tion or even to eliminate it entirely. In this case a correction for the polarization resistance may be determined from the variation of the resistance with the frequency and applied to the results by the use of the equation $\Delta R = R_S - R_T = k/\sqrt{\omega}$.

Summary

1. The various criteria as to the quality and sufficiency of platinization in the measurement of the conductance of electrolytes are discussed and compared; and a test based on the variation of apparent resistance with frequency is recommended.

2. The addition of lead acetate to the platinizing solution, as recommended by Kohlrausch, is helpful.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 13, 1934

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

The Influence of the Concentration and Nature of the Solute on the Compressions of Certain Aqueous Solutions[1]

BY R. E. GIBSON

In continuation of a study of the effect of pressure on solutions,[2] we have determined over the whole range of concentration the compressions to 1000 bars[3] of aqueous solutions of the salts mentioned in Table I. It is the object of this paper to publish the thermodynamic data and call attention to several interesting generalizations which have been found. The apparatus, technique and method of calculating the results have already been described,[2a] but a few modifications made in the course of the work may be mentioned. By immersion of the manganin-wire pressure gage and the comparison coil in a well stirred oil thermostat, it was possible to eliminate a small but troublesome wandering of the zero point, traced to differences in the temperature coefficients of resistance of the two coils and also to avoid corrections for the change with temperature of the pressure coefficient of manganin which in our apparatus amounted to approximately the equivalent of 1 bar per degree at one thousand bars between 22 and 30°.

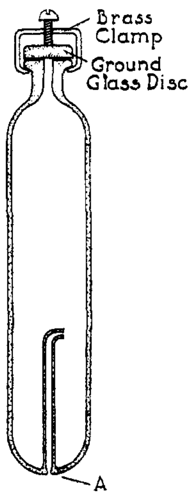

Fig. 1.—Flat-topped piezometer.

As a consequence of this improvement it was possible to make better observations of the freezing pressures of pure benzene, freshly distilled over phosphorus pentoxide, and it was found necessary to modify equation (1) given in the previous paper,[2a] which expressed the freezing pressure of benzene in bars as a quadratic function of the temperature.

$$P = 518.8 + 37.4(t - 20) + 0.104(t - 20)^2 \qquad (1)$$

Better values of the freezing pressures of benzene (according to the absolute gage in this Laboratory) are obtained by *subtracting* from the pressures calculated by equation (1) one, two and four bars at 20, 25 and 32°, respectively.

The reproducibility of the piezometers was noticeably improved when the glass stopper was replaced by a flat ground-glass cap (see Fig. 1), and the orifice at A was constricted to a diameter of 0.5 mm. During the work a significant result on the effect of heat treatment on the behavior of a Pyrex glass piezometer under pressure was noticed. A flat-topped piezometer which had not been specially annealed gave us a mean of seven observations 0.03890 for the compression of water, values of 0.00303 and 0.00399 being assumed for the compressions of Pyrex glass and mercury, respectively. The piezometer was heated slowly to 550° in a good furnace, held there for seven minutes, and then allowed to cool slowly. The temperature dropped to 539° in one hour and from 539 to 480° in two and a half hours. The mean of five observations of the compression of water in this piezometer now rose to 0.03916. The difference between these two sets of observations can only be satisfactorily accounted for by

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[1] Read in part before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society in Cleveland, September, 1934.

[2] Gibson, (a) THIS JOURNAL, **56**, 4 (1934); (b) *ibid.*, **56**, 865 (1934).

[3] To avoid cumbersome repetition the term compression will be used throughout this paper to mean the relative decrease in volume which a phase suffers when its pressure is increased from 1 to 1000 bars.

the assumption of a change in the *apparent* compression of the glass itself. Experience with glass piezometers indicates that accidental fluctuations in the results arise from details of design such as movement of stopper, size of orifice, and size of drop, but that the absolute value of the compression of the glass of the piezometer depends on its previous thermal treatment.

