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THE MOLAL VOLUMES OF ELECTROLYTES

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CONTENTS

I. INTRODUCTION

Molal volumes of solutes furnish some interesting information regarding molecular state and structure. The molal volumes of electrolytes, moreover, round off our understanding of the theory of electrolytes. Special attention may be paid to this topic since it demonstrates in a very clear manner the importance of the critical judgment of observations.

The molal volumes of nonelectrolytes in solutions vary little, and nearly linearly, with the concentration (53). Those of electrolytes vary appreciably. Masson (41) found that they can be represented over rather wide ranges by linear functions of the square root of the concentration. Redlich and Rosenfeld (51, 52) derived a linear square root relation from the theory of Debye and Hückel in 1931. Their relation predicts the slope for each valence type as a function of the temperature, the compressibility, the dielectric constant D of the solvent, and its pressure dependence dD/dP. The theory predicts only a limiting law, to be approached at low concentrations, but the common limiting slope does not depend on the nature of the electrolyte (except its valence type). According to Redlich and Rosenfeld, the individual differences in the slopes found by Masson are due to deviations from the limiting law at higher concentrations; consequently, Masson's equations with empirical slopes are unfit for extrapolation to zero concentration.

Though this quite simple situation has been clearly described more than 30 years ago, widespread misunderstanding has existed until now. On one hand, a wrong value of the limiting slope was derived from inaccurate determinations of dD/dP; on the other hand, the existence of a common limiting slope was often denied on the basis of density determinations of insufficient accuracy, or just disregarded.

Nothing can be easier than the measurement of a density with error limits of 10^{-3} or 10^{-4}, but considerable problems arise when the limits should be reduced to 10^{-6} or 10^{-7}. Yet such accuracy is required for the experimental proof or disproof of the theoretical limiting law.

In view of the thermodynamic connection, a failure of the limiting law for the molal volume implies a failure of the theory of Debye and Hückel. This inevitable conclusion has frequently been ignored.

The whole development was reviewed (54) in 1940. In the following, the attention will be concentrated mainly on later literature.

II. ELECTROSTATIC ENERGY AND THERMODYNAMIC QUANTITIES

As early as in 1894, Drude and Nernst (15) calculated the volume difference between undissociated molecules and their ions. They called this difference electrostriction. The contribution of N ions of radius r, carrying the charge $z\epsilon$, in a medium of dielectric constant D is given by

$$V_e = -(Nz^2\epsilon^2/Dr)\,(d \ln D/dP) \qquad \text{(Eq. 1)}$$

This is, of course, the derivative with respect to the pressure of the electrical free energy

$$F_e = Nz^2\epsilon^2/(Dr) \qquad \text{(Eq. 2)}$$

a relation discussed much later by Born (10).

Both relations are valid for isolated ions, *i.e.*, at infinite dilution. The interaction between ions, hence the concentration dependence of Eq. 2, is given by the theory of Debye and Hückel. In the same way in which Eq. 1 can be derived from Eq. 2, one can also derive the concentration dependence of the partial molal volume due to ionic interaction from the theory of Debye and Hückel.

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This derivation has been carried out by Redlich and Rosenfeld (51). It is convenient to introduce Traube's *apparent molal volume* ϕ, defined by the volume V of a solution containing n_1 moles of solvent (molal volume v_1^0) and n_2 moles of solute according to

$$V = n_1 v_1^0 + n_2\phi \qquad \text{(Eq. 3)}$$

Usually the apparent molal volume is computed from the molal weight of the solute w_2, its concentration c (moles/l.), and the densities s of the solution and s^0 of the solvent by

$$\phi = w_2/s^0 - 1000(s - s^0)/(cs^0). \qquad \text{(Eq. 4)}$$

The theory of electrolytes furnishes the limiting relation for low concentrations

$$\phi = \phi^0 + kw^{1.5}c^{0.5} \qquad \text{(Eq. 5)}$$

It shows the usual linear dependence on the square root of the concentration and the influence of the valence factor w, which is given by the number ν_i of ions of species i formed by one molecule of the electrolyte and the valence z_i according to

$$w = 0.5\sum_i \nu_i z_i^2 \qquad \text{(Eq. 6)}$$

The slope k for a uni-univalent electrolyte can be expressed by means of the gas constant R, the charge ϵ of a univalent ion, and the compressibility β of the solvent. If the molal volume is expressed in cc./mole, the coefficient is

$$k = N^2\epsilon^3(8\pi/1000D^3RT)^{0.5}(\mathrm{d}\ln D/\mathrm{d}P - \beta/3) \qquad \text{(Eq. 7)}$$

