electrolytes, the analysis in general involves additional terms for the interaction of ions of like charge, but Guggenheim and Turgeon accepted Bronsted's principle of specific interaction and ignored these terms. We now have good evidence that such terms are not negligible; hence, we must develop equations for these cell potentials on an adequate basis. First we express the potential for a cell of type B

$$E = E^{\circ} - \frac{RT}{F}\left[\ln K_w - 0.036\ (\varphi m) - \ln\frac{m_b}{m_a} - \ln\frac{\gamma_{X^-}}{\gamma_{OH^-}}\right] \qquad (13)$$

where $m = m_a + m_b$ and $K_w$ in the ionization constant for the solvent. Since we shall confine our use of data from this type of cell to solutions below 0.3 M, we shall ignore terms related to the third virial coefficient. Also the osmotic coefficient may be estimated with more than sufficient accuracy for the small term 0.036 ($\varphi m$). The activity-coefficient term may be expanded by substitution of either equations (41) and (42) or of (23), (27), (28) and (32) of paper I to yield

$$\ln \frac{\gamma_{X^-}}{\gamma_{OH^-}} = 2m\{(B_{MX}^{\gamma} - B_{MX}^{\varphi}) - (B_{MOH}^{\gamma} - B_{MOH}^{\varphi}) + (2y - 1)\theta_{X,OH}\} \quad (14)$$

where $y = m_a/m$ and terms in C and $\psi$ have been dropped as indicated above. Also we note that $B^{\gamma} - B^{\varphi} = B^{Gx}$ as defined in equation (56) of I or equation (7) of this paper.

For the particular case $y = 1/2$ which requires $m_a = m_b$, the last term in equation (14) disappears; then we can write

$$E' = E + \frac{RT}{F} \ln \frac{m_b}{m_a}$$

$$= E^\circ - \frac{RT}{F} [\ln K_w - 0.036(\varphi m) + 2m(B_{MOH}^{Gx} - B_{MX}^{Gx})] \quad (15)$$

Roberts[26] measured cells of type B with NaCl-NaOH solutions and $m_a = m_b$. His results are shown in the upper portion of figure 2. The solid line is calculated from the values of $\beta^{(0)}$ and $\beta^{(1)}$ derived for NaOH from the data of Akerlof and Kegeles[27] for type A cells together with isopiestic data (above 2 M) and parameters for NaCl from Table I. Type A cells with NaOH were also measured by Harned and Hecker[28] and their results lead to the dashed line on figure 2. It is apparent that the Akerlof and Kegeles curve agrees satisfactorily with the data of Roberts whereas the Harned and Hecker curve departs significantly in this concentration range. It did not seem worthwhile to attempt to improve the constants evaluated from Akerlof and Kegeles' data and they are included in Table I for NaOH.

The remaining series of experiments with Type B cells all hold $m_a$ fixed, usually at 0.01 M, and vary $m_b$. The results of Harned and Mannweiler[29] for NaOH-NaCl solutions are shown in the lower portion of figure 2. In these experiments $m_a = 0.01$ M; hence the value of $E'$ at $m = 0.02$ M should agree with that of Roberts. The difference of 0.5 mv seems large and standard cell calibration errors appear to be the only plausible explanation. Our primary interest, however, is in the slopes of the curves and the difference in slopes gives the value of $\theta_{Cl,OH}$. This may be seen by substituting equation (14) in (13). The result from figure 2 is $\theta_{Cl,OH} = -0.047$.

For the other alkali metals it seems best to consider the difference in potential for a given cell of type B from that of the corresponding cell with NaOH-NaCl or NaOH-NaBr solution of the same $m_a$ and $m_b$. This has the effect of cancelling the term in $\theta_{Cl,OH}$ or $\theta_{Br,OH}$. In most cases there are experimental potentials from the same laboratory for each cell of the pair but there is no difficulty in interpolating the values for the sodium cells when necessary. The difference in potential for such a pair of cells is

$$E_{M^+} - E_{Na^+} = \frac{RT}{F}\left[\ln\left(\frac{\gamma_{OH^-}}{\gamma_{X^-}}\right)_{M^+} - \ln\left(\frac{\gamma_{OH^-}}{\gamma_{X^-}}\right)_{Na^+}\right] \qquad (16)$$

If we substitute the appropriate expressions cited above for the activity coefficients, we obtain

$$mB_{MOH}{}^{Gx} + \delta = \left(\frac{F}{2RT}\right)(E_{M^+} - E_{Na^+}) + m(B_{MCl}{}^{Gx} + B_{NaOH}{}^{Gx} - B_{NaCl}{}^{Gx}) \qquad (17)$$

Here we have added a term $\delta$ to allow for the possibility of small differences in standard cell calibration between series of experiments carried out at different times, such as apparently arose in the experiments with NaOH-NaCl, or for differences between the AgX,Ag electrodes used in different series. Presumably $\delta$ is a very small constant for any series. The parameters for the alkali halides are taken from Table I. The results are shown in figure 3.

We consider first the values for KOH which were measured by Harned and Hamer[30] for both chloride and bromide solutions. The curve is drawn from the parameters for KOH from the amalgam cells (type A) measured by Akerlof and Bender[6] (with $\delta = 0$). The agreement is good and would become even better if a very small positive $\delta$ is assumed for the bromide solutions which would raise that curve, and if a very small negative $\delta$ correspondingly lowered slightly the curve for the chloride solutions. The measurements of amalgam cells with KOH by Harned and Cook[31] yield a curve which agrees less perfectly but still quite well. The parameters from Akerlof and Bender's type A cells are adopted for Table I.

The data for cesium hydroxide appear to be less precise than those for sodium or potassium hydroxides, and a careful consideration of the uncertainties indicated that $\beta^{(1)}$ could be determined only within very wide limits. We chose therefore to relate $\beta^{(1)}$ to $\beta^{(0)}$ by the curve established by most 1-1 electrolytes as shown in figure 3. Appropriate graphical presentation of the data for both types of cell then allowed the choice of values $\beta^{(0)} = 0.150$, $\beta^{(1)} = 0.30$ with no third virial coefficient. The resulting curve with an assumed $\delta$ of 0.005 is shown as the upper dashed line on figure 3 and yields agreement well within the scatter of the data. At higher concentrations the function is determined entirely by the data from the amalgam cell.

Unfortunately the situation for lithium hydroxide is less satisfactory even though the individual sets of data seem relatively precise. The type A cell values above 0.02 M are well represented by the function defined by $\beta^{(0)} = 0.015$ and $\beta^{(1)} = 0.14$ with no third virial coefficient, but this yields the lower dashed curve on figure 3 which, even with a substantial $\delta$ value, does not fit the type B cell values very well. The type B results for chloride[34] and bromide[35] solutions also diverge from one another and in the opposite direction from the smaller divergence shown by potassium solutions. The horizontal straight line corresponding to $\beta^{(0)} = \beta^{(1)} = 0$ gives a reasonable fit to all of the data at very low concentration but is clearly unsatisfactory for amalgam cells above 0.1 M. A set of constants in the vicinity of $\beta^{(0)} = -\beta^{(1)} = 0.06$ and a negative third virial coefficient would give a compromise forced-fit of all cell data.

Each of the above sets of constants for LiOH may be compared with the general pattern for 1-1 electrolytes as shown in figure 1. The first set (from type A cells) is very reasonable. The second set, $\beta^{(0)} = \beta^{(1)} = 0$ is at the lower boundary of the principal zone near the values for CsCl, CsBr, and CsI; thus it cannot be eliminated on this basis. The last set departs from the normal pattern substantially and, therefore, seems unlikely to be correct. Since other hydroxides and other lithium salts fall in the general pattern for 1-1 electrolytes, it seems rather probable that lithium hydroxide will conform also and on that basis we select the first set of constants for Table I. Further experimental work is needed to resolve these questions about LiOH.

Cells of type A or B could also be used for other hydroxides. We shall consider only the measurements of

Harned and Geary[36] on $Ba(OH)_2$-$BaCl_2$ solutions in type B cells. These cells were paired with NaOH-NaCl cells with equal concentrations of $OH^-$ and $Cl^-$. The mathematical analysis is slightly more complex and one must note that the ionic strength is no longer the same in the two solutions. The terms for interaction of like-charged ions still cancel. Good agreement is obtained for the constants $\beta^{(0)} = 0.172$, $\beta^{(1)} = 1.20$ which are included in Table VI.

## Organic Acids and Salts

There are isopiestic data for a large array of organic acids and salts. These were treated in essentially the manner already described and the results are given for carboxylate salts in Table II, for tetra-alkyl ammonium halides in Table III, for sulfonic acids and sulfonates in Table IV, and for some additional compounds in Table V. In the last two tables the maximum error in the osmotic coefficient within the indicated concentration range was 0.02 instead of 0.01.

For the methane and ethane sulfonates only activity coefficients are reported[40] (although they are based upon isopiestic measurements). By evaluating our constants from the ratios of activity coefficients over the range of experimental measurement, the results should be independent of the original extrapolation to zero concentration. The fit is generally very good (less than 1% deviation in $\gamma$) but there are a few discrepant points which may be typographical errors.

Figures 1 and 4 show the relationship of $\beta^{(1)}$ to $\beta^{(0)}$ for the solutes listed in Tables II, III, and IV. From figure 1 it is apparent that the carboxylate salts fall within the normal pattern. In figure 4 the range of "normal" behavior exhibited by the inorganic electrolytes and the carboxylate salts in figure 1 is shown. Figure 4 shows a considerably wider range of constants which is not surprising in view of the greater variety of interionic forces and the somewhat decreased accuracy of the data or of the ability of our equations to fit the data.

## 2-1 Electrolytes

The treatment of inorganic 2-1 and 1-2 electrolytes followed the same pattern as for 1-1 electrolytes and the results are given in Tables VI and VII. The accuracy of fit to max. m is 0.01 in Table VI and 0.02 in Table VII. Figure 5 shows the $\beta^{(0)}$ and $\beta^{(1)}$ values for 2-1 electrolytes. The general pattern is the same as was noted in figure 1 for the 1-1 type, but the range of $\beta^{(1)}$ values is much larger; this was discussed in I. Comments follow on the special situations arising among these solutes.

