

eucupin and vuzin and (2) quinine, quinidine, quinicine and quinic acid in aqueous solution all shift about  $200 \text{ cm.}^{-1}$ , to smaller wave numbers when 0.9 molar sulfuric acid is substituted as a solvent.

As the size of the group attached to position six of the quinoline nucleus of the alkaloids (1) increases from hydrogen to isooctoxyl, respectively, the absorption maxima broaden as the patterns shift toward smaller wave numbers. This also occurs when the secondary hydroxyl group of quinine at position four is replaced by a carbonyl group (quinicine) or by a carboxyl group (quinic acid).

The fluorescence spectra of most of these compounds excited by monochromatic radiation of  $\lambda$  366  $m\mu$  under comparable conditions in water and in sulfuric acid have been photographed and the spectrograms analyzed using a recording densitometer. No evidence of structure was observed, and all spectrograms were substantially identical.

These results have been interpreted to account in part for the low values of the quantum yield of the photochemical reduction of chromate by these compounds when excited by absorbed light.

CAMBRIDGE, MASSACHUSETTS

RECEIVED FEBRUARY 17, 1933  
PUBLISHED JULY 6, 1933

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## The Compressibility of Solutions. I. The Apparent Molal Compressibility of Strong Electrolytes

BY FRANK T. GUCKER, JR.

### Introduction

For many years a host of workers have investigated the conductivity and colligative properties of solutions of electrolytes, and from these studies we have developed our modern ideas of such solutions. Quite recently, the study of other properties of these same solutions has disclosed several important generalizations which must be considered in completing our theories of strong electrolytes. Randall and his co-workers<sup>1</sup> have showed that the apparent molal heat capacity of such solutions is a linear function of the square root of the molality over a wide range of concentration. Masson<sup>2</sup> has found that the apparent molal volume of solutions of strong electrolytes is also a linear function of the square root of the concentration. Scott and Geffcken<sup>3</sup> have verified this generalization in the case of many salts.

It seemed of interest to study the existing compressibility data, to see if the apparent molal compressibility of strong electrolytes showed the

(1) Randall and Ramage, *THIS JOURNAL*, **49**, 93 (1927); Randall and Rossini, *ibid.*, **51**, 323 (1929).

(2) Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(3) Scott, *J. Phys. Chem.*, **35**, 2315, 3379 (1931); *ibid.*, **37**, 1022 (1932); Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

same sort of regularity. This paper gives the results of these calculations, which show that the apparent molal compressibility is indeed a linear function of the square root of the concentration, over a wide range of concentration, temperature and pressure. The theoretical interpretation of these results will be the subject of a later paper.

The apparent molal compressibility of a solute is the compressibility of an amount of solution containing one mole of solute, minus the compressibility of the water. Thus

$$\Phi(K_2) = \beta V - \beta_1 V_1 \quad (1)$$

where  $\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$  is the coefficient of compressibility of the solution and  $\beta_1$  is that of the water.  $V$  and  $V_1$  are, respectively, the volume of solution occupied by one mole of salt and that occupied by the amount of solvent in which the mole of salt is dissolved. Expressing concentration on the weight basis, equation (1) becomes

$$\Phi(K_2) = \frac{\beta}{d} \left[ \frac{1000}{m} + M_2 \right] - \frac{\beta_1}{d_1} \frac{1000}{m} \quad (2)$$

where  $m$  is the number of moles of salt per 1000 g. of water,  $d$  and  $d_1$  the density of the solution and that of pure water, and  $M_2$  is the molecular weight of the solute.

Expressing concentration on the volume basis

$$\Phi(K_2) = \frac{\beta}{c} - \frac{\beta_1}{d_1} \left[ \frac{1000d}{c} - M_2 \right] \quad (3)^4$$

where  $c$  is the number of moles of solute per liter of solution.

From these equations we can see that for the same error in  $\beta$ , the uncertainty in  $\Phi$  becomes larger as the concentration decreases; hence very accurate data are needed to calculate  $\Phi$  with any reliability in dilute solutions. Furthermore, the values of  $\beta$  and  $\beta_1$ ,  $d$  and  $d_1$  must be *self-consistent*. Hence it is important to know the value of the compressibility of the solvent, obtained in the same apparatus in which that of the solution was measured. Errors in  $\beta$  will cause deviations in  $\Phi$  which may be either positive or negative; but an error in  $\beta_1$  will affect *all* values of  $\Phi$ , causing a deviation which is inversely proportional to the concentration. With these facts in mind, we have studied only the rather meager data in the literature in which the workers gave experimental values for  $\beta$ ,  $\beta_1$  and  $d$  at a number of different concentrations.

