

THE APPARENT MOLAL HEAT CAPACITY, VOLUME, AND COMPRESSIBILITY OF ELECTROLYTES

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INTRODUCTION

For the last fifty years, a great number of investigators have studied the activity of electrolytes in solution. Arrhenius' theory and the more recent interionic attraction theory were designed primarily to explain this property, yet any completely satisfactory solution theory must explain *all* properties of solutions. The Debye-Hückel theory has now been extended to explain the change of viscosity, conductivity, heats of dilution, and other properties of solutions of electrolytes. The validity of its basic postulates is strengthened by each such successful extension. All of these properties approach the simple laws demanded by theory only at *extremely low* concentration. In contrast to this, the three apparent molal properties which we will discuss exhibit simple relationships over the *whole range* of concentration. We will first present the experimental facts which show the similarity of the behavior of these properties and will then see how far our theories can explain this relationship. The correct interpretation of these facts must eventually lead to a more complete and satisfactory theory of solutions.

An *apparent molal property* of the solute may be defined by the equation:

$$\Phi(G) = \frac{G - n_1 \bar{G}_1^0}{n_2} \quad (1)$$

where G is any extensive property of a solution, \bar{G}_1^0 the corresponding molal property of the solvent, and n_1 and n_2 the number of moles of solvent and solute. Thus if we take a volume, V ,

of solution which contains *one mole* of solute, the apparent molal volume of the solute is equal to V minus the volume, V_1 , of the water which is used in making up the solution:

$$\Phi(V_2) = V - V_1 \quad (2)$$

Equation 2 shows us that the error in $\Phi(V_2)$ becomes larger as V increases, being nearly inversely proportional to the concentration c . This is true of any apparent molal property. The particular extensive property of the solution must be studied with great precision in order to determine with any certainty the value of Φ in dilute solutions.

APPARENT MOLAL HEAT CAPACITIES

Within the last four years several workers have studied the heat capacities of aqueous solutions of many typical electrolytes at 25°C. over a wide concentration range. These data are sufficiently accurate to furnish, even in fairly dilute solutions, satisfactory values of the apparent molal heat capacity defined by the equation

$$\Phi(C_{p_2}) = s \left[\frac{1000}{m} + M_2 \right] - \frac{1000}{m} \quad (3)$$

where s is the specific heat of the solution, m is the molality (moles of solute per 1000 g. of water), and M_2 is the molecular weight of the solute.

Randall and Rossini (1), from a careful study of the heat capacities of a number of solutions, confirmed the earlier statement of Randall and Ramage (2) that the apparent molal heat capacity is a linear function of $m^{\frac{1}{2}}$ from the lowest concentration studied up to about 2 molal. Work in this laboratory (3) has shown that this linear relationship undoubtedly holds in the case of five other uni-univalent electrolytes from 2 molal to about 0.2 molal. There is some uncertainty about the more dilute range. A marked departure from linearity was observed by Gucker and Schminke (3a) in the case of two solutes (potassium hydroxide and hydrochloric acid) below 0.2 molal. Similar

irregularities in the very dilute range have been noted by La Mer and Cowperthwaite (4) and by Young (5). La Mer and Cowperthwaite studied the E.M.F. of suitable cells over a wide range of temperature and calculated \bar{C}_{p_2} for zinc sulfate below 0.01 molal. They conclude that even as low as 0.0005 molal it is not a linear function of $m^{\frac{1}{2}}$. Young calculated the apparent molal heat capacity of sodium chloride in very dilute solutions from a determination of the heat of dilution at two different temperatures and concluded that for this salt also Φ is not a linear function of $m^{\frac{1}{2}}$ in very dilute solutions. An exact determination of the limiting law for apparent molal heat capacity must await precise data for a large number of electrolytes in the very dilute range. The necessary accuracy cannot be realized by direct determination of the specific heat, but undoubtedly can be obtained by a study of the temperature coefficient of the heat of dilution. Such a study is being continued by Professor Young at the University of Chicago and is also being carried out in this laboratory by a slightly different procedure.

Despite the uncertainty in the very dilute range, linear extrapolation of the apparent molal heat capacity curves gives values at infinite dilution which are additive for the ions. This does not, of course, prove that the extrapolation is correct, since all of the lines might show similar curvature in the very dilute range. It is interesting to note that the additivity of apparent ionic heat capacities at infinite dilution was shown thirty years ago by Lamb (6) from a study of the rather meager data in the literature at that time.