Although the zinc halides show anomalous behavior indicating a high degree of association at high concentration, they appear to follow the normal pattern for 2-1 electrolytes in dilute solution. Hence we fitted the regular equations to the data for these solutes but with weighting patterns emphasizing the dilute range. The results in each case are quite reasonable in that (1) the values of $\beta^{(0)}$ and $\beta^{(1)}$ fall in the normal band in figure 5 and (2) a large negative value of $C^{\varphi}$ is obtained which indicates strong three particle association presumably to the neutral $ZnX_2$ species. At still higher concentration further association to $ZnX_3^-$ and $ZnX_4^{=}$ appears to occur. Apparently there is no significant association to $ZnX^+$ ion pairs. In all cases the primary source of experimental values is the galvanic cell $Zn,Hg|ZnX_2(m)|AgX,Ag$ where the two phase amalgam is used for the zinc electrode, but there are also isopiestic measurements above 0.1 M.

In the case of $ZnCl_2$ there are cell measurements by Scatchard and Tefft[46] and by Robinson and Stokes[47] who also made isopiestic measurements. The constants selected were obtained from Scatchard and Tefft's potentials with equal weighting below $I = 1$ and weights of $(1/I)^4$ at higher concentration. The osmotic coefficients from these constants fit the experimental values up to 1.2 M which is also the range of good fit to the cell measurements. The standard $E_o = 0.9845$ v falls well within the range 0.9843 to 0.9851 calculated from the present best value[48] for the zinc electrode (saturated with Hg) $E_o = 0.7619$ v together with the values 0.2224 and 0.2232 for the silver-silver chloride electrode obtained in our treatment of hydrochloric acid.

For $ZnBr_2$ the cell measurements of Stokes and Stokes[49] extend only to 0.99 M and were weighted equally to yield the constants of Table VI. This function fits the measured osmotic coefficients[50] (within 0.01) through 1.6 M. The standard potential $E_o$ = 0.8333 v again agrees satisfactorily with the values 0.8328 or 0.8329 calculated from the potentials of the zinc and silver-silver bromide electrodes.

The cell measurements of Bates[51] for $ZnI_2$ extend only to 0.8 M; these were used along with the osmotic coefficients[52] in the same concentration range with appropriate weights to yield the constants adopted. The osmotic data are well fitted through 0.8 M while the cell potentials agree reasonably except for the most dilute solution (0.0012 M) which deviates by 0.0018 v. The standard potential again agrees well, $E_o$ = 0.6097 which is exactly the value obtained from the separate values for the zinc and silver-silver iodide electrodes. In this case the value of $C^{\varphi}$, although negative, is not particularly large--indeed it is somewhat smaller than the value for $BaI_2$. Thus the association to neutral $ZnI_2$ is not particularly strong. The trend of the osmotic coefficients above 0.8 M, however, indicates strong association of more than three ions presumably to $ZnI_3^-$ and $ZnI_4^=$.

Among the organic salts and acids of the 2-1 type are several disulfonates[55]. When the two ionizing groups are not too widely separated the electrolyte properties are fitted satisfactorily and the resulting constants depart from the normal pattern only moderately (in the direction of abnormally large $\beta^{(1)}$). In the case of 4,4' dibenzyldisulfonic acid we accept the older data listed by Robinson and Stokes[3] which follow the general pattern of these electrolytes, rather than the more recent results of Bonner and Rogers[55], which seem anomalous, but this discrepancy should be resolved by additional experiments.

### 3-1, 4-1, and 5-1 Electrolytes

The same general methods discussed for 1-1 and 2-1 electrolytes were used for the higher valence types and the results for 3-1 electrolytes are given in Table VIII while the parameters for 4-1 and 5-1 solutes are in Table IX. The allowable deviation up to max. m is 0.002 except for the 5-1 salt $K_5P_3O_{10}$ where 0.03 was accepted. While the maximum molality values are lower for the high valence types the maximum ionic strengths are about the same as were obtained for 1-1 and 1-2 solutes. Figure 6 shows that $\beta^{(0)}$ and $\beta^{(1)}$ values are about as closely interrelated for 3-1 electrolytes as for lower valence types; the corresponding data for 4-1 and 5-1 types are too few to have much meaning.

Among these cases a few require special comment. For $Co(en)_3Cl_3$ there are in addition to isopiestic data[3], the measurements for very dilute solutions of concentration cells with transference and of transference numbers by Karl and Dye[56]. The constants in Table VIII were obtained by appropriate weighting of both sets of data in a combined calculation. Our equations with these constants yield good agreement with all of the experimental points.

In the case of $InCl_3$ the potential of the cell $In|InCl_3(m)|AgCl,Ag$ was measured by Covington, Hakeem, and Wynne-Jones[57] for concentrations from 0.001 to 0.01 M. These results yield lower activity coefficients than are typical for 3-1 salts and suggest some tendency toward ion association. Nevertheless, the data can be fitted very well by our equations with a negative value of the second virial coefficient. The data do not extend over a wide enough concentration range to determine both $\beta^{(0)}$ and $\beta^{(1)}$ unambiguously. The value $3/2\ \beta^{(0)} = -3.8$ with $\beta^{(1)} = 0$ yields a good fit. If the straight line on figure 6 which agrees well with the properties of other 3-1 electrolytes is extrapolated, one can obtain even slightly better agreement with the $InCl_3$ data for the values: $3/2\ \beta^{(0)} = -1.68$, $3/2\ \beta^{(1)} = -3.85$ which are entered in Table VIII.

## A Convenient Approximation

For many purposes only a rough estimate of an activity coefficient is needed. Since $\beta^{(1)}$ has been shown to be determined within rather narrow limits if $\beta^{(0)}$ is known and the effect of the third virial coefficient is small, a convenient approximation becomes possible. Figure 7 shows the activity coefficient as a function of molality for 1-1 electrolytes for a series of values of $\beta^{(0)}$. In each case $\beta^{(1)}$ was given a value in the middle of the band in figure 1 and $C^{\varphi}$ was neglected.

By taking the value of $\beta^{(0)}$ from Tables I through V and interpolating between the appropriate curves on figure 7 one can read directly an approximate value of the activity coefficient for any 1-1 electrolyte.

Similar graphs could, of course, be prepared for higher valence types, but the more extreme departures from unity of these activity coefficients reduces the utility of this procedure. Hence such graphs are omitted.

## Discussion

Up to this point the emphasis has been upon convenient and accurate representation of data for thermodynamic purposes. Let us now consider the interpretation of the results in terms of interionic forces. In I it was shown that $B^{\varphi}$ is a second virial coefficient arising from short-range forces between pairs of ions although its interpretation is complicated by the presence of the term for long-range electrostatic forces and the ionic strength dependence of the radial distribution functions. Thus much of the discussion will be qualitative in nature.

The second virial coefficient may be either positive or negative depending on the net predominance of repulsive or attractive short-range forces, respectively. Also the second virial coefficient for an electrolyte is a weighted mean of the interactions of pairs of ions with signs ++, +-, and -- and it was shown in I that the relative weighting of +- interactions is greatest at low ionic strength. At higher ionic strength the ++ and -- terms become more important but never equal to the weight of the +- interaction. Since multiply charged ions of the same sign will rarely approach one another closely, we can expect that the ++ or -- terms for such ions will be even smaller than for singly charged ions of the same sign and same size.

In view of this difference in weighting of +- compared to ++ and -- interactions it is possible to determine two parameters for the short-range binary interactions of a single electrolyte--but only two. In our formulation these are $\beta^{(0)}$ and $\beta^{(1)}$. Ramanathan and Friedman[61] included more parameters in their model but, in accordance with these ideas, found that only two could be evaluated from osmotic or activity data and that any others had to be set to zero or to some other arbitrary value unless they were known from different sorts of measurements.

The simplest molecular model presenting effectively two parameters is one of rigid spherical ions of varying size. The thermodynamic properties depend primarily on the sum of radii for unlike ions $(R_+ + R_-)$ but there is a secondary dependence on the absolute magnitude of the difference $|R_+ - R_-|$. The excluded volumes depend on the cubes of the distances of closest approach; hence, we expect a larger repulsive effect for like-charged ions when there is a difference in size. Rasaiah and Friedman[62] made statistical calculations for this model and we evaluated our parameters to fit several of their examples; the results are in Table X and pertain to aqueous solution at room temperature. We see that for constant $(R_+ + R_-)$ a shift from equal to unequal sized ions increases $\beta^{(0)}$ and decreases $\beta^{(1)}$; thus it moves a point on figure 1 downward and to the right. While no combination of the available examples corresponds exactly to a change of $\beta^{(1)}$ with $\beta^{(0)}$ constant, the comparison of the third line with the second line of Table X approaches this case and indicates the approximate reduction in $(R_+ + R_-)$ required for a particular increase in $|R_+ - R_-|$.

While it is formally possible to discuss the parameters we have obtained for real electrolytes in terms of ionic hard-core radii, this does not seem promising. The ambiguity between the radius of the simple ion and the solvated ion is well known. Also there seems to be no correlation of the parameters in Table I with the expectations based upon ionic radii determined from crystals.

In their model for the intermolecular potential Ramanathan and Friedman[61] assumed electrostatic and repulsive terms based upon independent knowledge of charges and of radii in crystals and then evaluated empirically coefficients of a term, first introduced by Gurney,[63] which can be considered to represent the net effect of solvation, dispersion forces, and any other effects of similar range. Our results support this general concept that the second virial coefficients for electrolytes are best discussed in terms of a combination of repulsive radii determined from crystals or other sources and slightly longer range forces which arise from solvation effects, from dispersion forces, and in some cases also from such other effects as would arise from permanent dipoles or multipoles (for example with $OH^-$ or $NO_3^-$). The contribution of each of these various types of short-range forces to ++ and -- interactions will not follow the same relationship as its contribution to +- interactions; hence $\beta^{(1)}$ will not be exactly determined by $\beta^{(0)}$. But the relationship is complex and we do not expect any simple pattern related to ionic size.

In figures 1, 4, 5 and 6 we have noted that in each case the points for most solutes fall in a band with positive slope; this indicates that these short-range forces follow similar patterns for ++ and -- as compared to +-

interionic interactions. In some cases the points outside these bands are individually labelled. Thus in figure 1 the point for $RbNO_2$ falls below the band while the points for other nitrites are within but near the lower boundary of the band. Since these data for nitrites do not appear to be of very high accuracy, it is probable that $RbNO_2$ is not really anomalous. The results for all nitrites, however, indicate more repulsive or less attractive forces between pairs of nitrite ions than is typical for most anions. Corresponding statements can be made about the labelled points above the band with the conclusion that like ion interactions are less repulsive or more attractive than normal for $BrO_3^-$, $ClO_3^-$, and $H_2AsO_4^-$.