**The Experimental Data Reviewed.**—About the earliest reliable data are those of W. C. Röntgen and J. Schneider<sup>5</sup> for potassium chloride and

(4) The symbol  $\Phi$  has long been used for the *apparent molal volume* of a solute. With the definition and use of other apparent molal quantities, the meaning of  $\Phi$  has been generalized. In order to avoid confusion, the particular molal quantity may conveniently be indicated in parentheses after the  $\Phi$ . Thus  $\Phi(V_2)$ ,  $\Phi(C_{p_2})$  and  $\Phi(K_2)$  would symbolize the apparent molal volume, heat capacity (at constant pressure) and compressibility, of constituent 2 (the solute). In this paper  $\Phi$  is used for  $\Phi(K_2)$  wherever the abbreviation may be made without ambiguity.

(5) Röntgen and Schneider, *Wied. Ann.*, **29**, 165 (1886); *ibid.*, **31**, 36 (1887).

sodium chloride. They used a *differential* apparatus, in which were two piezometers, the first containing water and the second the solution. Each was made from a 60-cc. glass cylinder to the top of which was fused a fine calibrated capillary, in which the height of the liquid could be observed. A pressure of about eight atmospheres was applied, forcing the liquid in the capillary down 5 or 6 cm. The level was read to 0.005 cm., so that the error from this source would be about 0.2% in any one experiment. Usually several experiments were carried out with each solution. The differential arrangement tended to minimize any error due to heat of compression, or any change in the temperature of the apparatus. The corresponding contraction, when the second piezometer contained water, was known from a previous experiment. The ratio of the two is the *apparent* coefficient of compressibility of the solution, relative to that of water.

$$x = (\beta - \beta_2)/(\beta_1 - \beta_2) \quad (4)$$

where  $\beta$ ,  $\beta_1$  and  $\beta_2$  are the coefficients of compressibility of the solution, water and piezometer, respectively. Knowing  $\beta_2$ , it is easy to calculate the *actual* relative compressibility

$$y = \beta/\beta_1 \quad (5)$$

We have calculated the values of  $\beta$  for sodium chloride and potassium chloride solutions from those of  $x$  or  $y$  and  $\beta_1$  and  $\beta_2$  given in the same paper. The data are, therefore, self-consistent.

Röntgen and Schneider studied the compressibility of a number of other solutions; but most of them at only one or two concentrations, so that the results are not useful here.

Berkeley, Hartley and Burton<sup>6</sup> measured the compressibility of solutions of calcium ferrocyanide at 0°, from 1.0 to 1.5 *c*, in order to calculate osmotic pressure from vapor pressure measurements. Their piezometer was a glass cylinder of 15 cc. capacity with a graduated capillary tube at the bottom and a ground stopper at the top, through which it was filled. It was put into a pressure cylinder and the position of the mercury column in the capillary was read by means of a cathetometer. Pressure was applied in steps of 20.4 atmospheres, and the mean value of  $\bar{\beta}$  (1–62.1 at.) was used for these computations. They discarded some experiments because the mercury column did not return to the same position with falling pressure as with rising pressure. This was due to a change in the position of the plug, which is a difficulty in this type of apparatus. The error of reading in any experiment was about 1%.

Perman and Urry<sup>7</sup> made an exhaustive investigation of the compressibilities of potassium chloride and calcium chloride solutions at ten-degree intervals from 30 to 80°. They used a glass piezometer of about 20 cc.

(6) Berkeley, Hartley and Burton, *Phil. Trans. Roy. Soc.*, **A209**, 198 (1909).

(7) Perman and Urry, *Proc. Roy. Soc. (London)*, **A126**, 44 (1930).

capacity with a capillary tube into which a mercury thread was forced by hydrostatic pressure, measured by standardized gages. They discarded the ground plug of Berkeley and Burton, and filled the piezometer by evacuating it and drawing the solution in through the capillary. The position of the mercury meniscus, relative to an etched mark, was read by means of a cathetometer. They worked up to 200 atmospheres, and tabulated the mean values of  $\beta$  from 0 to 100 and from 100 to 200 atmospheres, and of  $\beta_1$  from 0 to 100 atmospheres. They estimated their error in the final value of  $\beta$  as not more than 0.25%.