Some other interesting generalizations now emerge. While the apparent molal heat capacity of non-electrolytes or weak electrolytes is *positive*, that of all strong electrolytes in dilute solutions is *negative*. A comparison of different salts shows that those of

${}^1\bar{C}_{p_2} = \left(\frac{\partial \bar{C}_p}{\partial n_2} \right)_{n_1}$, the *partial* molal heat capacity of the solute. Partial and apparent molal quantities are equal at zero concentration and proportional in the dilute range (cf. equation 17). Their conclusions regarding \bar{C}_{p_2} therefore apply also to $\Phi(C_{p_2})$.

higher valence type have progressively more negative values of Φ^0 and progressively steeper slopes against $m^{\frac{1}{2}}$. We have plotted in figure 1 a number of typical apparent molal heat capacity curves which illustrate the general principles discussed above. We have

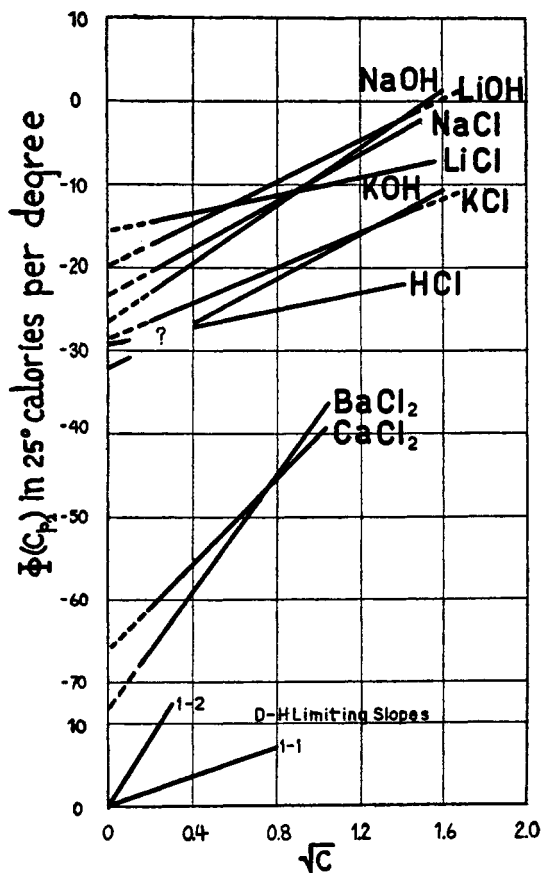


FIG. 1. APPARENT MOLAL HEAT CAPACITIES AT 25°C.

used as abscissa $c^{\frac{1}{2}}$ (which is nearly proportional to $m^{\frac{1}{2}}$ at low concentration), in order to make these lines strictly comparable with those in other figures.

Rossini (7) has made a careful survey of the literature and has calculated the apparent molal heat capacity of nearly all the salts

for which sufficiently accurate heat capacity data were available. As he has shown, these values are a most concise and accurate way of representing heat capacity data and the linear relationship is very convenient for interpolating and extrapolating such data.

APPARENT MOLAL VOLUMES

The apparent molal volume of a solute is most conveniently calculated from the density of the solution, using the equation

$$\Phi(V_2) = \frac{1000}{c} \left(\frac{d_1 - d}{d_1} \right) + \frac{M_2}{d_1} \quad (4)$$

where c is the concentration in moles per liter, and d and d_1 are the density of the solution and of pure water. This function has been studied for a long time and values of Φ are tabulated in Landolt-Börnstein, but it was only in 1929 that Masson (8) discovered that for most electrolytes Φ is a linear function of $c^{1/2}$. The experimental evidence has been studied very carefully by Scott (9) and also by Geffcken (10), who made additional density measurements in very dilute solutions. Both authors conclude that the linear relationship is valid for most of the univalent electrolytes studied, though a number of the lines, particularly those for lithium salts, show an appreciable deviation from the linear relationship in fairly concentrated solutions. Linear extrapolation of Φ for the alkali halides at many different temperatures was shown by Geffcken and Scott to indicate additive apparent ionic volumes at infinite dilution. Linear extrapolation of Φ from moderate concentrations ($0.2 c$) also gave results which were in good agreement with the values obtained by Lamb and Lee (11), who studied the density of sodium, lithium, and potassium chloride solutions down to $0.0001 c$ by means of an ingenious sinker method.

Masson, Geffcken, and Scott all concluded that the linear relationship held for any given electrolyte up to a high concentration, but that the slopes were appreciably different for individual electrolytes of the same valence type. On the other hand, Redlich and Rosenfeld (12) concluded from an examination of the best experimental data that the lines were all curved at high concentra-

tion and approached the *same slope* at great dilution. Which of these two views is correct can only be decided by further extremely precise density measurements, particularly in the dilute range.