A question of fundamental significance had been clarified by Gross and Halpern (27) several years before Eq. 5 had been derived. In the first paper of Debye and Hückel, the electrical free energy of an electrolyte solution was obtained from the energy of the *electrostatic model* by an integration carried out with a temperature-independent dielectric constant. Gross and Halpern, who were the first to derive the concentration dependence of the heat content, showed that this procedure is correct but that the energy or heat content of the total *solution* is obtained from the free energy by differentiation with temperature-dependent dielectric constant. The same is, of course, true for the pressure dependence. Suppression of the variation of the dielectric constant results in wrong values and even in wrong signs of the coefficients for both volume and heat content.

The relations between the equations of Born, Drude, and Nernst, and the limiting laws for the activity coefficients and molal volumes have been commented on by Gross (28).

As a matter of course, a relation such as Eq. 5 cannot be more than a limiting law for low concentrations. But the limiting law of Debye and Hückel has been well established and Eq. 5 for the molal volume has been derived from it by straightforward thermodynamics. Therefore, no objections should have been expected.

III. THE COEFFICIENT

Equation 5 comprises statements regarding concentration dependence or valence dependence which can be separately examined (52, 54), but the most significant test and application is based on the comparison of the value of the coefficient k as calculated from Eq. 7 with the limiting slope deduced from observed densities according to Eq. 5.

Until recently a weak point in the computation of k was the pressure dependence of the dielectric constant of the solvent. Even for water at room temperature, the earlier observations by Falckenberg (18) and Kyropoulos (37) differed so much that the corresponding values of k were 1.8 (from Falckenberg at 16.3°) and 2.53 (from Kyropoulos at 20°). Later measurements by Harris, Haycock, and Alder (32) were in favor of Falckenberg's result, but they were not accurate enough for a final decision.

In this situation and in view of the difficulties inherent in the determination of the pressure dependence of the dielectric constant, the reasonable procedure was to start from available data on the densities of electrolyte solutions. Equations 5 and 7 require that the limiting slope of the apparent molal volumes in a $c^{0.5}$-diagram is independent of the nature of the electrolyte (except for the valence factor); thus, the coefficient k is given by the common limiting slope if such a common slope exists.

Older data by Baxter and Wallace (5) gave (52) a value $k = 1.7 \pm 0.2$ (25°); later more accurate data by Geffcken, Gibson, Jones, Wirth, and their co-workers led (54) to $k = 1.86 \pm 0.02$ (25°). The decisive point in the scrutiny of the density data was that precisely the *best* determinations were found to be in excellent agreement with the requirement of a common limiting slope. The value 1.86 could therefore be considered to be final within rather narrow limits of error. A little later, new precise measurements (55, 56) on potassium chlorate and hydrochloric acid confirmed this value. It is in reasonably good agreement with Falckenberg's measurements.

Owen and Brinkley (45), Owen (46), and Harned and Owen in their textbook (31) chose to ignore these plain and definite facts. They also ignored the much earlier published derivation (51) of Eq. 5, and they did not mention Falckenberg's measurements (18). Instead, they derived the value $k = 2.517$ from Kyropoulos' results and called it the "theoretical coefficient," a name that appears to have unduly influenced later authors. It was never explained why the results of Falckenberg, who, working in Heydweiller's laboratory, was used to high standards of accuracy, should be disregarded. Similarly the clearly demonstrated, striking