**The Apparent Molal Compressibilities.**—From the experimental results, discussed above, the apparent molal compressibilities were calculated by means of equation (2). The actual details of computation are illustrated in Table I, which contains all the figures necessary to find the apparent molal compressibility of sodium chloride in aqueous solutions at 18°.

Values of  $\Phi$  which were calculated in this way were plotted against the square root of the concentration. These values were found to lie along straight lines, within experimental error. Values of  $\Phi$  were computed from the equations for these lines, and the corresponding values of  $\beta$  calculated by means of equation (2). These were compared with the observed values of  $\beta$ . The excellent agreement is illustrated in Table II.

We tried plotting  $\Phi$  against the square root of the concentration, expressed in two different ways. The apparent molal compressibilities of the uni-univalent electrolytes first investigated were plotted against the square root of the *molality* and the best straight lines were found to represent the data satisfactorily at all points, up to 6 *m*. The data for calcium chloride, which is more soluble, extended to 8 *m* and at all temperatures the values of  $\Phi$  fell below the straight line from about 5 *m* up. However, when we calculated the corresponding *volume concentrations* and plotted  $\Phi$

TABLE I  
CALCULATION OF APPARENT MOLAL COMPRESSIBILITY  
Data of Röntgen and Schneider for NaCl Solutions at 18°.  $M_2 = 58.37^a$

Expt.	$m^c$	$\frac{1000}{m}$	$\frac{M}{\frac{1000}{m} + M_2}$	Density <sup>b</sup>	$\frac{\gamma}{\beta/\beta_1^b}$	$\frac{10^6 s}{46.7y}$	$\frac{10^8}{\beta V}$	$\frac{10^8}{\beta_1 V_1}$	$10^3 \Phi$	$10^3 \Phi$ (calcd.) <sup>d</sup>
	0.0			0.9987	1.000	46.70				
1	0.724	1381	1439	1.0278	0.920	42.96	60.14	64.58	-4.44	-4.46
2	1.544	647.7	706.1	1.0585	.844	39.41	26.29	30.29	-4.00	-3.97
3	2.805	356.5	414.9	1.1022	.754	35.21	13.25	16.67	-3.42	-3.43
4	4.300	232.6	291.0	1.1493	.670	31.29	7.92	10.88	-2.96	-2.97
5	6.145	162.7	221.1	1.2011	.593	27.69	5.10	7.61	-2.51	-2.52

<sup>a</sup> Their value of  $M_2$  was used in the calculations, for the sake of consistency. <sup>b</sup> These values are taken directly from their paper. <sup>c</sup> They tabulate  $n$  (moles salt per 1000 kg. water), from which  $m$  is obtained by dividing by 1000. <sup>d</sup> Calculated from the equation  $10^3 \Phi = -5.57 + 1.31c^{1/2}$ .

TABLE II  
 AGREEMENT BETWEEN OBSERVED AND CALCULATED COMPRESSIBILITY  
 Data of Röntgen and Schneider at 18°

Expt.	$c^{1/2}$	NaCl solutions			$c^{1/2}$	KCl solutions		
		$10^6\beta$ (obs.)	$10^6\beta$ (calcd.) <sup>a</sup>	$10^6\Delta\beta =$ obs.-calcd.		$10^6\beta$ (obs.)	$10^6\beta$ (calcd.) <sup>b</sup>	$10^6\Delta\beta =$ obs.-calcd.
1	0.845	42.96	42.94	-0.02	0.342	45.64	45.56	+0.08
2	1.224	39.41	39.45	- .04	.582	44.48	44.45	+ .03
3	1.630	35.21	35.18	+ .03	.822	42.75	42.78	- .03
4	1.987	31.29	31.28	+ .01	1.029	41.07	41.14	- .07
5	2.331	27.69	27.65	+ .04	1.184	39.68	39.71	- .03
6					1.490	36.70	36.70	.0
7					1.743	34.15	34.15	.0
8					2.008	31.48	31.48	.0

Average  $10^6\Delta\beta = .03$  (0.1%) .03 (0.1%)  
 Maximum  $10^6\Delta\beta = .04$  (0.12%) .07 (0.17%)

Their error in a tabulated value is about 0.1%.