Materials

Except where otherwise mentioned, the solutions were all made up directly from weighed amounts of salt and water. *Potassium chloride, bromide, thiocyanate, nitrate, chlorate* and *chromate, sodium bromide, barium chloride* and *barium nitrate* were prepared by recrystallization of J. T. Baker C. P. Analyzed preparations and subsequent dehydration by heat and vacuum desiccation. Potassium thiocyanate was dried *in vacuo* in the same flask that was used for the gravimetric preparation of a stock solution from which the other solutions were prepared by quantitative dilution. Solutions of *barium thiocyanate* were prepared directly from Baker and Adamson Reagent barium thiocyanate dihydrate and analyzed by gravimetric titration against silver nitrate. *Lithium chloride* and *lithium iodide* were prepared by dissolving J. T. Baker C. P. Analyzed carbonate, carefully washed with water, in the appropriate acid and recrystallizing the products from aqueous solution. The compositions of the lithium chloride solutions were computed from the observed densities with the aid of the density-concentration table in the "International Critical Tables"[4] and checked by a solution prepared from carefully dehydrated salt and water. The percentage of lithium iodide in the solutions was determined by gravimetric analysis, by density measurements and by making solutions of weighed amounts of the trihydrate and water. All methods gave substantially the same results. C. P. cesium hydroxide from the Foote Mineral Company was dissolved in C. P. Analyzed hydrobromic acid. From the solution *cesium bromide* was crystallized. The salt was dried in an oven and a vacuum desiccator. Anhydrous *sodium carbonate* was obtained by heating the monohydrate (Mallinckrodt) to 300°. The hexahydrate of *cerium chloride* was prepared from cerium nitrate, obtained from the Foote Mineral Company in 1917, by the method described by Hönigschmid and Holch.[5] The chloride in the solutions was determined as silver chloride. J. T. Baker C. P. Analyzed glacial acetic acid and distilled water were used in the preparation of the acetic acid solutions. The concentration of the solutions was checked by titration against a standard barium hydroxide solution.

Results

The experimental results,[6] all of which were obtained at 25°, are recorded in Table I. The specific volumes marked by an asterisk represent new values determined during the course of this work in the pycnometers which have been used in this Laboratory for fifteen years. During the work experiments with water were made at intervals to check the reproducibility of the piezometers. It was assumed that the bulk compression of pure water from 1 to 1000 bars was 0.03935 cc.[7] and hence the apparent compression of the Pyrex glass was computed. The results in Table I are all based on this value for water. No piezometer giving values for the compression of water whose mean deviation exceeded 1×10^{-4} was used, and all the observations are given in Table I.

Discussion of Results

Representation of Results.—It has been found[8] that the volume changes under pressure of aqueous solutions of sulfates could be represented within the error of experiment as a function of the concentration by an equation of the form[2a]

$$A = a'r_2 + b'r_2^{3/2} \qquad (2)$$

Such an equation was also found to fit, within experimental error over the whole concentration range, the data for solutions of the salts[9] recorded in Table II, but it proved inadequate when applied to solutions of the other salts.

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[4] "International Critical Tables," Vol. 3.

[5] Hönigschmid and Holch, *Z. anorg. allgem. Chem.*, **177**, 94 (1928).

[6] The symbols used in this series of papers may be summarized as follows:

x_1 = weight fraction of water in solution
x_2 = weight fraction of salt in solution
$r_1 = x_1/x_2$
$r_2 = x_2/x_1$
c_1 = concentration of water in g. per cc. of solution = $x_1\rho$
c_2 = concentration of salt in grams per cc. of solution = $x_2\rho$
P = pressure in kilobars (10^9 dynes per sq. cm.)
k = decrease in volume per unit volume
$-\Delta_P v$ = specific compression of a solution
$-\Delta_P v_w$ = specific compression of pure water
$-\Delta_P v_s$ = specific compression of solid salt
$-\Delta_P v_2$ = partial compression of salt in solution
$-\Delta_P \phi_2$ = apparent compression of salt in solution = $\dfrac{A}{r_2}$
$-\Delta_P \phi_1$ = apparent compression of water in solution
For an increase of pressure from 1 to 1000 bars
v = specific volume of solution
v_2 = partial volume of salt in solution
v_s = specific volume of solid salt
ρ = density of solution
ρ_w = density of water
$A = -\Delta_P v_w + \dfrac{\Delta_P v}{x_1}$
m = moles of solute per 1000 grams water
C_1 = moles of water per liter of solution
C_2 = moles of solute per liter of solution
M_1 = molecular weight of water
M_2 = molecular weight of solute

[7] Adams, THIS JOURNAL, **53**, 3769 (1931).