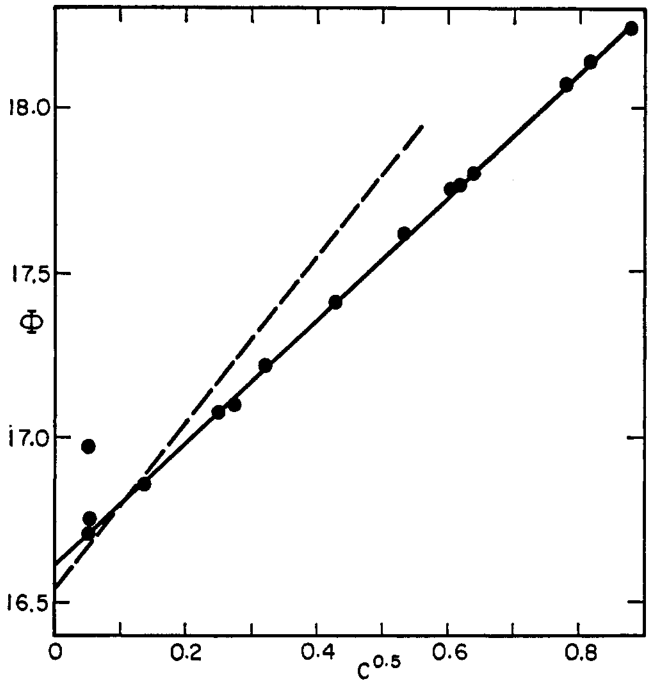

Fig. 1.—Apparent molal volume of NaCl at 25°: ●, data by Kruis (36); full line, $\phi = 16.61 + 1.86c^{0.5}$ (53); broken line, $\phi = 16.538 + 2.517c^{0.5}$ (45).

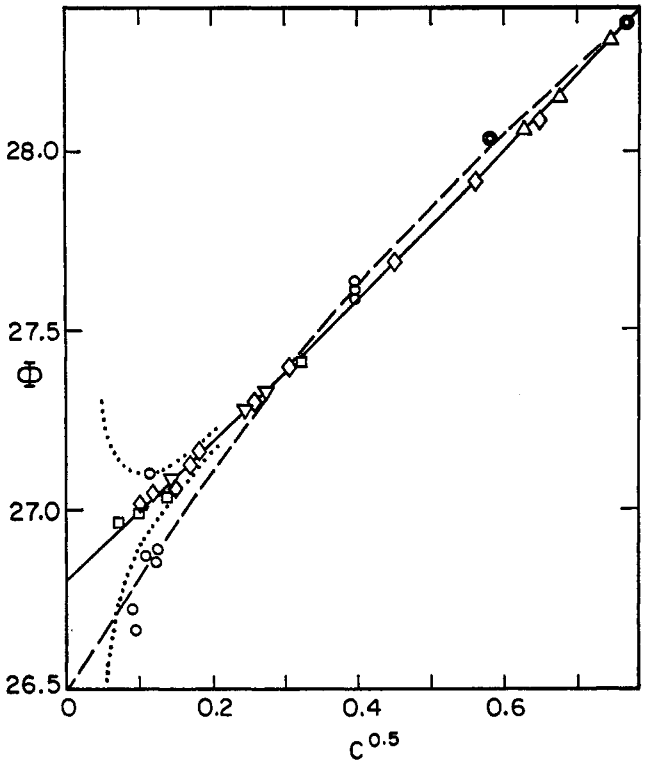

Fig. 2.—Apparent molal volume of KCl at 25°: ∇, Geffcken and Price, △ Kruis, □ Brodskii, ○ MacInnes and Dayhoff, ◊ Ayers. The full line represents the curve $\phi = 26.81 + 1.86c^{0.5} + 0.20c$; the broken line, the equation (MacInnes and Dayhoff) $\phi = 26.50 + 3.26c^{0.5} - 1.12c$. The dotted lines indicate an error of $\pm 10^{-6}$ in the density.

convergence of the best data to a common slope value 1.86 was never mentioned.

The discrepancy between Owen's "theoretical coefficient" and all available good experimental data could not escape anybody's attention. Agreement was enforced by the introduction of an arbitrary second-order term (linear in c). Actually the influence of a finite ionic radius on the molal volume was given up to the second-order term in Eq. 14 of our first paper (51) in 1931. We rejected a detailed discussion as meaningless, mainly because a consistent calculation of second-order terms would have to include the derivatives with respect to c of d ln $D/\mathrm{d}P$ and β. Any theoretical calculation must be expected to be quite sensitive to these entirely unknown second derivatives. Thus it was concluded that only a limiting law for high dilution such as Eq. 5 was really significant.