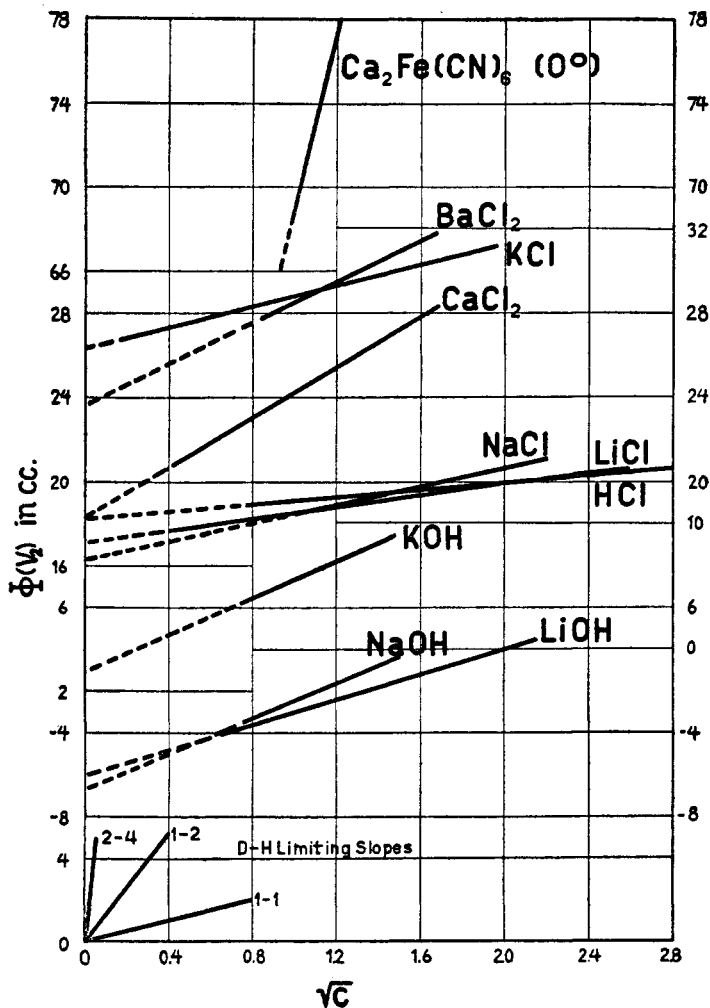


FIG. 2. APPARENT MOLAL VOLUMES AT 25°C.

Only a few solutes other than 1-1 electrolytes have been investigated. Geffcken (10b) includes the results for barium chlo-

ride solution, and Cantelo and Pfffer (13) give results for cobalt sulfate and cadmium iodide at 25°C. We have calculated values for the apparent molal volume of several other higher valence type electrolytes from the data in the literature. We find that the slope of these curves is markedly steeper with the higher valence ions, just as in the case of the apparent molal heat capacity curves. These general characteristics are shown by the typical lines plotted in figure 2.

APPARENT MOLAL COMPRESSIBILITIES

Recently we have studied the coefficient of compressibility of salt solutions from the point of view of the apparent molal compressibility. This function is defined by the equation

$$\Phi(K_2) = \beta V - \beta_1 V_1 \tag{5}$$

or

$$\Phi(K_2) = \beta \frac{1000}{c} - \frac{\beta_1}{d_1} \left[\frac{1000d}{c} - M_2 \right] \tag{6}$$

where $\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ and β_1 are the coefficients of compressibility of solution and water, and V and V_1 have the same meaning as in equation 2. A review (14) of the rather meager data in the literature shows that $\Phi(K_2)$ is also a linear function of $c^{\frac{1}{2}}$ over a very wide range of concentration and temperature. We have recently learned that Scott (15) has independently reached conclusions very similar to our own. He has just completed an experimental study of the compressibility of the alkali halides. This will be the most complete set of data on the compressibility of salt solutions, and its publication (16) should greatly broaden our knowledge of the compressibility of solutions and should be very valuable for solution theory.

Our own study shows that the values of the apparent molal compressibility are *negative* for electrolytes. Now it can be shown that from our definition

$$\Phi(K_2) = -\frac{\partial \Phi(V_2)}{\partial P} \tag{7}$$

and if the apparent molal compressibility is negative the apparent molal volume must *increase* with pressure. This fact, which is as striking as the negative value of $\Phi(C_p)$, has been noted by several investigators (17, 18). Adams found that, except in the