<sup>a</sup> Calculated from the equation  $10^6\Phi = -5.57 + 1.31c^{1/2}$     <sup>b</sup> Calculated from the equation  $10^6\Phi = -4.89 + 1.32c^{1/2}$ .

against  $c^{1/2}$ , the linear relationship held up to the highest concentration for which data were available (a solution practically saturated at 30°).

The two methods of plotting are illustrated in Fig. 1, which clearly shows the superiority of the volume concentration plot. The average deviation of *all* the observed values of  $\beta$  from those calculated from the *upper* line is  $1 \times 10^{-7}$ . The *lower* line is based on the first seven points and the average deviation of the observed values of  $\beta$  at these concentrations is only  $0.4 \times 10^{-7}$ . At the three highest concentrations, however, the deviations become increasingly larger and amount to 6, 9 and  $19 \times 10^{-7}$ . Even in the case of the uni-univalent electrolytes, slightly better agreement was found when  $\Phi$  was plotted against  $c^{1/2}$  than when plotted against  $m^{1/2}$ ; although below 4  $m$  there is little choice between the two abscissas.

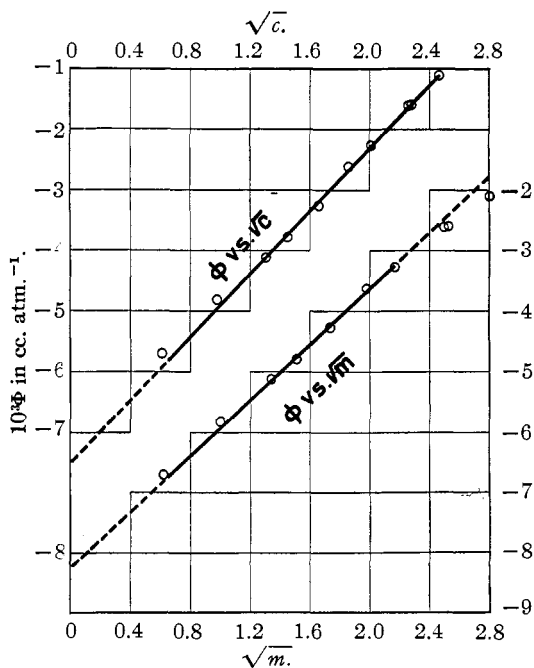


Fig. 1.—Calcium chloride at 60°, comparison of abscissas.

It is interesting to note that L. H. Adams, in the course of an exhaustive study of the properties of binary systems under pressure, used a relation very similar to the  $\Phi-m^{1/2}$  plot.<sup>7a</sup> He found that the change with pressure of the "apparent specific volume" of potassium sulfate and potassium chloride was a linear function of the square root of the *weight fraction* up to about 0.6 *m* and 3.6 *m*, respectively.

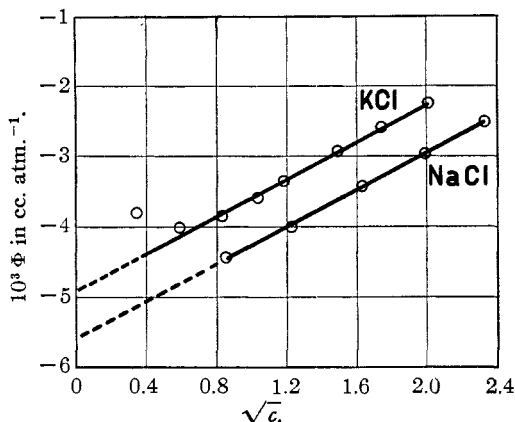


Fig. 2.—Data of Röntgen and Schneider at 18°.

Since this paper was submitted to THIS JOURNAL we have learned from A. F. Scott that he has also reached conclusions very similar to our own as to the linearity of the  $\Phi-c^{1/2}$  plot. He is at present completing a study of the

compressibility of solutions of six alkali halides over a wide range of concentration. We are awaiting with interest the publication and interpretation of these results.

The accuracy with which the linear relationship between  $\Phi$  and  $c^{1/2}$  fits the observed compressibility data is shown in Figs. 1 to 3, which illustrate typical cases.