Owen and Brinkley (45) derived an equation for the influence of the ionic radius which in second order is identical with our earlier one. Since their equation did not fit the data with a reasonable ionic radius, they introduced an additional second-order term with an empirical coefficient. The introduction of such a term is, of course, perfectly justified, but the significance of a supposedly theoretical term of *equal* order cannot be understood. Figure 1 shows the experimental apparent molal volumes of sodium chloride of Kruis (36) and, as a broken line, Owen's limiting slope. It is not surprising that the data (below $c^{0.5} = 0.7$) can be represented by a parabola with a limiting slope prescribed by the broken line, but such a representation is convincing neither in Fig. 1 nor in the corresponding Fig. 2 of Owen and Brinkley (45).

In a similar manner, Benson's (6) discussion of Mayer's theory suffers from the use of the wrong value of k (see his Fig. 4).

Although the value $k = 1.86$ has been safely established since 1940, a recent direct confirmation has been very welcome. Owen and his co-workers (47) reported obviously excellent measurements of the dielectric constant of water as a function of pressure and temperature. The new values of k were computed and compared with the older ones in a short note (59). However, this computation was still based on the measurements of the compressibility of water by Smith and Keyes (67). Dr. George Kell of the Canadian National Research Council, Ottawa, kindly pointed out to us that the interpolation formula of Smith and Keyes differed appreciably from recent measurements by Peña and McGlashan (50). The results of these authors are in good agreement with previous authors quoted by them and also with unpublished measurements by Kell and Whalley (34).

The values of the coefficient k based on the results of Owen and his co-workers for D and $\mathrm{d}D/\mathrm{d}P$ and on the results of Kell and Whalley for the compressibility β of water are shown in Table I.

TABLE I

COEFFICIENT k

Temp., °C.	10^{12} d ln D/dP, dyne^{-1} cm.^{2} (Owen)	$10^{12}\beta$, dyne^{-1} cm.^{2} (McGlashan)	$10^{12}\beta$, dyne^{-1} cm.^{2} (Kell)	cm.^{3} $l.^{0.5}$ mole$^{-1.5}$
0	45.14	—	50.98	1.444
5	45.48	49.79	49.28	1.529
10	45.84	—	47.89	1.613
15	46.23	47.16	46.78	1.697
20	46.65	—	45.91	1.782
25	47.10	45.62	45.24	1.868
30	47.58	—	44.75	1.955
35	48.09	44.42	44.42	2.046
40	48.62	44.25	44.22	2.138
45	49.19	44.25	44.15	2.234
50	49.78	44.12	44.17	2.333
55	50.40	—	44.29	2.435
60	51.05	44.19	44.50	2.542
65	51.73	—	44.79	2.653
70	52.43	—	45.15	2.768

The interpolation formula

$$k = 1.445 + 0.01663t + 46.10^{-6}t^3 \qquad \text{(Eq. 8)}$$

deviates from the results by not more than 0.002. Also given in Table I are the values of the compressibilities of Peña and McGlashan.

The new value $k = 1.867$ (25°) agrees with the old value 1.86 ± 0.02 of 1940 even better than the value 1.884 derived (59) with the aid of the compressibilities of Smith and Keyes.

Much less satisfactory is the state of our knowledge regarding the limiting slope at temperatures lower and higher than 25°. Density data for very low concentrations of sufficiently high accuracy are not available. Our early discussion (52) of the data of Baxter and Wallace (5) on alkali halides led to $k = 2.8$ at 0° (calcd. 1.45 by Eq. 8) and $k = 1.5$ at 50° (calcd. 2.334). Thus the density data would indicate a *decrease* of k with the temperature while the calculated values *increase.* The dilatometric measurements of solutions of potassium nitrate between 5 and 30° by Halasey (29) also indicate a decrease of k. Results of Rodnyanskii and coworkers (61) between 25 and 340° indicate a strong increase of the coefficient, but the concentrations are too high for a final conclusion.

Other measurements of densities at varying temperatures (25, 71) furnish hardly substantial evidence concerning the limiting slope.

New accurate measurements of the expansion of dilute electrolyte solutions between 0 and 70° are needed to clarify this discrepancy.