It is not surprising that the magnitude of these effects is greater for the salts involving large organic groups shown in figure 4. For the electrolytes involving multiply charged ions in figures 5 and 6 it is surprising that the points farthest from the principal band involve only the very common univalent ions $Na^+$ and $K^+$ which cannot be the cause of the deviation since most salts with these ions are normal. Thus the short-range forces between pairs of multiply charged ions must be responsible. In all cases the ions are polyatomic with the negative charge distributed among several peripheral atoms; hence it is not too surprising that they approach one another close enough for short-range forces to have some effect.

The location of a given point along the band for that type of electrolyte is, of course, the more important factor, and it will be discussed in terms of the value of $\beta^{(0)}$. This quantity is determined primarily by the short-range forces between ions of opposite charge. Our results show various trends of interest, but many of these have been discussed previously by Gurney[63] and Frank[64] among others. These authors emphasize a classification of both cations and anions with respect to a tendency to enhance or to disrupt the solvent structure. Then it is shown that the activity coefficient curves, or our $\beta$ values, are the higher the more dissimilar are the ions in this respect and the lower the more similar they are.

We find that the multiply charged cations are readily added to this system. Then the most "structure-making" ions are the smaller multiply charged ions with the sequence $Mg^{++}$,$Ca^{++}$,$Sr^{++}$,$Ba^{++}$,$Li^{+}$,$Na^{+}$,$K^{+}$,$Rb^{+}$,$Cs^{+}$ continuing to the "structure-breaking" ions $Rb^{+}$ and $Cs^{+}$. The corresponding anion sequence is $OH^{-}$,$F^{-}$,$Cl^{-}$,$Br^{-}$,$I^{-}$,$ClO_4^{-}$ wherein we have added perchlorate as the most "structure-breaking" ion to those usually given heretofore.

The divalent ions $Zn^{++}$, $Mg^{++}$, $Ca^{++}$ and $Sr^{++}$ each have $\beta^{(0)}$ values in increasing order for $Cl^{-}$, $Br^{-}$, $I^{-}$, and $ClO_4^{-}$; while for $Ba^{++}$ as for $Li^{+}$ the values for $ClO_4^{-}$ drop between $Br^-$ and $I^-$. For other simple divalent cations the data are less extensive but there seems to be no contradiction of this pattern. The complex but compact ion $UO_2^{++}$ also follows this trend, but large cobalt complex ions show the opposite sequence and may be classified as "structure-breakers".

When one ion is of intermediate character, for example $Na^+$ or $K^+$, then the sequence may be irregular. For potassium there is a smooth trend of $\beta^{(0)}$ from $OH^-$ down through $F^-$ to $Cl^-$ and then back upward for $Br^-$ and $I^-$. But for sodium the hydroxide and perchlorate both take intermediate values. Hydrogen ion in strong acids is a "structure-maker" with properties close to those of $Li^+$. The sulfate ion appears to fall between $F^-$ and $Cl^-$; its $\beta^{(0)}$ values drop from $Li^+$ to $Na^+$ and then rise through $K^+$, $Rb^+$ and $Cs^+$.

The $\beta^{(0)}$ values for nitrates are relatively low in all cases regardless of the structure making or breaking character of the cation. This suggests some tendency toward ion pair formation as is also indicated by spectroscopic data in several cases. Lemley and Plane[65] report a particularly complete spectral study for zinc nitrate while Peleg[66] reports a similar study of magnesium nitrate; these authors refer to work on other nitrates.

The electrolytes involving $ClO_3^-$, $BrO_3^-$, $H_2PO_4^-$, $H_2AsO_4^-$, $BO_2^-$, $BF_4^-$, and $PF_6^-$ all have low $\beta^{(0)}$ values but data are available for only one or two cations in most cases. Presumably these large anions are structure breakers and in addition tend toward ion pair formation as do nitrates. Nevertheless, their behavior is well represented by our equations and it is not necessary to assume incomplete dissociation.

It has been noted previously that acetate is a weak "structure-maker" and our results agree. The values for nitrite follow those for chlorides rather closely; hence nitrite is a weak "structure-breaker". The electrolytes involving large organic ions have been measured recently and the papers presenting these results are accompanied in most cases by discussions making use of recent theory; hence we shall not comment further on these cases.

Bromley[67] has independently developed a system of representation and estimation for activity coefficients of strong electrolytes and I have enjoyed discussions with him. His system, although developed simultaneously, may be described as a simplification of the present system. The third virial coefficient is omitted and the second virial coefficient is modified into a form, still dependent on ionic strength, but with a single parameter B. This is, in effect, a relationship between our $\beta^{(1)}$ and $\beta^{(0)}$. He further shows that his B values can be approximated from two parameters for each ion $B_M$ and $\delta_M$ or $B_X$ and $\delta_X$ by the equation

$$B = B_M + B_X + \delta_M \delta_X$$

Structure-making cations have positive $\delta_M$ while structure-breakers have negative $\delta_M$. For anions the signs are reversed with structure-makers having negative $\delta_X$ and the structure breakers having positive $\delta_X$. Thus the last term gives the effect just discussed in which $\delta_M\delta_X$ is the more positive the more dissimilar are pairs of ions with respect to this quality and is negative for pairs in which both ions have the same characteristic (either structure-making or structure-breaking).

Although less accurate than our equations, Bromley's system is quite effective and will be useful for many purposes. He also compares his results with a somewhat similar system of Meissner and Tester.[68]

Electrolytes of the 2-2 type and others involving ion pairing will be treated in a subsequent paper. Also we are proceeding to calculations for mixed electrolytes based upon the constants here obtained; indeed the convenience of our equations as applied to mixed electrolytes was a primary incentive for this work.

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Table I: Inorganic Acids, Bases, and Salts of 1-1 Type.

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| HCl | 0.1775 | 0.2945 | 0.00080 | 6 | a | t |
| HBr | .1960 | .3564 | .00827 | 3 | a | t |
| HI | .2362 | .392 | .0011 | 3 | b | t |
| $HClO_4$ | .1747 | .2931 | .00819 | 5.5 | .002 | 3 |
| $HNO_3$ | .1119 | .3206 | .0010 | 3 | .001 | 3 |
| LiCl | .1494 | .3074 | .00359 | 6 | .001 | 3 |
| LiBr | .1748 | .2547 | .0053 | 2.5 | .002 | 3 |
| LiI | .2104 | .373 | --- | 1.4 | .006 | 3 |
| LiOH | .015 | .14 | --- | 4 | c | t |
| $LiClO_4$ | .1973 | .3996 | .0008 | 3.5 | .002 | 3 |
| $LiNO_2$ | .1336 | .325 | -.0053 | 6 | .003 | 4 |
| $LiNO_3$ | .1420 | .2780 | -.00551 | 6 | .001 | 3 |
| NaF | .0215 | .2107 | --- | 1 | .001 | 3 |
| NaCl | .0765 | .2664 | .00127 | 6 | .001 | 3 |
| NaBr | .0973 | .2791 | .00116 | 4 | .001 | 3 |
| NaI | .1195 | .3439 | .0018 | 3.5 | .001 | 3 |
| NaOH | .0864 | .253 | .0044 | 6 | b | t |
| $NaClO_3$ | .0249 | .2455 | .0004 | 3.5 | .001 | 3 |
| $NaClO_4$ | .0554 | .2755 | -.00118 | 6 | .001 | 3 |
| $NaBrO_3$ | -.0205 | .1910 | .0059 | 2.5 | .001 | 3 |
| NaCNS | .1005 | .3582 | -.00303 | 4 | .001 | 3 |
| $NaNO_2$ | .0641 | .1015 | -.0049 | 5 | .005 | 4 |
| $NaNO_3$ | .0068 | .1783 | -.00072 | 6 | .001 | 3 |
| $NaH_2PO_4$ | -.0533 | .0396 | .00795 | 6 | .003 | 3 |
| $NaH_2AsO_4$ | -.0442 | .2895 | --- | 1.2 | .001 | 3 |

Table I Continued Page 2

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| $NaBO_2$ | -.0526 | .1104 | .0154 | 4.5 | .004 | 5 |
| $NaBF_4$ | -.0252 | .1824 | .0021 | 6 | .006 | 5 |
| KF | .08089 | .2021 | .00093 | 2 | .001 | 3 |
| KCl | .04835 | .2122 | -.00084 | 4.8 | .0005 | t |
| KBr | .0569 | .2212 | -.00180 | 5.5 | .001 | 3 |
| KI | .0746 | .2517 | -.00414 | 4.5 | .001 | 3 |
| KOH | .1298 | .320 | .0041 | 5.5 | b | 6 |
| $KClO_3$ | -.0960 | .2481 | --- | 0.7 | .001 | 3 |
| $KBrO_3$ | -.1290 | .2565 | --- | 0.5 | .001 | 3 |
| KCNS | .0416 | .2302 | -.00252 | 5 | .001 | 3 |
| $KNO_2$ | .0151 | .015 | .0007 | 5 | .003 | 7 |
| $KNO_3$ | -.0816 | .0494 | .00660 | 3.8 | .001 | 3 |
| $KH_2PO_4$ | -.0678 | -.1042 | --- | 1.8 | .003 | 3 |
| $KH_2AsO_4$ | -.0584 | .0626 | --- | 1.2 | .003 | 3 |
| $KPF_6$ | -.163 | -.282 | --- | 0.5 | .001 | 8 |
| RbF | .1141 | .2842 | -.0105 | 3.5 | .002 | 9 |
| RbCl | .0441 | .1483 | -.00101 | 5 | .001 | 3 |
| RbBr | .0396 | .1530 | -.00144 | 5 | .001 | 3 |
| RbI | .0397 | .1330 | -.00108 | 5 | .001 | 3 |
| $RbNO_2$ | .0269 | -.1553 | -.00366 | 5 | .002 | 4 |
| $RbNO_3$ | -.0789 | -.0172 | .00529 | 4.5 | .001 | 3 |
| CsF | .1306 | .2570 | -.0043 | 3.2 | .002 | 9 |
| CsCl | .0300 | .0558 | .00038 | 5 | .002 | t |
| CsBr | .0279 | .0139 | .00004 | 5 | .002 | 3 |

Table I Continued Page 3

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| CsI | .0244 | .0262 | -.00365 | 3 | .001 | 3 |
| CsOH | .150 | .30 | --- | --- | --- | t |
| $CsNO_2$ | .0427 | .060 | -.0051 | 6 | .004 | 4 |
| $CsNO_3$ | -.0758 | -.0669 | --- | 1.4 | .002 | 3 |
| $AgNO_3$ | -.0856 | .0025 | .00591 | 6 | .001 | 3 |
| $TlClO_4$ | -.087 | -.023 | --- | 0.5 | .001 | 3 |
| $TlNO_3$ | -.105 | -.378 | --- | 0.4 | .001 | 3 |
| $NH_4Cl$ | .0522 | .1918 | -.00301 | 6 | .001 | 3 |
| $NH_4Br$ | .0624 | .1947 | -.00436 | 2.5 | .001 | 10 |
| $NH_4ClO_4$ | -.0103 | -.0194 | --- | 2 | .004 | 11 |
| $NH_4NO_3$ | -.0154 | .1120 | -.00003 | 6 | .001 | 3 |

Explanation of symbols: t means "discussed in the text with references given there"; a, b, and c indicate high, intermediate, and low accuracy, respectively, in cases where some or all of the experimental data are other than isopiestic measurements of $\varphi$.