The data of Berkeley and Burton for calcium ferrocyanide at 0° (Fig. 3) are represented by the equation

$$10^3\Phi = -32.00 + 14.04c^{1/2}$$

with a maximum deviation of 1.2% and an average of 0.4%. The average error of a single experiment is about 1%.

The data of Perman and Urry for potassium chloride and calcium chloride solutions at different temperatures are represented by the equations given in Table III. In every case the deviations are about what would be expected from experimental error.

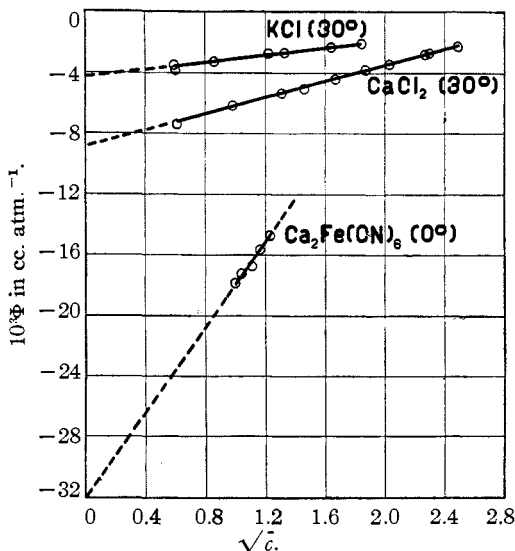


Fig. 3.—Apparent molal compressibility of salts of various valence types.

(7a) Adams, THIS JOURNAL, 54, 2233 (1932), equation (7).

TABLE III  
THE APPARENT MOLAL COMPRESSIBILITIES AS FUNCTIONS OF  $c^{1/2}$   
Data of Perman and Urry

Temp., °C.	10 <sup>3</sup> Φ for KCl solutions	10 <sup>3</sup> Φ for CaCl <sub>2</sub> solutions
30	-4.26 + 1.18 <i>c</i> <sup>1/2</sup>	-8.86 + 2.66 <i>c</i> <sup>1/2</sup>
40	-3.00 + 0.59 <i>c</i> <sup>1/2</sup>	-7.98 + 2.38 <i>c</i> <sup>1/2</sup>
50	-3.06 + 0.63 <i>c</i> <sup>1/2</sup>	-8.31 + 2.52 <i>c</i> <sup>1/2</sup>
60	-4.15 + 1.23 <i>c</i> <sup>1/2</sup>	-8.48 + 2.58 <i>c</i> <sup>1/2</sup>
70	-3.81 + 1.06 <i>c</i> <sup>1/2</sup>	-8.65 + 2.66 <i>c</i> <sup>1/2</sup>
80	-4.09 + 1.10 <i>c</i> <sup>1/2</sup>	-9.20 + 2.84 <i>c</i> <sup>1/2</sup>
Of the 36 experimental values of β,	Of the 59 experimental values of β,	
1 differs by 3 × 10 <sup>-7</sup>	1 differs by 3 × 10 <sup>-7</sup>	
5 differ by 2 × 10 <sup>-7</sup>	16 differ by 2 × 10 <sup>-7</sup>	
17 differ by 1 × 10 <sup>-7</sup> and	23 differ by 1 × 10 <sup>-7</sup> and	
13 agree exactly with the calculated values.	19 agree exactly with the calculated values.	

In all these experiments, the maximum deviations amount to only 0.9% and the average deviations to 0.3%. The estimated error of any value of β is 0.25%.

The concentration range over which the linear relationship holds is indeed remarkable. In the case of 6 *c* calcium chloride solutions, the coefficient of compressibility is only half that of pure water; yet the apparent molal compressibility is still a linear function of  $c^{1/2}$ .

The only irregularity which we have observed in the apparent molal compressibility, in the work of reliable investigators, is in the values for sulfuric acid solutions obtained by Röntgen and Schneider. These experiments cover the whole concentration range, but there were only three below 6 *m*. These show no linearity or regularity. It is to be hoped that this acid will receive detailed and accurate study in the near future, to clear up this question.