At present, the most likely explanation rests on the lack of accurate density data for sufficiently low concentrations and the resulting probability of wrong extrapolation. Only a float method (Kohlrausch or Baxter and Wallace) can furnish data of sufficient accuracy.

IV. THE INTERPRETATION OF DENSITY DATA

It is interesting to see that up to now Eq. 5 to 7 have not been generally accepted. Authors who would never think of doubting the limiting relation of Debye and Hückel quite often represent their results by a linear square root relation with individually different coefficients as proposed by Masson (41) in 1929. Quite a few authors believe that their experimental results either confirm Masson's individual coefficients rather than Eq. 5 to 7, or at least are better represented by Masson's empirical relation. Actually it can be easily seen that individual coefficients are the result of insufficient accuracy, and it can be demonstrated that Eq. 5 with an additional individual term containing c certainly furnishes for moderately concentrated solutions a better representation of any data than does Masson's relation.

Geffcken and his co-workers in the laboratory of Fajans in Munich developed the most accurate method for determining the density of solutions and were the first to discuss the influence of experimental errors.

One derives easily from Eq. 4 and 5 that the direct influence on the coefficient k exerted by an error δs in the density is quite high even at moderately low concentrations (Table II). The values for δk are for single measurements, the value of ϕ^0 being assumed to be known. The order of magnitude is the same for a set of measurements and unknown ϕ^0. Estimates for the uncertainty of k due to terms higher than the linear term in $c^{0.5}$ are given in Table II under "Nonlinearity." They are based on the largest deviations found for alkali halides (52).

TABLE II

ERROR IN THE COEFFICIENT k

	c			
	0.1	0.3	0.6	0.1
δk for $\delta s = 10^{-6}$	2.0	0.12	0.033	0.002
δk for $\delta s = 10^{-7}$	0.2	0.012	0.003	0.000
Nonlinearity	0.003	0.029	0.11	0.30

It is obvious from Table II that significant results for k require error limits below 10^{-6} in the density. The influence of errors is shown in Fig. 2. The data for potassium chloride, just as well as those for sodium chloride, have made an important contribution in the determination of the limiting slope. The excellent agreement of the results of Kruis (36), Geffcken and Price (24), Brodskii and co-workers (66), and Ayers (1) leaves no possible doubt in the representation by

$$\phi = 26.81 + 1.86c^{0.5} + 0.20c \qquad \text{(Eq. 9)}$$

(full line in Fig. 2).

The data of MacInnes and Dayhoff (39) illustrate the problem of the best representation of data. Their error limits of about $\pm 2 \times 10^{-6}$ are wider than those of the four other sets. Yet the accuracy of their results is still far superior to the great majority of available data. Obviously their data (Fig. 2) would have been smoothed much better with the aid of an equation of the type

$$\phi = \phi^0 + 1.86c^{0.5} + hc \qquad \text{(Eq. 10)}$$

with *two* empirical parameters ϕ^0 and h than by means of their equation

$$\phi = 26.50 + 3.26c^{0.5} - 1.12c \qquad \text{(Eq. 11)}$$

with *three* parameters (MacInnes and Dayhoff use the molality m instead of c, but the difference is insignificant in this discussion). Such a conclusion is, of course, valid and still more important for data of lesser accuracy, provided the range below $c = 0.5$ is to be covered by interpolation or extrapolation. It is also obvious that in this case Eq. 10 furnishes necessarily a better representation than Masson's relation (both contain two parameters). Except for the exclusive representation of higher concentrations, there is never any reason to prefer Masson's relation.

Quite naturally, extrapolations to zero concentrations are especially sensitive to the choice of the slope. Unfortunately, very few computations have been carried out with the correct value, but extensive data are available which would furnish much better information if appropriately represented although their accuracy is not sufficient for an independent determination of the limiting slope (11–13, 22, 38, 42, 49, 60, 69, 76). Such an extrapolation equation was suggested for calcium nitrate [quoted by Ewing and Herty (16)]. Baker's measurements (2) on copper sulfamate are well represented by

$$\phi = 55.22 + 3^{1.5} \times 1.86c^{0.5} + 0.46c \qquad \text{(Eq. 12)}$$

while he computes the square root coefficient from the data. The extensive and obviously accurate data of Ayers (1) [see also (64)] for the nitrates and chlorides of ytterbium, erbium, neodymium, and lanthanum certainly deserve an attempt at consistent representation by means of 13 empirical parameters (five limiting molal volumes and eight c-coefficients). A revision and extension of the values of ϕ^0 suggested by Fajans and Johnson (17) more than 20 years ago would be very useful.