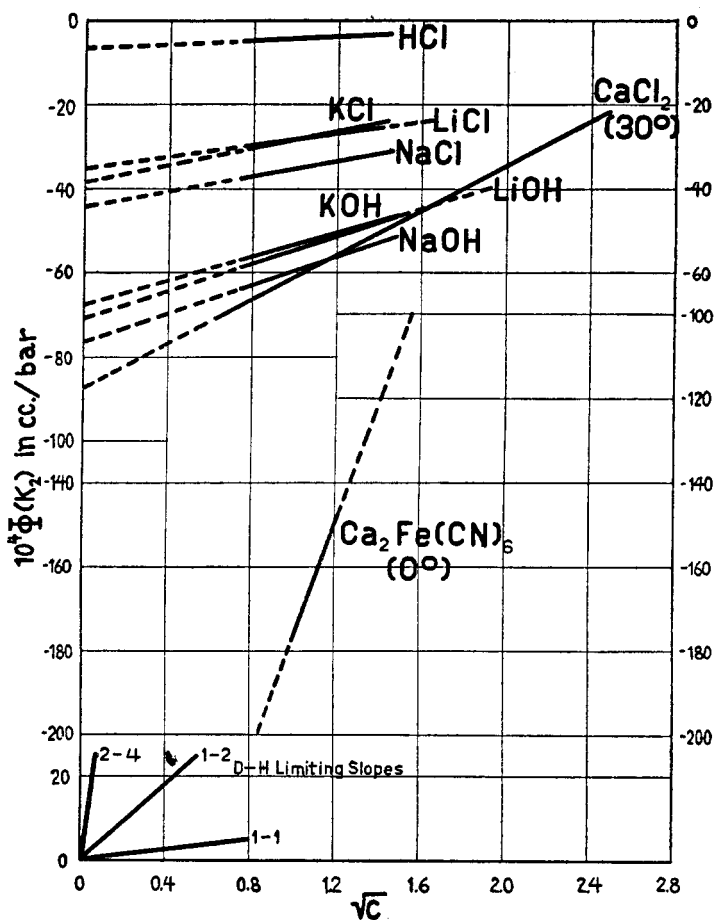


FIG. 3. APPARENT MOLAL COMPRESSIBILITIES AT 25°C.

most concentrated solutions, the partial molal volume of sodium chloride *increases* with pressure up to about ten thousand atmospheres.

Most of the discussion of apparent molal compressibilities in

the present paper is based upon experimental data obtained by Dr. B. J. Mair and Miss Edith Lanman at Bryn Mawr College four years ago. This work will appear shortly in the Journal of the American Chemical Society. We are very grateful to these authors for their kind permission to make use of the data at the present time.

A comparison of the extrapolated values shows that the apparent ionic compressibility is also additive at infinite dilution. Once more the higher valence electrolytes show progressively steeper slopes, as can be seen in figure 3.

THEORETICAL INTERPRETATION OF THE RESULTS

A completely satisfactory theory of electrolytic solutions must account for the results which we have discussed as well as the activity and conductivity of such solutions. There are really two problems involved. First, we must explain the widely different values for the apparent molal properties at infinite dilution; the fact that the apparent molal volume increases with pressure and that the apparent molal heat capacity is negative in most strong electrolytes. Second, we must explain why all of these apparent molal properties are linear functions of the square root of the concentration; why the slope is characteristic of a particular solute and so distinctly different for different valence types. An encouraging start has been made in the theoretical treatment, although we are still very far from a complete solution of the problem.

Many years ago Tammann (19) advanced the stimulating hypothesis that an internal pressure (Binnendrucke) existed in solutions. The properties of the solution were, therefore, those of water under high pressure. This hypothesis explains qualitatively many observed facts. More recently several attempts have been made to calculate the electrostrictive force exerted by the ions upon the water molecules and thus to calculate quantitatively the properties of electrolytic solutions. Probably the most complete theoretical treatment is that of F. Zwicky (20) who has calculated the heat capacity and, more recently with Evjen (21), the compressibility and expansion of such solutions.

They start with a general expression, derived by Dällenbach, for the force exerted on an isotropic dielectric medium in which the electric field, charge density, and polarization are known from point to point. They combine this with the well-known expression for potential derived by Debye and Hückel:

$$\psi = \frac{\nu\epsilon}{D} \cdot \frac{e^{-\kappa r}}{r}$$

Thus they calculate the characteristics of the field and the pressure at any distance from the ion. In a 0.1 *c* solution of a uni-univalent electrolyte the pressures are of the order of 70,000 kg. per cm.² at 1 Å. from the center of the ion and fall off very rapidly to 23 kg. per cm.² at 10Å. These pressures, combined with Bridgeman's data for the different properties of water under pressure, give the corresponding properties for a solution.

At present the agreement between theory and experiment is by no means quantitative, although the general electrostrictive picture seems illuminating, since it correlates these properties and predicts that the specific heat and coefficient of compressibility of electrolytes are *less* than those of water. In addition to the mathematical difficulties, the theory is handicapped because a value of $\bar{\mu}$, the average dipole moment of the water molecules in liquid water, enters into the calculations. This value must be much less than the dipole moment of water vapor, else electrical saturation would result at room temperature, but the exact value can only be inferred.

The value of the apparent molal heat capacity of a uni-univalent electrolyte calculated by the theory is -117 calories per degree, whereas the values obtained by linear extrapolation of the Φ curves illustrated in figure 1 range from -15 to -32 calories per degree for the uni-univalent electrolytes. This agreement is hardly satisfactory. The theory predicts a greater pressure around a higher valence ion, which explains the more negative value of $\Phi^0(C_{p_2})$ for barium and calcium chloride. However, Zwicky does not include a numerical value for the 2-1 electrolyte.