[8] Ref. (a), Table II. In this paper the molality was used as argument but it is obvious that r_2 and m are connected by a constant factor.

[9] The values for compression data of sodium chloride solutions are those of Adams, *op. cit.*

TABLE I

THE COMPRESSIONS AND SPECIFIC VOLUMES OF AQUEOUS SOLUTIONS OF CERTAIN SALTS. EXPERIMENTAL RESULTS OVER A PRESSURE RANGE OF 1 TO 1000 BARS AT 25°

$100x_2$	10^4k	v	$-\frac{\Delta pv}{x_1} \times 10^4$	Deviation ($A_{\text{obs.}} - A_{\text{calcd.}}$) $\times 10^4$
		KCl		
0.00	393.5	1.0029	394.6	...
5.88	363.2	0.9682	373.7	0.0
10.91	342.2	.9365	359.7	− .9
13.79	330.2	.9198	352.3	−1.0
16.84	316.7	.9023	343.7	0.2
20.00	303.9	.8844	336.0	1.0
23.22	292.9	.8665	330.5	0.2
25.52	284.6	.8554	326.8	.2
		KBr		
0.00	393.5	1.0029	394.6	...
8.26	369.4	0.9446	380.3	−0.1
13.79	353.1	.9063	371.2	.2
20.00	334.9	.8636	361.5	.8
26.47	317.2	.8196	353.6	− .1
32.88	299.1	.7762	345.9	− .3
39.02	281.7	.7354	339.8	− .6
		KCNS		
0.00	393.5	1.0029	394.6	...
8.29	366.2	0.9634*	384.7	−0.3
14.82	345.2	.9332*	378.1	.5
26.49	311.3	.8806*	372.9	− .5
38.95	274.8	.8263*	372.0	1.0
44.37	260.3	.8033*	375.9	0.8
54.97	233.5	.7594*	393.7	.0
64.54	211.4	.7210*	429.8	−1.5
		KNO_3		
0.00	393.5	1.0029	394.6	...
8.16	366.3	0.9535	380.3	−0.2
13.68	348.2	.9210	371.5	.5
20.22	328.3	.8835	363.6	− .1
26.53	309.2	.8484	357.0	− .4
		$KClO_3$		
3.10	385.1	0.9831	390.7	...
7.06	373.0	.9595	385.1	...
		K_2CrO_4		
0.000	393.5	1.00293	394.6	...
13.782	322.0	0.89845*	335.5	−0.1
19.908	292.4	.85451*	312.0	.2
26.502	262.8	.80864*	289.1	− .2
32.900	235.8	.76566*	269.0	− .8
37.689	215.1	.73408*	253.4	1.1
		$K_3Fe(CN)_6$		
5.23	374.3	0.9749*	385.0	...
19.95	321.5	.8998*	361.4	...
		LiCl		
0.00	393.5	1.0029	394.6	...
4.44	361.1	0.9778	369.5	−0.3
7.66	340.0	.9605	353.7	.1
9.82	326.4	.9492	343.5	.9
15.06	298.6	.9227	323.9	.6
	297.8			
19.66	277.5	.9002	310.8	− .6
27.91	246.1	.8594	293.4	− .9
34.62	222.2	.8265	280.8	6.6^a
39.30	206.1	.8035	272.3	18.0^a
	205.3			
		LiI		
0.00	393.5	1.0029	394.6	...
9.62	375.0	0.9326	386.9	−0.1
25.58	342.4	.8166	375.7	− .3
33.87	322.9	.7582	370.2	− .1
46.37	293.4	.6649	363.8	.2
53.33	275.7	.6137	362.5	.6
		NaBr		
0.00	393.5	1.0029	394.6	...
5.00	375	0.9648	380.9	0.1
15.00	341	.8901	357.1	−1.0
25.00	304	.8167	331.1	1.2
35.00	270	.7446	309.2	0.3
45.00	236	.6743	289.3	− .6
		Na_2CO_3		
0.00	393.5	1.0029	394.6	...
3.86	354.3	0.9646	355.5	−0.4
8.39	311.8	.9205	313.3	− .6
13.88	268.0	.8745*	272.2	.6
16.78	246.5	.8505*	251.9	− .9
20.26	221.4	.8231*	228.3	− .1
	221.1			
		CsBr		
0.00	393.5	1.00293	394.6	...
9.88	377.0	0.92596*	387.4	0.0
20.05	360.0	.8472	381.5	− .5
29.94	341.8	.77138*	375.4	.1
	340.5			
40.00	320.5	.69465*	370.7	.4
	319.8			
45.69	308.1	.6513	369.4	.2
49.77	298.2	.6204	368.5	.7
		$BaCl_2$		
0.00	393.5	1.0029	394.6	...
5.00	371.9	0.9593	375.6	0.4
9.96	350.8	.9167	357.5	.5
	351.7			
15.00	331.2	.8741	340.6	.0
19.70	311.9	.8346	324.2	− .2
24.79	290.8	.7924	305.5	.4
	289.2			
		$Ba(NO_3)_2$		
0.00	393.5	1.0029	394.6	
4.53	379.7	0.96634*	384.3	
7.98	368.9	.93890*	376.4	
		$Ba(CNS)_2$		
0.00	393.5	1.0029	394.6	
5.62	376.7	0.9654*	385.3	
16.29	344.7	.8904*	366.6	
22.21	324.6	.8490*	354.3	