Table II: Salts of Carboxylic Acids (1-1 Type)

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| Li Acetate | 0.1124 | 0.2483 | -0.00525 | 4 | 0.001 | 3 |
| Na Formate | .0820 | .2872 | -.00523 | 3.5 | .001 | 3 |
| Na Acetate | .1426 | .3237 | -.00629 | 3.5 | .001 | 3 |
| Na Propionate | .1875 | .2789 | -.01277 | 3 | .001 | 3 |
| NaH Malonate | .0229 | .1600 | -.00106 | 5 | .002 | 3 |
| NaH Succinate | .0354 | .1606 | .00040 | 5 | .001 | 3 |
| NaH Adipate | .0472 | .3168 | --- | 0.7 | .001 | 3 |
| K Acetate | .1587 | .3251 | -.00660 | 3.5 | .001 | 3 |
| KH Malonate | -.0095 | .1423 | .00167 | 5 | .004 | 3 |
| KH Succinate | .0111 | .1564 | .00274 | 4.5 | .002 | 3 |
| KH Adipate | .0419 | .2523 | --- | 1 | .001 | 3 |
| Rb Acetate | .1622 | .3353 | -.00551 | 3.5 | .001 | 3 |
| Cs Acetate | .1628 | .3605 | -.00555 | 3.5 | .001 | 3 |
| Tl Acetate | .0082 | .0131 | -.00127 | 6 | .001 | 3 |

## Table III: Tetraalkylammonium Halides

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| $Me_4NF$ | 0.2677 | 0.2265 | 0.0013 | 3 | .002 | 37 |
| $Et_4NF$ | .3113 | .6155 | .0349 | 2 | .002 | 37 |
| $Pr_4NF$ | .4463 | .4090 | .0537 | 2 | .002 | 37 |
| $Bu_4NF$ | .6092 | .402 | -.0281 | 1.7 | .005 | 37 |
| $Me_4NCl$ | .0149 | -.083 | .0057 | 3.4 | .005 | 38 |
| $Et_4NCl$ | .0336 | -.153 | .0084 | 3 | .002 | 38 |
| $Pr_4NCl$ | .1065 | -.354 | .0098 | 2.5 | .002 | 38 |
| $Bu_4NCl$ | .2058 | -.464 | -.0588 | 2.5 | .001 | 38 |
| $Me_4NBr$ | -.0363 | -.201 | .0084 | 3.5 | .004 | 38 |
| $Et_4NBr$ | -.0457 | -.448 | .0135 | 4 | .001 | 38 |
| $Pr_4NBr$ | .0108 | -.826 | .0078 | 3.5 | .003 | 38 |
| $Bu_4NBr$ | -.0558 | -.579 | -.0010 | 4.5 | .007 | 38 |
| $Me_4NI$ | .0345 | -.585 | --- | 0.3 | .003 | 38 |
| $Et_4NI$ | -.1930 | -.599 | .0401 | 2 | .007 | 38, 39 |
| $Pr_4NI$ | -.2839 | -.863 | --- | 0.5 | .005 | 38 |

### Table IV: Sulfonic Acids and Salts (1-1 Type)

(SA = sulfonic acid; S = sulfonate)

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| Methane SA | 0.1298 | 0.629 | 0.0052 | 4 | --- | 40 |
| Li methane S | .1320 | .271 | -.0030 | 4 | --- | 40 |
| Na methane S | .0787 | .274 | -.0024 | 4 | --- | 40 |
| K methane S | .0581 | .165 | -.0046 | 4 | --- | 40 |
| $NH_4$ methane S | .0661 | .191 | -.0041 | 4 | --- | 40 |
| $Me_4N$ methane S | .1458 | .168 | -.0043 | 4 | --- | 40 |
| $Et_4N$ methane S | .1548 | .090 | -.0034 | 4 | --- | 40 |
| $Bu_4N$ methane S | .2145 | .235 | -.0392 | 4 | --- | 40 |
| Ethane SA | .1536 | .341 | -.0056 | 4 | --- | 40 |
| Li ethane S | .1799 | .319 | -.0118 | 4 | --- | 40 |
| Na ethane S | .1316 | .374 | -.0082 | 4 | --- | 40 |
| K ethane S | .0965 | .250 | -.0074 | 4 | --- | 40 |
| $NH_4$ ethane S | .1142 | .179 | -.0114 | 4 | --- | 40 |
| $Me_4N$ ethane S | .1796 | .083 | -.0116 | 4 | --- | 40 |
| $Et_4N$ ethane S | .1805 | .075 | -.0040 | 4 | --- | 40 |
| $Bu_4N$ ethane S | .1827 | .445 | -.0374 | 4 | --- | 40 |
| Benzene SA | .0526 | .445 | .0036 | 5 | .002 | 41 |
| Li benzene S | .1134 | .466 | -.0075 | 4.5 | .002 | 41 |
| Na benzene S | .0842 | .351 | -.0181 | 2.5 | .001 | 41 |
| p-toluene SA | -.0366 | .281 | .0137 | 5 | .002 | 3 |
| Li p-toluene S | .0189 | .399 | .0046 | 4.5 | .004 | 3 |
| Na p-toluene S | -.0344 | .396 | .0043 | 4 | .003 | 3 |
| K p-toluene S | -.0985 | .453 | .0122 | 3.5 | .002 | 3 |

Table IV Continued Page 2

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| 2,5 $Me_2$ benzene SA | -.0965 | .141 | .0210 | 4.5 | .01 | 3 |
| Li 2,5 $Me_2$ benzene S | -.0098 | .361 | .0039 | 3.5 | .002 | 41 |
| Na 2,5 $Me_2$ benzene S | -.0277 | .228 | --- | 1 | .005 | 41 |
| p-Et benzene SA | -.1736 | .435 | .0383 | 2 | .007 | 3 |
| Li p-Et benzene S | -.1438 | .804 | .0317 | 5 | .01 | 41, 42 |
| Na p-Et benzene S | -.2240 | .895 | .0355 | 2.5 | .01 | 41, 42 |
| Mesitylene SA | -.2209 | .248 | .0432 | 2 | .01 | 41 |
| Li Mesitylene S | -.1998 | .871 | .0456 | 2 | .004 | 41 |
| Na Mesitylene S | -.2018 | .767 | --- | 1 | .003 | 41 |

## Table V: Additional 1-1 Type Organic Salts

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| Choline Cl | 0.0457 | -0.196 | 0.0008 | 6 | 0.004 | 43 |
| Choline Br | -.0066 | -.227 | .0036 | 6 | .004 | 43 |
| $Me_3BzNCl$ | -.0821 | -.178 | .0162 | 3.5 | .01 | 43 |
| $Me_3BzNBr$ | -.1517 | -.545 | .0187 | 3 | .01 | 43 |
| $Me_2OEtBzNCl$ | -.0879 | -.343 | .0134 | 4 | .01 | 43 |
| $Me_2OEtBzNBr$ | -.1518 | -.778 | .0177 | 3 | .01 | 43 |
| $(HOC_2H_4)_4NF$ | .0938 | .128 | -.0030 | 4 | .001 | 44 |
| $(HOC_2H_4)_4NBr$ | -.0474 | -.259 | .0106 | 3 | .002 | 44 |
| $Me_3SCl$ | .0314 | -.184 | .0023 | 6 | .005 | 45 |
| $Me_3SBr$ | -.0228 | -.245 | .0044 | 6 | .004 | 45 |
| $Me_3SI$ | -.0601 | -.604 | .0006 | 3 | .01 | 45 |
| $Bu_3SCl$ | .0726 | -.245 | -.0099 | 6 | .01 | 45 |
| $Bu_3SBr$ | -.0803 | -.616 | .0053 | 6 | .01 | 45 |

## Table VI: Inorganic Compounds of 2-1 Type

| | $\frac{4}{3}\beta^{(0)}$ | $\frac{4}{3}\beta^{(1)}$ | $(2^{\frac{5}{2}}/3)C^{\varphi}$ | Max. m | σ | ref. |
|---|---|---|---|---|---|---|
| $MgCl_2$ | 0.4698 | 2.242 | 0.00979 | 4.5 | 0.003 | 3 |
| $MgBr_2$ | .5769 | 2.337 | .00589 | 5 | .004 | 3 |
| $MgI_2$ | .6536 | 2.4055 | .01496 | 5 | .003 | 3 |
| $Mg(ClO_4)_2$ | .6615 | 2.678 | .01806 | 2 | .002 | 3 |
| $Mg(NO_3)_2$ | .4895 | 2.113 | -.03889 | 2 | .003 | 3 |
| $CaCl_2$ | .4212 | 2.152 | -.00064 | 2.5 | .003 | 3 |
| $CaBr_2$ | .5088 | 2.151 | -.00485 | 2 | .002 | 3 |
| $CaI_2$ | .5839 | 2.409 | -.00158 | 2 | .001 | 3 |
| $Ca(ClO_4)_2$ | .6015 | 2.342 | -.00943 | 2 | .005 | 3 |
| $Ca(NO_3)_2$ | .2811 | 1.879 | -.03798 | 2 | .002 | 3 |
| $SrCl_2$ | .3810 | 2.223 | -.00246 | 4 | .003 | 3 |
| $SrBr_2$ | .4415 | 2.282 | .00231 | 2 | .001 | 3 |
| $SrI_2$ | .5350 | 2.480 | .00501 | 2 | .001 | 3 |
| $Sr(ClO_4)_2$ | .5692 | 2.089 | -.02472 | 2.5 | .003 | 3 |
| $Sr(NO_3)_2$ | .1795 | 1.840 | -.03757 | 2 | .002 | 3 |
| $BaCl_2$ | .3504 | 1.995 | -.03654 | 1.8 | .001 | 3 |
| $BaBr_2$ | .4194 | 2.093 | -.03009 | 2 | .001 | 3 |
| $BaI_2$ | .5625 | 2.249 | -.03286 | 1.8 | .003 | 3 |
| $Ba(OH)_2$ | .229 | 1.60 | --- | 0.1 | --- | 36 |
| $Ba(ClO_4)_2$ | .4819 | 2.101 | -.05894 | 2 | .003 | 3 |
| $Ba(NO_3)_2$ | -.043 | 1.07 | --- | 0.4 | .001 | 3 |
| $MnCl_2$ | .4363 | 2.067 | -.03865 | 2.5 | .003 | 3 |
| $FeCl_2$ | .4479 | 2.043 | -.01623 | 2 | .002 | 3 |