In Zwicky's original treatment he calculated the pressure

around a *single* ion. Now as he pointed out, an oppositely charged ion tends to neutralize this pressure, so that half way between the two it must actually be zero. Only an approximate correction was made for this effect. Since reading this manuscript, he has again taken up the problem and states in a private communication that, by calculating the pressure distribution around a *pair* of ions, one positive and the other negative, he obtains for a 1-1 electrolyte the much more satisfactory value $\Phi^0 C_{p_2} = -30$ calories per degree. He will discuss this question in a letter to the Physical Review, which should throw considerable light on the problem outlined here.

Another weakness of Zwicky's theory at the present time is that it does not predict quantitatively the differences in $\Phi^0(C_{p_2})$ for different salts of the same valence type. Actually this difference is very marked, as a glance at figure 1 will show. Zwicky attributes such specific differences to the amount of chemical hydration of the individual ions.

A somewhat more satisfying suggestion is offered by Webb (22) in a discussion of the apparent molal volume of salts at infinite dilution. He considers this volume is the result of two factors: first, the actual volume of the cavity (with a radius r_0 about 1.5 times that of the ion) in the water around the individual ion; second, a decrease in the solvent volume, due to electrostriction. The ion-solvent force he finds is very sensitive to a change in r_0 , increasing greatly as r_0 decreases. This idea can afford an explanation not only for the individual values of $\Phi^0(V_2)$ but also for those of $\Phi^0(C_{p_2})$. Unfortunately, a quantitative calculation of the individual apparent molal volumes requires other data which are not known at the present time.

Perhaps the most serious objection is that the electrostriction theory does not predict the simple linear relationship between the apparent molal property and $c^{\frac{1}{2}}$.² Strangely enough such a linear relationship can be derived quite simply from the Debye-Hückel limiting law (23) in the case of each of the three apparent molal properties discussed here. The limiting law for the differ-

² Zwicky states, however, that his new method of calculation also gives this linear relationship.

ence between the partial molal free energy of an electrolyte at any concentration c and that at infinite dilution is

$$\bar{F}_2 - \bar{F}_2^0 = (\Sigma \nu_i) RT \ln c - \frac{A}{D^{3/2} T^{1/2}} \cdot (\Sigma \nu_i z_i^2)^{3/2} c^{1/2} \quad (8)$$

where

$$A = \left(\frac{\pi \epsilon^3 N^3}{1000k} \right)^{1/2}$$

ν_i is the number of ions per molecule of charge z_i , N is Avogadro's number, ϵ the electronic charge, k Boltzmann's constant, and D the dielectric constant of the medium; the other symbols have their usual meaning. $(\Sigma \nu_i z_i^2)^{3/2}$ is the important *valence factor*. Substituting the values in the International Critical Tables gives $A = 2.457 \times 10^{-14}$ (in c.g.s. units).

The other properties are derived from equation 8 by thermodynamic reasoning. Randall and Rossini (1) obtained the equation for the partial molal heat capacity through the thermodynamic relationship

$$\bar{C}_{p_2} - \bar{C}_{p_2}^0 = -T \frac{\partial^2}{\partial T^2} (\bar{F}_2 - \bar{F}_2^0) \quad (9)$$

In carrying out the differentiation they assumed that the concentration was independent of the temperature, which would be true only for measurements at constant volume. The Debye-Hückel equation is derived at constant volume, while the experimental measurements are made at constant pressure. Scatchard (24) discussed this discrepancy and showed that it was easily removed by including a term for the thermal expansion in the theoretical equation. The complete equation for heat capacity was derived by La Mer and Cowperthwaite (reference 4, p. 1007).

$$\bar{C}_{p_2} - \bar{C}_{p_2}^0 = 3/4 A (\Sigma \nu_i z_i^2)^{3/2} \frac{f(D, V, T)}{(DT)^{3/2}} c^{1/2} \quad (10)$$

where

$$f(D, V, T) = 1 + 2 \frac{T}{D} \frac{\partial D}{\partial T} + 5 \left(\frac{T}{D} \frac{\partial D}{\partial T} \right)^2 + \frac{2T^2}{DV} \cdot \frac{\partial D}{\partial T} \cdot \frac{\partial V}{\partial T} + \frac{2}{3} \frac{T}{V} \frac{\partial V}{\partial T} + \left(\frac{T \partial V}{V \partial T} \right)^2 - 2 \frac{T^2}{D} \frac{\partial^2 D}{\partial T^2} - \frac{2}{3} \frac{T^2}{V} \frac{\partial^2 V}{\partial T^2}$$

The equation of Randall and Rossini differs only in that their $f(D, T)$ omits the last three terms of La Mer and Cowperthwaite's $f(D, T, V)$. The value of $f(D, T)$ is 16 per cent higher than that of $f(D, T, V)$ at 25°C., which illustrates the importance of the thermal expansion term.