In addition to the data to which reference has already been made, we also studied the (unpublished) data of Dr. B. J. Mair and Miss E. H. Lanman. They investigated solutions of lithium, sodium and potassium chlorides and hydroxides, hydrochloric and acetic acids and potassium acetate, with an estimated accuracy of about 0.2%. We are indebted to them for their kindness in communicating these results to us and in allowing us to publish conclusions drawn from them. Their results cover only three concentrations of each solution, and hence do not furnish a rigorous test of the linear relationship between the apparent molal compressibility and the square root of the concentration; but the fact that they can all be correlated on this basis, well within the estimated experimental error, is a confirmation of the generality of this relationship. These data also cover enough compounds to indicate that linear extrapolation of the Φ curves of *strong* electrolytes to zero concentration gives values of Φ<sup>0</sup> which are additive for the ions. This fact does not, of course, preclude the possibility that *all* of these lines may show parallel curvature in the dilute

region. Fuller discussion of these results will be useful only when the data have been published.

**Salts of Different Valence Types.**—The compressibility data here assembled were obtained under varying conditions of temperature and pressure; but, although  $\beta$  changes greatly with changing conditions,  $\Phi$  does not. The small effect of temperature on  $\Phi$  is shown by the equations derived from the data of Perman and Urry (Table III). Pressure also has little influence on  $\Phi$ , although  $\beta$  changes as much as 1% in the dilute solutions between (0-100) and (100-200) atmospheres. This is illustrated in Table IV.

TABLE IV  
THE APPARENT MOLAL COMPRESSIBILITIES OF POTASSIUM CHLORIDE AT DIFFERENT PRESSURES (DATA OF PERMAN AND URRY AT 30°)

$c^{1/2}$	$10^6\beta_1 = 44.6$ (0-100 at.) $10^3\Phi$	$10^6\beta_1 = 42.8^a$ (100-200 at.) $10^3\Phi$
0.592	-3.5	-3.2
.595	-3.8	-3.6
.861	-3.25	-2.63
1.217	-2.78	-2.36
1.328	-2.71	-2.37
1.636	-2.33	-2.23
1.845	-2.08	-1.90

<sup>a</sup> Not tabulated by Perman and Urry, but given in graph on p. 63.

We are therefore justified in comparing the  $\Phi$  curves for potassium chloride and calcium chloride at 30° and for calcium ferrocyanide at 0°. Such a comparison is made in Fig. 3. It shows that, as far as these salts are concerned, the value of  $\Phi^0$  decreases and the slope of the  $\Phi-c^{1/2}$  curve *increases* as we go from the 1-1 to the 2-1 and 2-4 electrolytes.<sup>7b</sup> This effect is also observed in the apparent molal heat capacities of salts of different valence types.<sup>8</sup>

The apparent molal compressibility of all the *strong* electrolytes is *negative*.

In the hope of determining the apparent molal compressibility of a larger number of salts, we studied the data of M. Schumann,<sup>9</sup> who had investigated the chlorides of sodium, potassium, ammonium, barium, strontium and calcium. Values of  $\Phi$  for all these solutions were calculated and plotted, but were not precise enough to be included here. His curves of  $\beta$  against percentage of salt, instead of being smooth, were zigzag and quite unusual. J. Drucker<sup>10</sup> pointed out discrepancies as large as 10%

(7b) Since this paper was submitted to THIS JOURNAL, we have derived from the Debye-Hückel theory an equation which predicts the change of slope with valence type. This was presented at the Symposium on Electrolytes held during the Washington meeting of the American Chemical Society and will be published in a paper on the apparent molal heat capacities, volumes and compressibilities of salt solutions in the August number of *Chemical Reviews*.

(8) Rossini, *Bur. Standards J. Research*, **4**, 325 (1930).

(9) Schumann, *Wied. Ann.*, **31**, 36 (1887).

(10) Drucker, *ibid.*, **34**, 963 (1888).



between Schumann's values and his own and those of Röntgen and Schneider. Drucker's data for potassium chloride and calcium chloride were not used since they were obtained by an indirect method (measuring the adiabatic coefficient of compressibility) and at different temperatures. His interpolated values at 20° are, therefore, open to some uncertainty.