Table VI: Inorganic Compounds of 2-1 Type - Page 2

| | $\frac{4}{3}\,\beta^{(0)}$ | $\frac{4}{3}\,\beta^{(1)}$ | $(2^{\frac{5}{2}}/3)C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| $CoCl_2$ | 0.4857 | 1.967 | -0.02869 | 3 | 0.004 | 3 |
| $CoBr_2$ | .5693 | 2.213 | -.00127 | 2 | .002 | 3 |
| $CoI_2$ | .695 | 2.23 | -.0088 | 2 | .01 | 3 |
| $Co(NO_3)_2$ | .4159 | 2.254 | -.01436 | 5.5 | .003 | 3 |
| $NiCl_2$ | .4639 | 2.108 | -.00702 | 2.5 | .002 | 3 |
| $CuCl_2$ | .4107 | 1.835 | -.07624 | 2 | .003 | 3 |
| $Cu(NO_3)_2$ | .4224 | 1.907 | -.04136 | 2 | .002 | 3 |
| $ZnCl_2$ | .3469 | 2.190 | -.1659 | 1.2 | .006 | t |
| $ZnBr_2$ | .6213 | 2.179 | -.2035 | 1.6 | .007 | t |
| $ZnI_2$ | .6428 | 2.594 | -.0269 | 0.8 | .002 | t |
| $Zn(ClO_4)_2$ | .6747 | 2.396 | .02134 | 2 | .003 | 3 |
| $Zn(NO_3)_2$ | .4641 | 2.255 | -.02955 | 2 | .001 | 3 |
| $Cd(NO_3)_2$ | .3820 | 2.224 | -.04836 | 2.5 | .002 | 3 |
| $Pb(ClO_4)_2$ | .4443 | 2.296 | -.01667 | 6 | .004 | 3 |
| $Pb(NO_3)_2$ | -.0482 | 0.380 | .01005 | 2 | .002 | 3 |
| $UO_2Cl_2$ | .5698 | 2.192 | -.06951 | 2 | .001 | 3 |
| $UO_2(ClO_4)_2$ | .8151 | 2.859 | .04089 | 2.5 | .003 | 3 |
| $UO_2(NO_3)_2$ | .6143 | 2.151 | -.05948 | 2 | .002 | 3 |
| $Li_2SO_4$ | .1817 | 1.694 | -.00753 | 3 | .002 | 3 |
| $Na_2SO_4$ | .0261 | 1.484 | .00938 | 4 | .003 | 3 |
| $Na_2S_2O_3$ | .0882 | 1.701 | .00705 | 3.5 | .002 | 3 |
| $Na_2CrO_4$ | .1250 | 1.826 | -.00407 | 2 | .002 | 3 |
| $Na_2CO_3$ | .2530 | 1.128 | -.09057 | 1.5 | .001 | 3 |

# Table VI: Inorganic Compounds of 2-1 Type - Page 3

| | $\frac{4}{3}\beta^{(0)}$ | $\frac{4}{3}\beta^{(1)}$ | $(2^{\frac{5}{2}}/3)C^{\phi}$ | Max. m | σ | ref. |
|---|---|---|---|---|---|---|
| $Na_2HPO_4$ | -0.0777 | 1.954 | 0.0554 | 1 | 0.002 | 3 |
| $Na_2HAsO_4$ | .0407 | 2.173 | .0034 | 1 | .001 | 3 |
| $K_2SO_4$ | .0666 | 1.039 | --- | 0.7 | .002 | 3 |
| $K_2CrO_4$ | .1011 | 1.652 | -.00147 | 3.5 | .003 | 3 |
| $K_2Pt(CN)_4$ | .0881 | 3.164 | .0247 | 1 | .005 | 53 |
| $K_2HPO_4$ | .0330 | 1.699 | .0309 | 1 | .002 | 3 |
| $K_2HAsO_4$ | .1728 | 2.198 | -.0336 | 1 | .001 | 3 |
| $Rb_2SO_4$ | .0772 | 1.481 | -.00019 | 1.8 | .001 | 3 |
| $Cs_2SO_4$ | .1184 | 1.481 | -.01131 | 1.8 | .001 | 3 |
| $(NH_4)_2SO_4$ | .0545 | 0.878 | -.00219 | 5.5 | .004 | 3 |
| cis$[Co(en)_2NH_3NO_2](NO_3)_2$ | -.0928 | 0.271 | --- | 0.6 | .002 | 54 |
| trans$[Co(en)_2NH_3NO_2](NO_3)_2$ | -.0901 | .249 | --- | .8 | .002 | 54 |
| cis$[Co(en)_2NH_3NO_2]Cl_2$ | -.0327 | .684 | .0121 | 2.8 | .005 | 54 |
| trans$[Co(en)_2NH_3NO_2]Cl_2$ | .0050 | .695 | .0066 | 2.4 | .005 | 54 |
| cis$[Co(en)_2NH_3NO_2]Br_2$ | -.1152 | .128 | .0158 | 1 | .004 | 54 |
| trans$[Co(en)_2NH_3NO_2]Br_2$ | -.0912 | .424 | .0223 | 2.4 | .005 | 54 |
| cis$[Co(en)_2NO_3NO_2]I_2$ | -.1820 | .594 | --- | 0.6 | .004 | 54 |
| trans$[Co(en)_2NO_3NO_2]I_2$ | -.1970 | 1.003 | --- | .3 | .003 | 54 |

## Table VII: Organic Electrolytes of 2-1 Type

(SA = Sulfonic acid; S = sulfonate)

| | $\frac{4}{3}\beta^{(0)}$ | $\frac{4}{3}\beta^{(1)}$ | $(2^{\frac{5}{2}}/3)C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| m-Benzenedi SA | 0.5611 | 2.637 | -0.0463 | 1.6 | 0.004 | 55 |
| $Li_2$ m-Benzenedi S | .5464 | 2.564 | -.0622 | 2.5 | .004 | 55 |
| $Na_2$ m-Benzenedi S | .3411 | 2.698 | -.0419 | 3 | .004 | 55 |
| 4,4'bibenzyldi SA | .1136 | 2.432 | .0705 | 2 | .01 | 3,t |
| $Li_2$ 4,4'bibenzyldi S | .1810 | 1.755 | .0462 | 1.2 | .007 | 55 |
| $Na_2$ 4,4'bibenzyldi S | .0251 | 1.969 | --- | 0.4 | .01 | 55 |
| $Na_2$ fumarate | .3082 | 1.203 | -.0378 | 2 | .003 | 3 |
| $Na_2$ maleate | .1860 | 0.575 | -.0170 | 3 | .004 | 3 |

## Table VIII: 3-1 Electrolytes

| | $\frac{3}{2}\beta^{(0)}$ | $\frac{3}{2}\beta^{(1)}$ | $(3^{\frac{3}{2}}/2)C^{\varphi}$ | Max. m | σ | ref. |
|---|---|---|---|---|---|---|
| $AlCl_3$ | 1.0490 | 8.767 | 0.0071 | 1.6 | 0.005 | 3 |
| $SrCl_3$ | 1.0500 | 7.978 | -.0840 | 1.8 | .005 | 3 |
| $YCl_3$ | 0.9599 | 8.166 | -.0587 | 1.8 | .007 | 3 |
| $LaCl_3$ | .9158 | 8.231 | -.0831 | 1.8 | .007 | 3 |
| $CeCl_3$ | .9187 | 8.227 | -.0809 | 1.8 | .01 | 3 |
| $PrCl_3$ | .9030 | 8.181 | -.0727 | 2 | .006 | 3 |
| $NdCl_3$ | .9175 | 8.104 | -.0737 | 1.8 | .007 | 3 |
| $SmCl_3$ | .9330 | 8.273 | -.0728 | 1.8 | .01 | 3 |
| $EuCl_3$ | .9370 | 8.385 | -.0687 | 1.8 | .007 | 3 |
| $CrCl_3$ | 1.1046 | 7.883 | -.1172 | 1.2 | .005 | 3 |
| $Cr(NO_3)_3$ | 1.0560 | 7.777 | -.1533 | 1.4 | .004 | 3 |
| $Ga(ClO_4)_3$ | 1.2381 | 9.794 | .0904 | 2 | .008 | 3 |
| $InCl_3$ | -1.68 | -3.85 | --- | 0.01 | --- | t |
| $Na_3PO_4$ | .2672 | 5.777 | -.1339 | 0.7 | .003 | 3 |
| $Na_3AsO_4$ | .3582 | 5.895 | -.1240 | 0.7 | .001 | 3 |
| $K_3PO_4$ | .5594 | 5.958 | -.2255 | 0.7 | .001 | 3 |
| $K_3P_3O_9$ | .4867 | 8.349 | -.0886 | 0.8 | .004 | 60 |
| $K_3AsO_4$ | .7491 | 6.511 | -.3376 | 0.7 | .001 | 3 |
| $K_3Fe(CN)_6$ | .5035 | 7.121 | -.1176 | 1.4 | .003 | 3 |
| $K_3Co(CN)_6$ | .5603 | 5.815 | -.1603 | 1.4 | .008 | 3 |
| $Co(en)_3Cl_3$ | .2603 | 3.563 | -.0916 | 1 | .003 | t |
| $Co(en)_3(NO_3)_3$ | .1882 | 3.935 | --- | 0.3 | .01 | 58 |
| $Co(en)_3(ClO_4)_3$ | .1619 | 5.395 | --- | 0.6 | .007 | 59 |
| $Co(pn)_3(ClO_4)_3$ | .2022 | 3.976 | --- | 0.3 | .003 | 58 |