The interpretation of the limiting values ϕ^0 has been discussed by Mukerjee (43) and by Benson and Copeland (7).

V. NONAQUEOUS SOLUTIONS

Since our early review (52) of solutions of calcium chloride in methanol, a few sets of data have been reported.

Filippova (19) reviewed data for nonaqueous solutions in 1940. She and her co-workers (20) determined the molal volumes of sodium acetate in aqueous ethanol (68.9%) at 20°. From Falckenberg's results (18) we estimate $k = 20.7$ for ethanol at 20°, or by a crude and uncertain interpolation $k = 14.9$ for the 68.9% mixture. The data of Filippova and co-workers appear to approach this limit slope (Fig. 3).

MacInnes and Dayhoff (40) represent their measurements on potassium iodide in methanol at 25° by means of a coefficient 11.5 in a term containing the square root of the molality. This means a value 13.0 for the concentration. From Falckenberg's data we obtain $k = 17.5$ at 18°. The agreement is probably as good as one can expect.

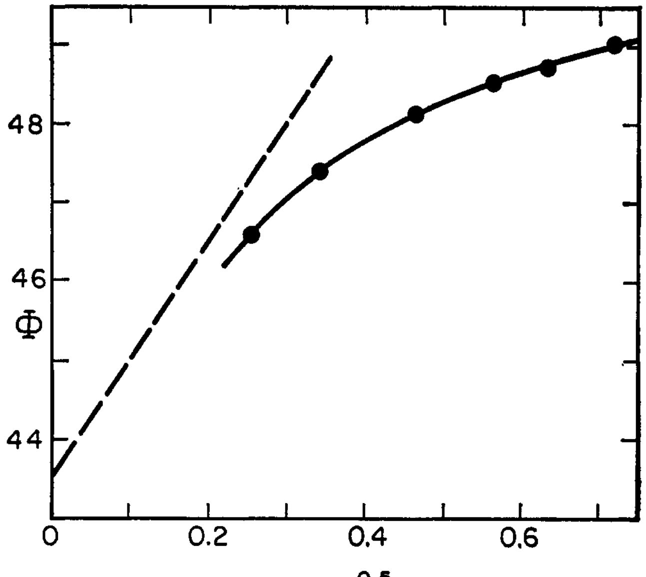

Fig. 3.—Apparent molal volume of CH_3COONa in ethanol at 20.00°: ● data by Filippova, *et al.* (20); broken line, estimated limiting slope.

Molal volumes of strontium and barium chlorides in aqueous ethanol (0 to 80%) at 25° have been determined by Bateman (4). Unfortunately, there is an unexplained discrepancy between his results for strontium chloride and those of Kruis (36). An attempt should be made to represent his results and those of Padova (48) on various salts by Eq. 5.

Molal volumes of sodium bromide in aqueous methanol have been determined by Baron (3) and those of hydrochloric acid in methyl, ethyl, and propyl alcohol by Minc and his co-workers (68).

Data (14) for moderately dilute solutions of silver chloride, sodium bromide, silver nitrate, and mercuric fluoride in ethylenediamine show a decrease of the molal volumes with increasing concentrations. If confirmed, this surprising result would indicate that $d \ln D/dP$ for this solvent is smaller than $\beta/3$.

Gunn and Green (26) find that the variation of the molal volumes with the concentration is represented by the same function for sodium chloride, sodium and potassium iodides, and barium nitrate in liquid ammonia. Barium nitrate may well be dissociated as a uni-univalent electrolyte. The identity goes even beyond the expected common limiting slope.

The lower the dielectric constant of a solvent, the larger is the effect of ionic interaction. Unfortunately, not only the slope values but, in general, also the deviations from the limiting law increase with decreasing dielectric constant.