The theoretical slope evidently requires an accurate knowledge of the dielectric properties of water, which are still in considerable doubt. The values obtained by different investigators, particularly for the derivatives, may be very different. Thus Randall and Rossini, employing E. Q. Adams' exponential representation of Kockel's data for D , obtained $f(D, T) = 1.75$, while La Mer and Cowperthwaite, using the Wyman (25) formula for the dielectric constant, obtained $f(D, T) = 4.535$ and $f(D, T, V) = 3.802$. Using La Mer and Cowperthwaite's value of $f(D, T, V)$,

$$\bar{C}_{p_2} - \bar{C}_{p_2}^0 = 4.69 (\sum \nu_i z_i^2)^{3/2} c^{1/2} \text{ calories per degree}$$

In deriving the theoretical slope of the partial molal volume curve, Redlich (26) and Rosenfeld used the thermodynamic equation

$$\bar{V}_2 - \bar{V}_2^0 = \frac{\partial}{\partial P} (\bar{F}_2 - \bar{F}_2^0) \tag{11}$$

Performing the indicated differentiation upon equation 8 gave them

$$\bar{V}_2 - \bar{V}_2^0 = \frac{A}{2} \frac{(\sum \nu_i z_i^2)^{3/2}}{D^{3/2} T^{1/2}} \left[\frac{3\partial D}{D\partial P} - \beta \right] c^{1/2} \tag{12}$$

Using the pressure coefficient determined by Falkenberg (27)

$$\frac{1}{D} \frac{\Delta D}{\Delta P} = 46 \times 10^{-6} \text{ (at 16.3°C.)}$$

and the value

$$\beta = 49.2 \times 10^{-6}$$

they find

$$\frac{3}{D} \frac{\Delta D}{\Delta P} - \beta = 89 \times 10^{-6}$$

and

$$\bar{V}_2 - \bar{V}_2^0 = 0.96 (\Sigma \nu_i z_i^2)^{3/2} c^{1/2}$$

More recently S. Kyropoulos (28) has studied the dielectric constant of water under pressure at 20°C. We find that his values for D at 1, 500, and 1000 kg. per cm.² give the equation

$$D = 80.79 + 4.80 \times 10^{-6}P - 3.11 \times 10^{-7}P^2 \quad (13)$$

where P is expressed in bars.³ The corresponding value for $\frac{1}{D} \frac{\partial D}{\partial P} = 59.4 \times 10^{-6}$ bars⁻¹. His value at atmospheric pressure is 0.5 per cent above that calculated from Wyman's formula (80.36). The equation for the volume of water under pressure at 20°C. we calculated from Bridgeman's data (31) at 0, 500, and 1000 atmospheres.

$$V = 1.0016 - 44.5 \times 10^{-6}P + 5.25 \times 10^{-9}P^2 \quad (14)$$

where P is in bars, whence $\beta = 44.4 \times 10^{-6}$ bars⁻¹. Based on the most recent experimental data, we therefore find at 20°C.

$$\left[\frac{3}{D} \cdot \frac{\partial D}{\partial P} - \beta \right] = 134 \times 10^{-6} \text{ bars}^{-1}$$

and

$$\bar{V}_2 - \bar{V}_2^0 = 1.34 (\Sigma \nu_i z_i^2)^{3/2} c^{1/2} \text{ cc.}$$

In the course of our study of the partial molal compressibility, we derived an equation for the slope of this curve, which is here published for the first time. Differentiating equation 8 twice with respect to P gives

$$\frac{\partial^2}{\partial P^2} (\bar{F}_2 - \bar{F}_2^0) = \frac{\partial}{\partial P} (\bar{V}_2 - \bar{V}_2^0) = -(\bar{K}_2 - \bar{K}_2^0) \quad (15)$$

where \bar{K}_2 represents the partial molal compressibility. The procedure yields

$$\bar{K}_2 - \bar{K}_2^0 = \frac{A}{4} (\Sigma \nu_i z_i^2)^{3/2} f(D, P, V) c^{1/2} \quad (16)$$

³ 1 bar = 10⁻⁶ dynes per cm.² = 1.0197 kg. per cm.² = 0.9869 atmosphere.

where

$$f(D, P, V) = \beta^2 + 2 \frac{\partial \beta}{\partial P} - 6 \frac{\beta}{D} \frac{\partial D}{\partial P} + 15 \left(\frac{1}{D} \frac{\partial D}{\partial P} \right)^2 - \frac{6}{D} \frac{\partial^2 D}{\partial P^2}$$

Computing the numerical values for the additional differential coefficients from equations 13 and 14,

$$\frac{\partial \beta}{\partial P} = -1.03 \times 10^{-8} \quad \text{and} \quad \frac{\partial^2 D}{\partial P^2} = -62.2 \times 10^{-8}$$

whence

$$f(D, P, V) = 6.49 \times 10^{-14} \text{ em.}^2 \text{ dynes}^{-1} \text{ bars}^{-1}$$

and

$$\bar{K}_2 - \bar{K}_2^0 = 3.23 \times 10^{-4} (\Sigma \nu_i z_i^2)^{3/2} c^{1/2} \text{ cc. per bar}$$

All the terms except the first are of about the same size and, because of the uncertainty, particularly of the second pressure

TABLE 1
Theoretical slopes for different valence types

VALENCE TYPE	$(\Sigma \nu_i z_i^2)^{3/2}$	THEORETICAL SLOPES		
		$\bar{V}_2 (20^\circ)$	$10^4 \bar{K}_2 (20^\circ)$	$\bar{C}_{p_2} (25^\circ)$
1-1	2.828	3.8	9.1	13.2
2-1	14.69	19.7	47.5	67.8
2-4	117.6	158	380	551

coefficients, the numerical value of $f(D, P, V)$ must be rather tentative.