## Table IX: 4-1 and 5-1 Electrolytes

| 4-1 Solute | $\frac{8}{5}\beta^{(0)}$ | $\frac{8}{5}\beta^{(1)}$ | $\frac{16}{5}C^{\varphi}$ | Max. m | $\sigma$ | ref. |
|---|---|---|---|---|---|---|
| $ThCl_4$ | 1.622 | 21.33 | -0.3309 | 1 | 0.006 | 3 |
| $Th(NO_3)_4$ | 1.546 | 18.22 | -.5906 | 1 | .01 | 3 |
| $Na_4P_2O_7$ | 0.699 | 17.16 | --- | 0.2 | .01 | 60 |
| $K_4P_2O_7$ | .977 | 17.88 | -.2418 | 0.5 | .01 | 60 |
| $K_4Fe(CN)_6$ | 1.021 | 16.23 | -.5579 | 0.9 | .008 | 3 |
| $K_4Mo(CN)_8$ | 0.854 | 18.53 | -.3499 | 0.8 | .01 | 3 |
| $K_4W(CN)_8$ | 1.032 | 18.49 | -.4937 | 1 | .005 | 53 |
| $Me_4NMo(CN)_8$ | .938 | 15.91 | -.3330 | 1.4 | .01 | 53 |

| 5-1 Solute | $\frac{8}{3}\beta^{(0)}$ | $\frac{5}{3}\beta^{(1)}$ | $(5^{\frac{3}{2}}/3)C^{\varphi}$ |  |  |  |
|---|---|---|---|---|---|---|
| $Na_5P_3O_{10}$ | 1.869 | 36.10 | -1.630 | 0.4 | .01 | 60 |
| $K_5P_3O_{10}$ | 1.939 | 39.64 | -1.055 | 0.5 | .015 | 60 |

Table X: Rigid Sphere Models

| $R_+ + R_-$ | $\lvert R_+ - R_- \rvert$ | $\beta^{(0)}$ | $\beta^{(1)}$ |
|---|---|---|---|
| 2.90Å | 1.64Å | 0.1043 | 0.0200 |
| 2.90 | 0 | .0773 | .0497 |
| 2.76 | 0.86 | .0734 | .0188 |
| 4.6 | 0 | .3221 | .1431 |
| 4.6 | 1.0 | .3506 | .1063 |

# Figure Captions

Figure 1. The relationship of $\beta^{(1)}$ to $\beta^{(0)}$ for 1-1 electrolytes. Inorganic solutes appear as circles and carboxylate salts as triangles.

Figure 2. Cell potentials for NaOH-NaCl solutions; see equation 15 and accompanying text for details.

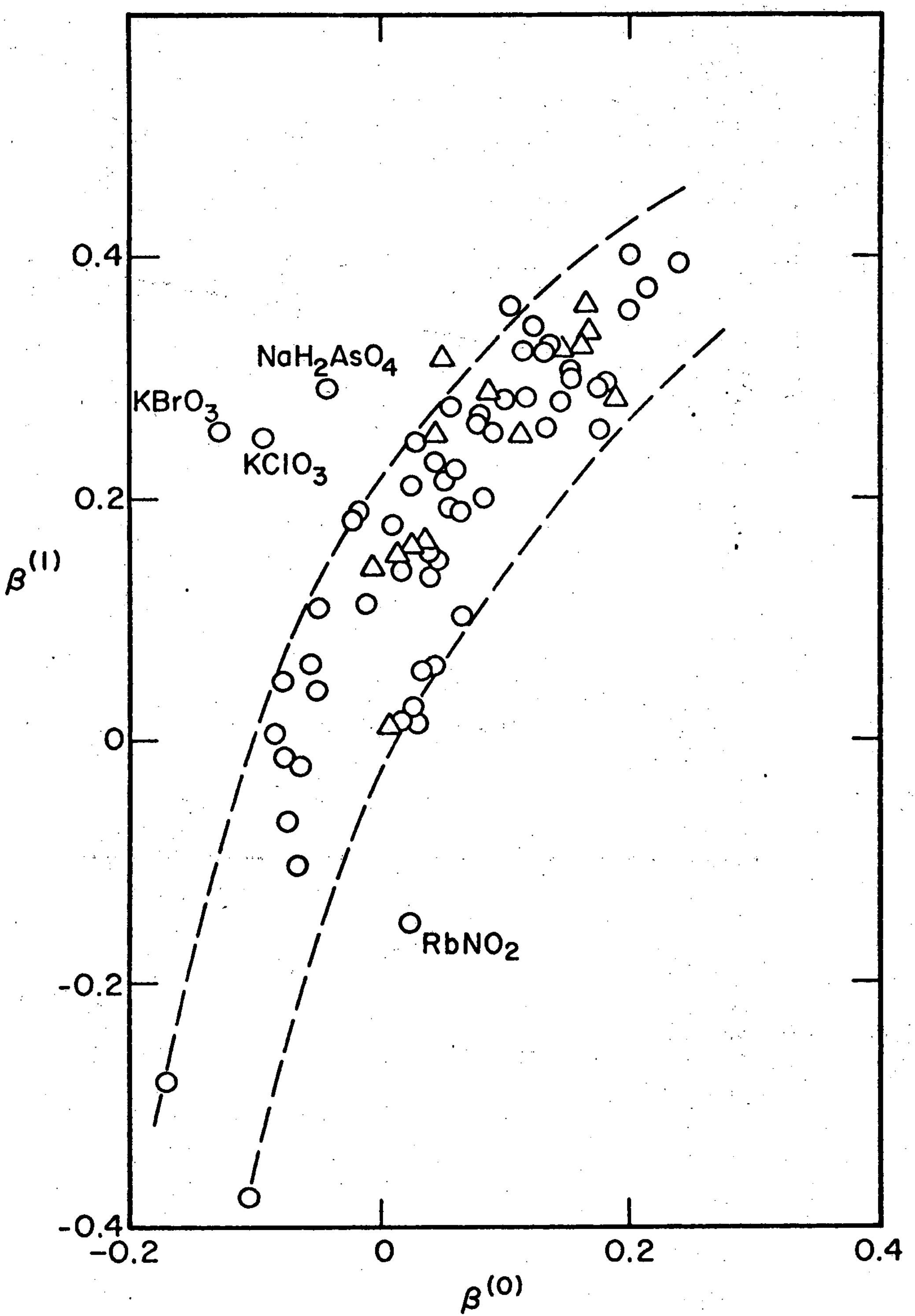
Figure 3. The second virial coefficient for alkali metal hydroxides; see text for details.

Figure 4. The relationship of $\beta^{(1)}$ and $\beta^{(0)}$ for organic electrolytes of 1-1 type. Sulfonates and sulfonic acids appear as circles and tetra-alkyl ammonium halides as triangles. The dashed curves here show the region similarly designated on figure 1.

Figure 5. The relationship of $\beta^{(1)}$ to $\beta^{(0)}$ for 2-1 electrolytes. Inorganic solutes appear as circles while those with organic groups as triangles.

Figure 6. The relationship of $\beta^{(1)}$ to $\beta^{(0)}$ for 3-1 electrolytes.

Figure 7. Activity coefficients for 1-1 electrolytes by the approximate method. The value of $\beta^{(0)}$ for each curve is indicated.



XBL 7212-7378

Figure 1. The relationship of $\beta^{(1)}$ to $\beta^{(0)}$ for 1-1 electrolytes. Inorganic solutes appear as circles and carboxylate salts as triangles.

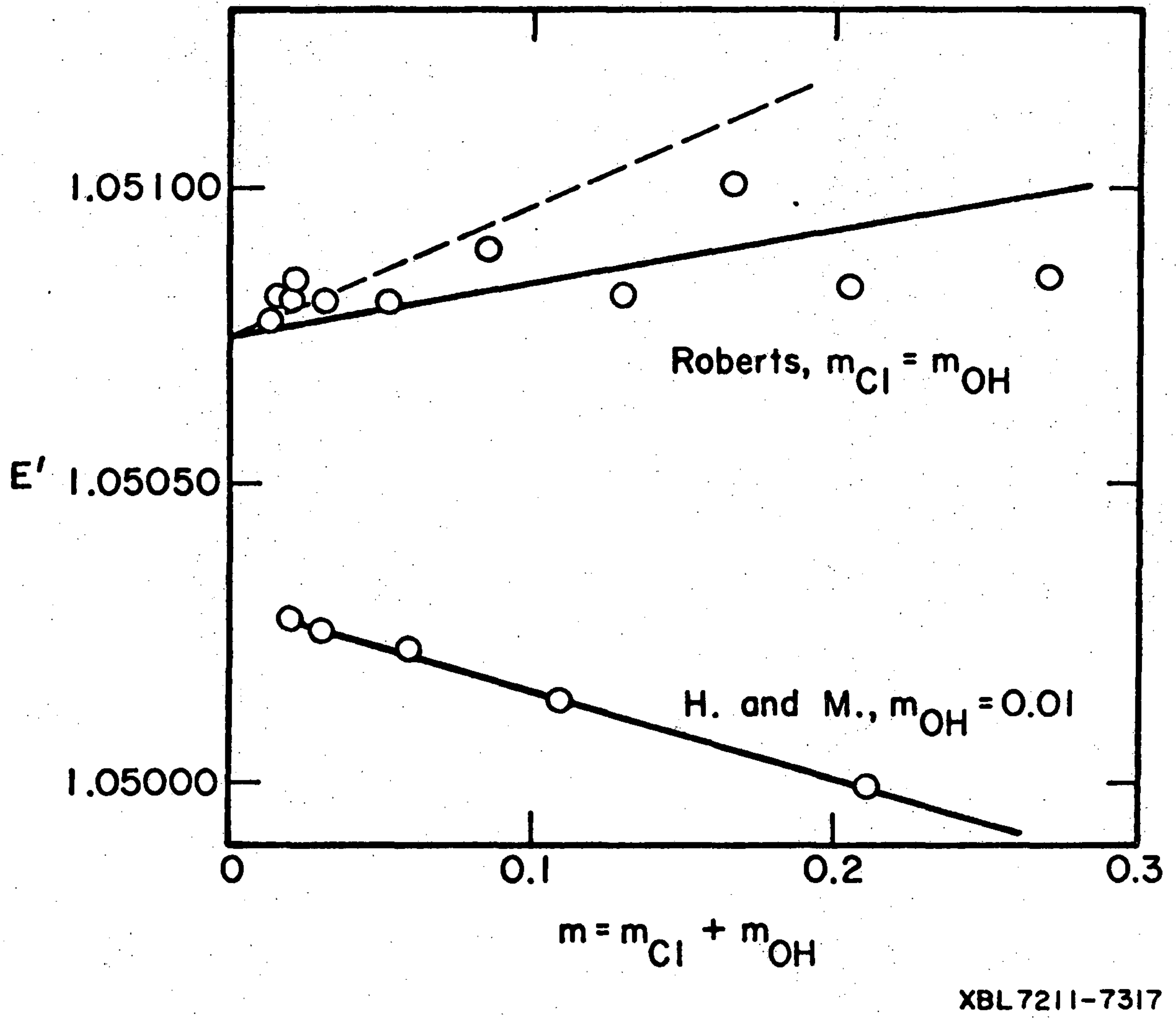


Figure 2. Cell potentials for NaOH-NaCl solutions; see equation 15 and accompanying text for details.