VI. APPLICATIONS

Root (62) early drew the conclusion from Eq. 4 and 5 that the relation

$$s = s^0 + Ac - Bc^{1.5} \qquad \text{(Eq. 13)}$$

should give a useful representation of the density of an electrolyte solution. Sometimes this equation was misunderstood to be a basic relation and Eq. 5 actually was derived from it (74).

For an ion with the charge z in a mixed dilute electrolyte solution, the thermodynamic properties depend on the ionic strength (on a volume basis)

$$\mu = 0.5\sum_i c_i z_i^2 \qquad \text{(Eq. 14)}$$

Equation 5 is to be replaced by

$$\phi = \phi_0 + kz^2\mu^{0.5} \qquad \text{(Eq. 15)}$$

This relation is quite well confirmed by Saegusa's measurements (65) on sodium carbonate in sodium chloride solutions. Large deviations have been found for potassium carbonate in sodium chloride solutions.

It is especially desirable to have rules that allow us to estimate molal volumes in mixtures at concentrations beyond the validity of the limiting law. Young and Smith (75) proposed that the experimentally observed mean apparent molal volume can be predicted as the molal average of the apparent molal volumes in those solutions of the components in which the ionic strength is equal to that in the mixture. They showed the usefulness of this mixture rule in an examination of the data of Wirth (72, 73), studied deviations from it, and discussed the relation between this rule and other mixture rules for thermodynamic properties as suggested by Brönsted, Scatchard, and Harned. A more general discussion of the molal volumes of mixed electrolyte solutions has been presented by Rush and Scatchard (63).

Molal volumes of mixed solutions (cesium chloride with lithium or sodium chloride) have been determined by Stakhanova and Vasilev (70).

The limiting value ϕ^0 at zero concentration is of interest for estimates of the ionic radii, according to Eq. 1 of Drude and Nernst, for comparisons of molal volumes in crystals and in standard solutions and for the determination of standard volume changes in chemical reactions or dissociations.

Particularly interesting is the change of volume connected with the ionization of water. Bodanszky and Kauzmann (9) revised the computation for the reaction (25°)

$$HCl(c) + NaOH(c) = NaCl(0.5c) + H_2O$$

and found

$$\Delta V = 21.28 - 2.30c^{0.5} + 0.40c$$

The improvement from the old value (44) $\Delta V^0 = 23.4$ to the new value 21.28 is due to correct extrapolation and to new, obviously very good measurements, on sodium hydroxide by Bodanszky and Kauzmann. Their result can still be a little improved by introducing the correct relation for NaCl

$$\phi = 16.61 + 1.86c^{0.5} \qquad \text{(Eq. 16)}$$

instead of Wirth's relation (72)

$$\phi = 16.435 + 2.010c^{0.5} + 0.052c \qquad \text{(Eq. 17)}$$

The final result is

$$\Delta V = 21.45 - 2.41c^{0.5} + 0.37c \qquad \text{(Eq. 18)}$$

The ionization volume of acetic acid was derived by Redlich and Bigeleisen (55) from their own measurements (56) and from measurements of Redlich and Nielsen (57). They found (25°)

$$HOAc + NaCl = HCl + NaOAc$$
$$\Delta V_0 = -11.47 \pm 0.05$$

This gave, according to Eq. 1 of Drude and Nernst, an average ionic radius $r = 0.725 \pm 0.006$ Å., while the change in heat capacity furnished the value 0.697 ± 0.023 according to Born's equation (Eq. 2). A similar calculation would be desirable for water.

The volume changes on ionization of numerous weak electrolytes have been determined by Hamann and Lim (30).

Molal volumes have been successfully used as a basis for the investigation of the second dissociation of sulfuric acid (21, 23, 33, 35) and sulfurous acid (33), and of the hydrolysis of sodium carbonate (23). Discussions of molal volumes (8, 58) have contributed also to the understanding of the dissociation of nitric and perchloric acids.

It was pointed out (52) in 1931 that there is some relation between electrostriction, its temperature dependence, the coefficients of the c-term, and the association of water. The same problem has been discussed later (*e.g.*, 64), but no quantitative relations have been proposed so far.

The application of molal volumes in investigations of molecular state and structure is particularly attractive because the intuitive interpretation appears to be so simple.

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