We have shown how the slopes for the different partial molal quantities have been derived. In table 1 we have summarized the valence factors and also the limiting slopes for salts for different types. Those for \bar{V}_2 and \bar{K}_2 refer strictly to 20°C . and that for \bar{C}_{p_2} to 25°C ., but the uncertainty in the calculated value of the first two properties makes this difference negligible. The slopes for the corresponding *apparent* molal quantities are now very easily computed through the relationship

$$\frac{\partial \bar{G}_2}{\partial c^{1/2}} = \frac{3}{2} \frac{\partial \Phi(G)}{\partial c^{1/2}} \quad (17)$$

which holds in dilute solution (10b).

Table 2 gives the experimental values for the apparent molal properties at infinite dilution and also for the slopes obtained by passing the best straight lines through the experimental points plotted against $c^{1/2}$. Only a few points for $\Phi(V_2)$ in concentrated solution were disregarded in this procedure. The theoretical Φ

TABLE 2
Experimental values for Φ^0 and $\partial\Phi/\partial c^{1/2}$ for ten solutes* at 25°C.

SOLUTE	Φ^0			$\partial\Phi/\partial c^{1/2}$		
	V_2	$-10^4 K_2$	$-C_{P_2}$	$\Phi(V_2)$	$10^4\Phi(K_2)$	$\Phi(C_{P_2})$
1-1 (theory)	—	—	—	2.5	6.1	8.8
HCl.....	18.20	6.6	(29.20)	0.83	2.3	5.10
LiCl.....	17.06	36.4	15.63	1.42	7.5	5.31
NaCl.....	16.28	44.2	23.30	2.22	9.1	13.95
KCl.....	26.36	38.3	28.50	2.41	9.9	10.56
LiOH.....	-6.0	67.8	19.98	3.00	14.2	12.53
NaOH.....	-6.7	76.7	26.59	4.18	17.0	17.49
KOH.....	2.9	71.0	(32.10)	4.35	16.1	13.32
2-1 (theory)	—	—	—	13.1	31.6	45
BaCl ₂	23.60	—	73.0	4.83	—	35.0
CaCl ₂	18.25	87.4†	66.0	5.99	26†	25.8
2-4 (theory)	—	—	—	105	260	368
Ca ₂ Fe(CN) ₆ (0°C.).....	25.3	316	—	43.4	139	—

* Sources: The values of $\Phi(V_2)$ are in cc. Those for HCl, LiCl, NaCl, KCl, and BaCl₂ are taken from Geffcken (10b); the others are calculated from density data; Ca₂Fe(CN)₆, from that of Berkeley and Burton (30); CaCl₂ and LiOH from the International Critical Tables, and NaOH and KOH from Mair and Lanman.

The values of $\Phi(K_2)$ are in cc. per bar. All are taken from Mair and Lanman except for CaCl₂ and Ca₂Fe(CN)₆ which are from Perman and Urry (29) and Berkeley and Burton (30), respectively.

The values for $\Phi(C_{P_2})$ are in 25°-calorie units. Those for NaCl and KCl are from Randall and Rossini (1), those for HCl, LiCl, LiOH, NaOH, and KOH from Gucker and Schminke (3), and those for CaCl₂ and BaCl₂ from Richards and Dole (32).

† Values at 30°C.

slopes for the different valence types are also included. This table shows that, for all three properties, the *actual* slopes are of the predicted magnitude and change with valence type in about the way that is predicted by the theory. However, there is often

as much difference between two electrolytes of the same type as between two of different valence types and the slopes of the few high valence type electrolytes are noticeably *less steep* than the theory demands.

One striking regularity is apparent. When the solutes are arranged in the order of the increasing slope of the apparent molal volume curve, the slopes of the other two properties follow the same order in almost every case. Of the 1-1 electrolytes only the three slopes in italics are exceptions. The difference in the slope for ions of the same type is due to some factor that our theory does not explain but which affects all the slopes in approximately the same way. Even if subsequent investigation shows that the lines for the same type all approach a common slope at

TABLE 3
Non-electrolytes at 30°C.