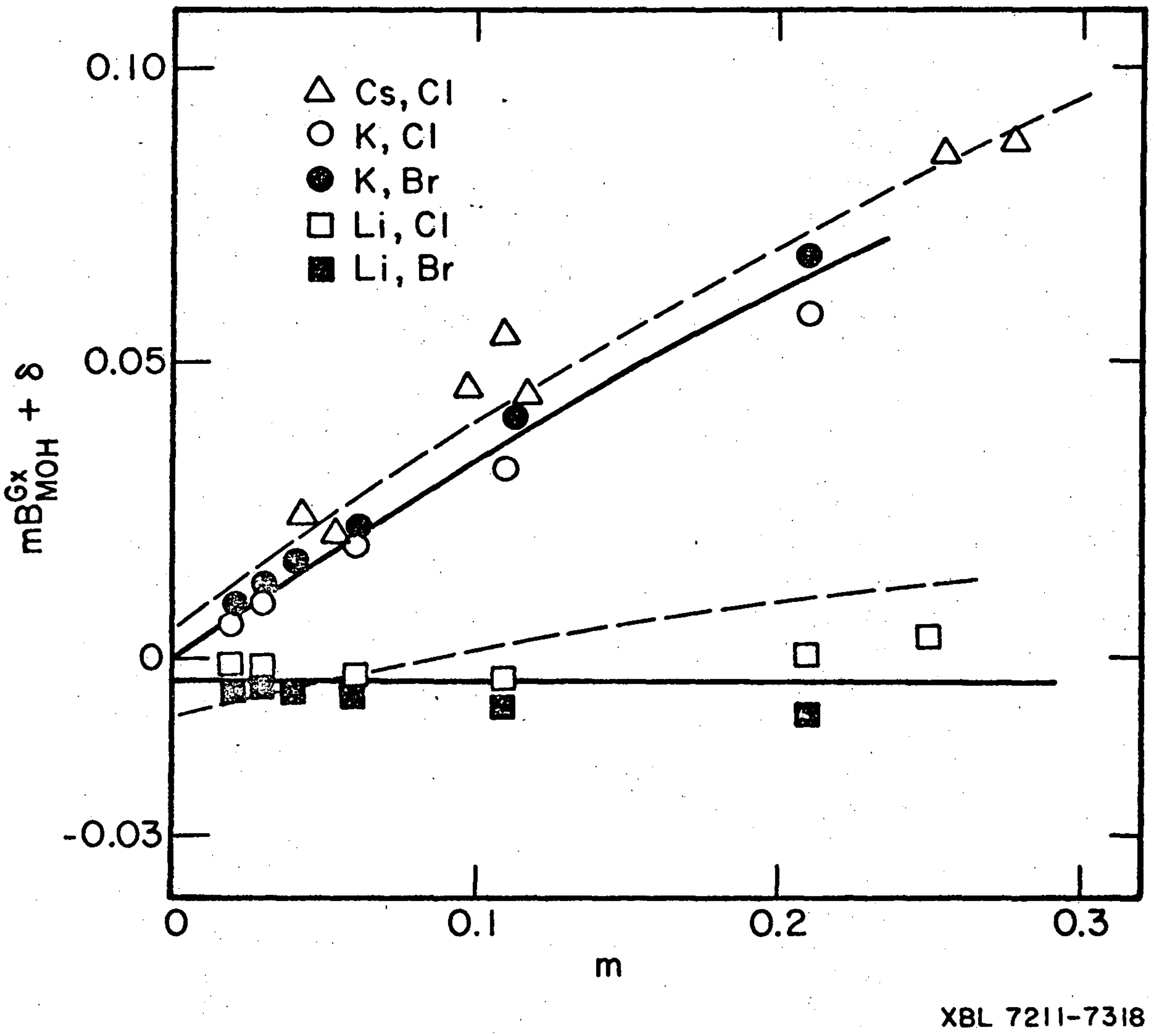
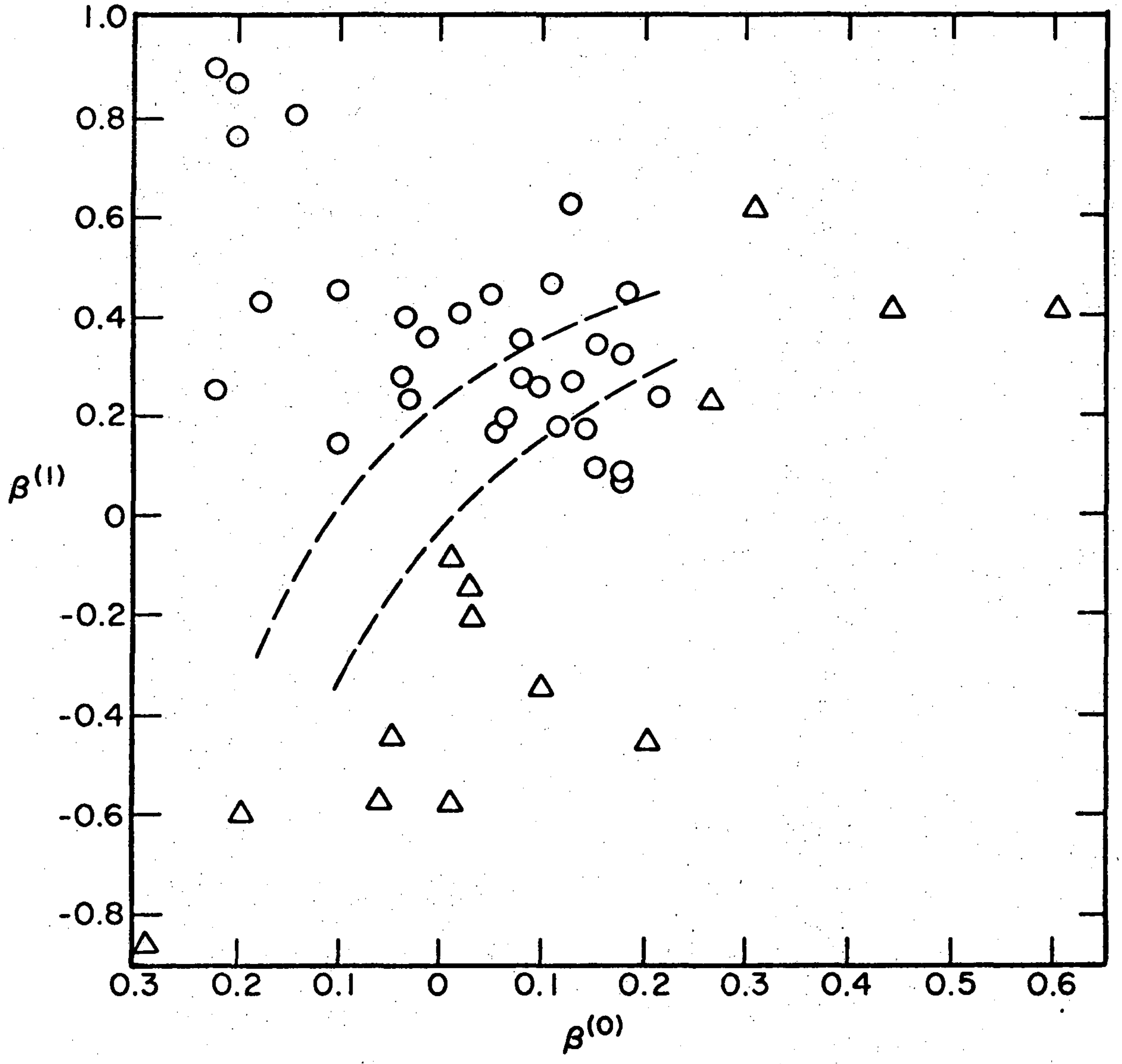
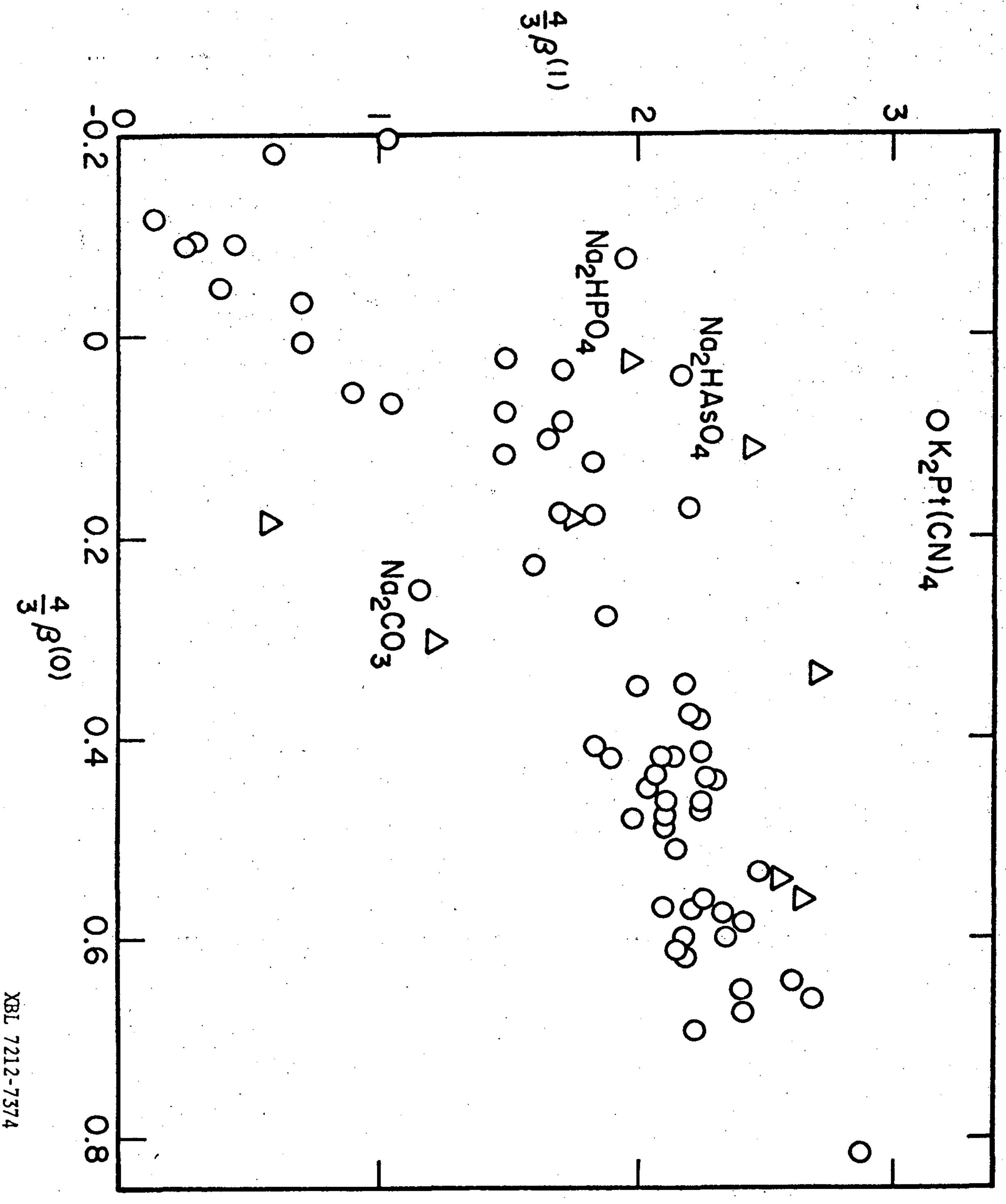