**$\beta$  as a Function of Concentration.**—To calculate  $\beta$  at any particular concentration requires the *density* of the solution in addition to the value of  $\Phi$ . Hence equations for  $\Phi(K_2)$  are less convenient in recording compressibility results than are equations for  $\Phi(C_{p_2})$  in recording heat capacity data.<sup>11</sup> Fortunately, a more convenient equation for recording data can be derived. W. C. Root<sup>12</sup> has recently shown that, for solutions in which the apparent molal volume is a linear function of the square root of the normality, the density may be represented by the equation

$$D = D_0 + C_1N + C_2N^{3/2} \quad (6)$$

where  $D_0$  is the density of water,  $N$  is the normality of the solution and  $C_1$  and  $C_2$  are constants. A similar equation holds true for the coefficient of compressibility of every solution in which the apparent molal compressibility *and* the apparent molal volume are both linear functions of the square root of the concentration. Then

$$\Phi(K_2) = \Phi^\circ(K_2) + a_1c^{1/2} \quad (7)$$

$$\Phi(V_2) = \Phi^\circ(V_2) + a_2c^{1/2} \quad (8)$$

Combination of these equations with (1) and the corresponding equation defining the apparent molal volume

$$\Phi(V_2) = V - V_1 \quad (9)$$

where  $V$  (in cc.) = 1000/ $c$ , gives the desired equation

$$\beta = \beta_1 + Ac + Bc^{3/2} \quad (10)$$

where

$$A = \frac{\Phi^\circ(K_2) - \beta_1\Phi^\circ(V_2)}{1000} \quad (11)$$

and

$$B = \frac{a_1 - \beta_1a_2}{1000} \quad (12)$$

The applicability of equation (10) has been tested in the case of calcium chloride solutions at 60°. Values of  $\Phi(V_2)$  were computed and plotted against  $c^{1/2}$ . They were found to fall along the straight line

$$\Phi(V_2) = 14.6 + 8.3c^{1/2} \text{ (in cc.)} \quad (13)$$

Equation (10) is therefore applicable in this case. Values of  $A$  and  $B$  were calculated from the coefficients in (13) and in the equation for  $\Phi(K_2)$  given in Table III.

The equation for the coefficient of compressibility was thus found to be

$$10^6\beta = 44.1_0 - 9.124c + 2.21_4c^{3/2}$$

(11) As suggested by Rossini, Ref. 8, p. 315.

(12) Root, THIS JOURNAL, 55, 850 (1933).

Values of  $\beta$  calculated from this equation agreed well with the ten experimental ones, showing three deviations of  $2 \times 10^{-7}$ , 3 of  $1 \times 10^{-7}$  and four cases of perfect agreement.

Equation (10) would be a convenient interpolation formula for representing compressibility data; for the coefficients could be evaluated directly from the data, without such a detailed study of  $\Phi(K_2)$  and  $\Phi(V_2)$ .

It is a pleasure to acknowledge our indebtedness to Dr. B. J. Mair and Miss E. H. Lanman for their kindness in allowing us to use their unpublished compressibility data, and to E. H. Gucker for invaluable assistance in the computations and in the preparation of this paper.

### Summary and Conclusions

The apparent molal compressibility is defined as  $\Phi(K_2) = \beta V - \beta_1 V_1$ . We have calculated this property for a number of solutions of electrolytes for which we could find in the literature accurate coefficients of compressibility over a suitably wide concentration range.

The apparent molal compressibility is a linear function of the square root of the volume concentration, up to the saturated solution. This relationship holds for all available data (11 different salts at 9 different temperatures) except for sulfuric acid (at  $18^\circ$ ). Further experiments are needed to see if this deviation is confirmed.

The apparent molal compressibility of all these electrolytes is negative but becomes less negative as the concentration increases. Salts of higher valence type are increasingly more negative and have progressively steeper slopes.

A long extrapolation indicates that within the limit of experimental error the apparent molal compressibilities are additive properties of the ions at infinite dilution.

These facts parallel in an interesting way what is already known of apparent molal heat capacities in aqueous solutions.

For all solutions in which  $\Phi(K_2)$  and  $\Phi(V_2)$  are linear functions of  $c^{1/2}$ , the following equation connects the coefficient of compressibility and concentration:  $\beta = \beta_1 + Ac + Bc^{3/2}$ , where the coefficients may be calculated from the equations for  $\Phi(K_2)$  and  $\Phi(V_2)$ .

EVANSTON, ILLINOIS

RECEIVED FEBRUARY 18, 1933  
PUBLISHED JULY 6, 1933