Urea.....	$\left\{ \begin{array}{l} \Phi(V_2) = 44.3 + 0.4 c^{1/2} \text{ cc.} \\ 10^4\Phi(K_2) = -0.5 + 2.4 c^{1/2} \text{ cc. per atmosphere} \end{array} \right.$
Sucrose.....	$\left\{ \begin{array}{l} \Phi(V_2) = 210.6 + 3.4 c^{1/2} \text{ cc.} \\ 10^4\Phi(K_2) = -26.8 + 24.0 c^{1/2} \text{ cc. per atmosphere} \end{array} \right.$

zero concentration, as Redlich and Rosenfeld postulate in the case of apparent molal volumes, our tabulation shows that the order of deviation at high concentration is essentially the same for all three properties.

Apparent molal properties of non-electrolytes

The observed linear relationship between the apparent molal properties of electrolytes and $c^{1/2}$ originates, according to the Debye-Hückel Theory, in the *ion atmosphere* which exists in such solutions. We might therefore expect that the apparent molal properties of non-electrolytes would show no such linear change with $c^{1/2}$. This is certainly true of some properties. In a study of the viscosity of solutions, Jones and Talley (33) showed that electrolytes differ from non-electrolytes in that the relative viscosity function of the former contains the square-root term, while that of the latter does not. No comprehensive study of

our apparent molal properties of non-electrolytes has been made, but these substances are often assumed to behave in a "normal" way in solution. Thus Zwicky (20a) considered the apparent molal heat capacity of non-electrolytes is independent of concentration. So far we have studied only two non-electrolytes, but the implications of these results are far-reaching and may greatly

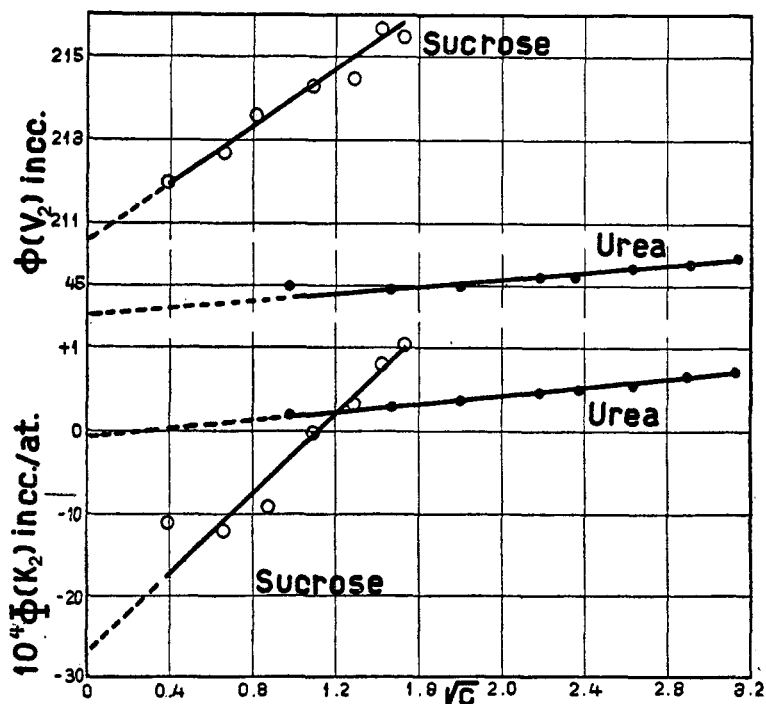


FIG. 4. APPARENT MOLAL VOLUMES AND COMPRESSIBILITIES OF NON-ELECTROLYTES.

affect our solution theory. Calculations from the data of Perman and Urry (29) show that the apparent molal volumes and compressibilities of sucrose and urea are linear functions of $c^{\frac{1}{2}}$ over the entire experimental range. For urea, the slope is small but the linear relationship holds from about 1 to 10 c . For sucrose, the slopes are much steeper—about those found for 2-1 electrolytes—and the linear relationship holds from 0.1 to 2.3 c . The equations

for these properties are given in table 3, and the results are plotted in figure 4. The individual experimental points are shown, since these calculations have not been published before. They fit the linear relationship in every case within the experimental error. Unfortunately we do not know the apparent molal heat capacities of these solutes, but the slopes of the other two properties parallel each other exactly like those of the electrolytes.

If, in the case of other non-electrolytes, the square-root term appears just as it does with electrolytes, we must explain it by some other picture than that of the ion atmosphere. Are we then justified in trying to explain all of the apparent molal properties of electrolytes as due to the ion atmosphere? How much of the individuality of the lines for different ions of the same type may be due to ion-solvent forces such as exist in non-electrolyte solutions? The only answer to these questions lies in a comprehensive study of solutions of non-electrolytes, which may perhaps give us a picture of a "normal" solution, upon which the interionic forces are superimposed in solutions of electrolytes. Such an investigation will be carried out in this laboratory in the near future. A concerted attack upon solutions of non-electrolytes should lay the foundation for a more unified and consistent solution theory.

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