Figure 3. The second virial coefficient for alkali metal hydroxides; see text for details.



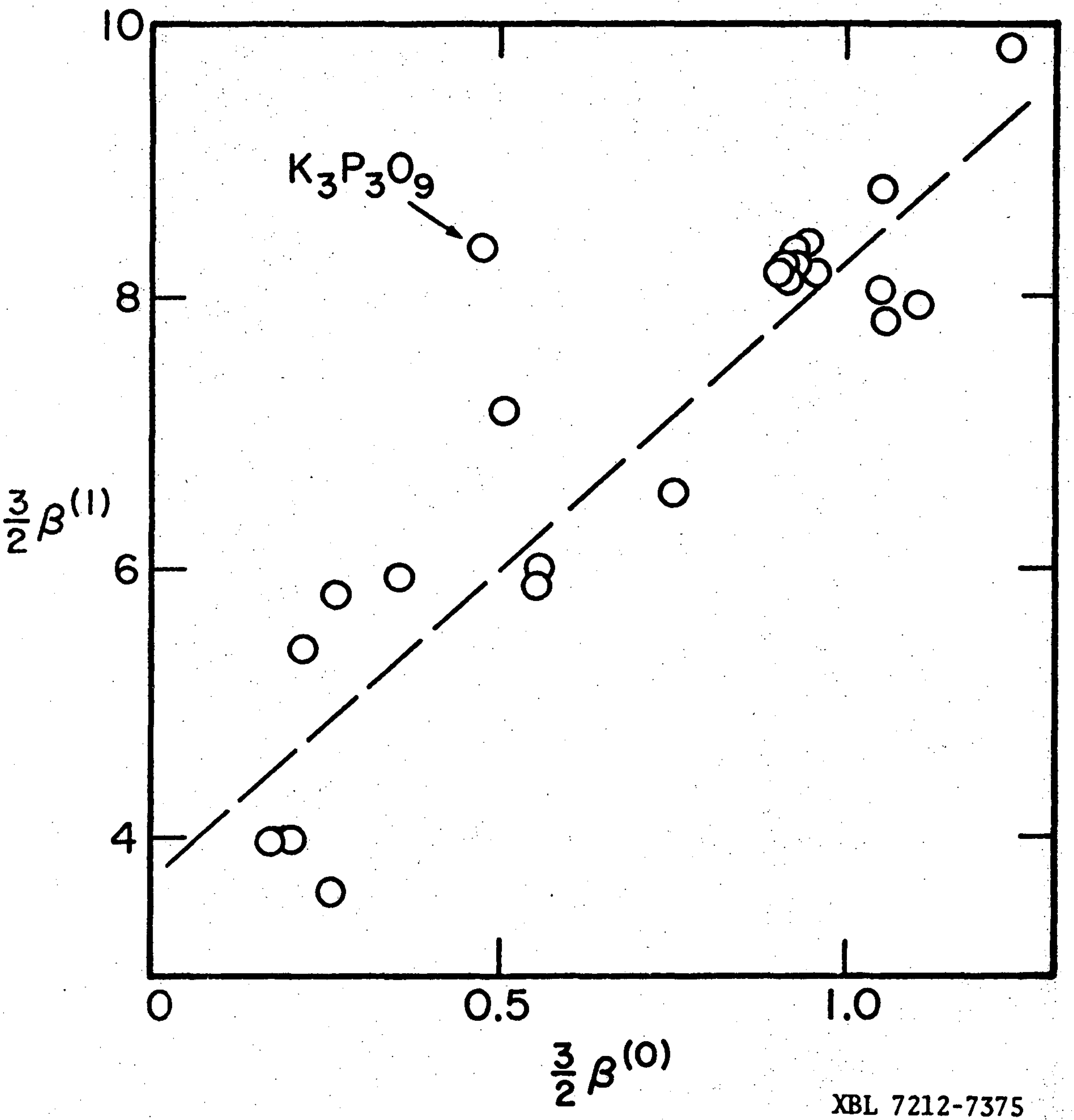
XBL 7212-7376

Figure 4. The relationship of $\beta^{(1)}$ and $\beta^{(0)}$ for organic electrolytes of 1-1 type. Sulfonates and sulfonic acids appear as circles and tetra-alkyl ammonium halides as triangles. The dashed curves here show the region similarly designated on figure 1.



XBL 7212-7374

Figure 5. The relationship of $\beta^{(1)}$ to $\beta^{(0)}$ for 2-1 electrolytes. Inorganic solutes appear as circles while those with organic groups as triangles.



XBL 7212-7375

Figure 6. The relationship of $\beta^{(1)}$ to $\beta^{(0)}$ for 3-1 electrolytes.

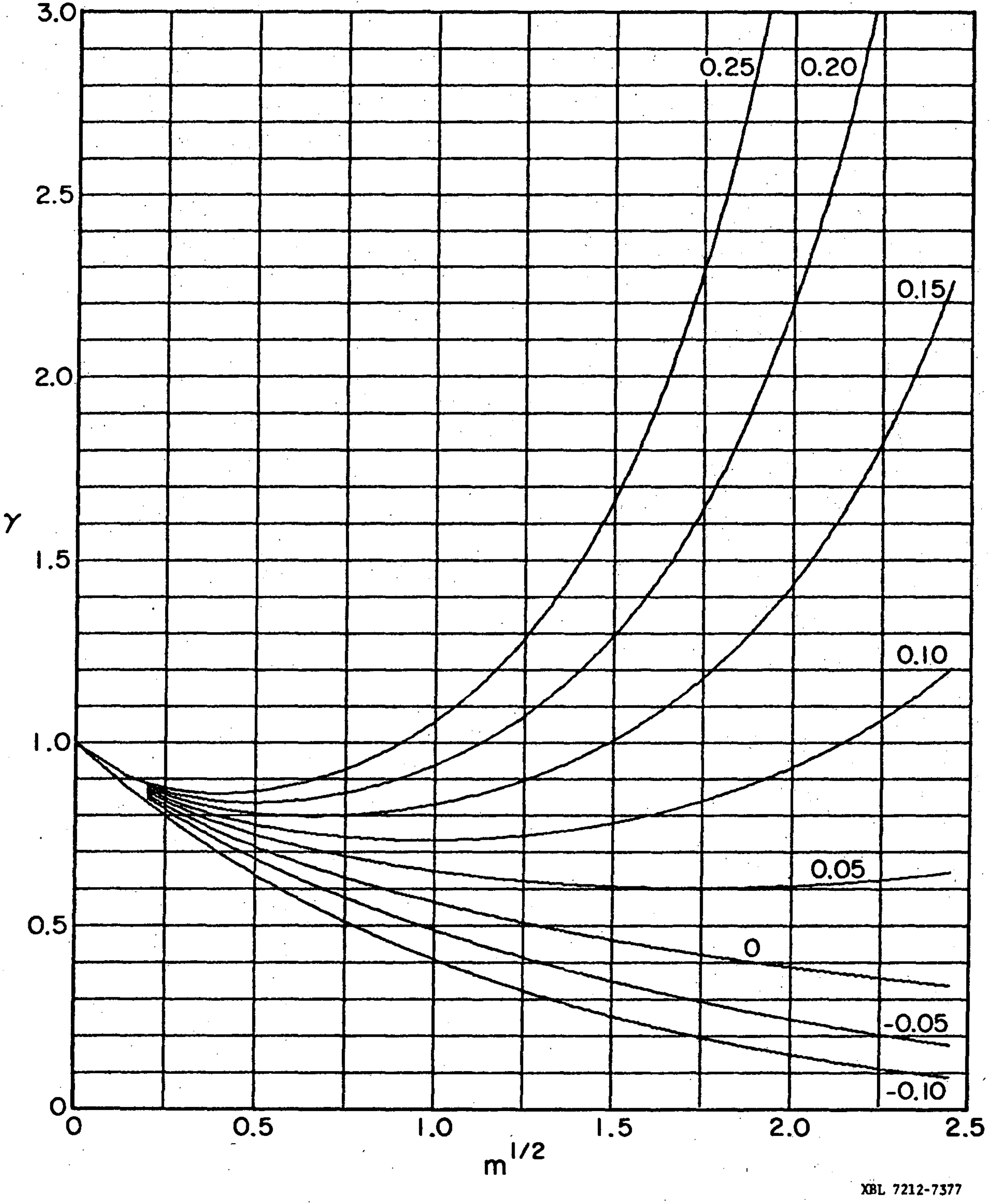


Figure 7. Activity coefficients for 1-1 electrolytes by the approximate method. The value of $\beta^{(0)}$ for each curve is indicated.

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