TABLE I (*Concluded*)

$100x_2$	10^4k	v	$-\frac{\Delta_P v}{x_1} \times 10^4$	Deviation ($A_{\text{obs.}} - A_{\text{calcd.}}$) $\times 10^4$
28.38	304.6	.8047*	342.1	
	304.4			
39.08	267.2	.7327*	321.7	
	267.9			
51.85	227.7	.6482*	306.5	
58.35	208.0	.6062*	303.5	
	209.0			
		$CeCl_3$		
0.00	393.5	1.0029	394.6	...
8.69	350.3	0.9232*	354.2	−0.1
16.97	309.3	.8514*	317.1	.7
23.36	280.0	.7961*	290.8	− .4
34.60	227.5	.6994*	243.3	1.0
44.09	188.0	.6234*	209.6	−0.3
		Acetic acid		
0.00	393.5	1.0029	394.6	...
6.81	382.7	0.9935	408.0	−0.2
11.62	377.7	.9874	421.9	.4
16.89	375.6	.9807	443.1	.3
31.16	375.3	.9650	526.0	−1.7
41.17	384.9	.9558	625.2	−2.1
50.53	399.8	.9489	766.7	
69.18	443.5	.9404	1353.0	
79.37	480.6	.9392	2188.1	
89.80	536.9	.9428	4962.7	
94.33	571.5	.9470	9548.5	
99.5	633.4	.9571	...	
	635.1			
	634.7			

[a] Points not used in fitting of equation.

TABLE II

REPRESENTATION OF COMPRESSION DATA BY THE EQUATION $A = a'r_2 + b'r_2^{3/2}$. TABLE OF COEFFICIENTS

Solute	$a' \times 10^4$	$-b' \times 10^4$
NaCl	599.5	460.0
NaBr	298.9	190.2
Na_2CO_3	1198.6	1083.4
KCl	433.6	404.4
KBr	206.5	151.6
KNO_3	220.5	193.4
K_2CrO_4[a]	521.9	379.5
CsBr	84.0	59.0
$BaCl_2$	420.3	265.6

[a] Deviation exceeds experimental error at highest concentration.

Now A is connected with the apparent compression of the solute by the relation $A/r_2 = \Delta_P\phi_2$, and it has been shown[10] that the apparent molal quantities of several substances are represented over a longer range of concentration more closely by a linear function of the volume concentration than by a linear function of the weight concentration. The observations recorded here confirm this view as far as apparent compressions are concerned. Equations of the form[10a]

$$\frac{A}{r_2} = a + bc_2^{1/2} \tag{3}$$

fitted the data for the salts in Table III over the entire range, as will be seen from the last column of Table I, where the deviations between the observed values of A or $\Delta_P v/x_1$ and those computed from the appropriate equation (3) are given. The scattering of these deviations gives an idea of the consistency of the experimental results. Although equation (3) is more generally useful in representing the data, it is more convenient to use equation (2) wherever possible, as the thermodynamic quantities, the partial compressions, are more readily computed from equation (2).[11] It is, however, possible to compute partial compressions directly from equation (3) by a method analogous to that described for partial volumes[12] if the coefficients in equation (3) are known.

Unlike the weight concentration, the volume concentration c_2 varies with the pressure, but no account has been taken of this in the expressions given here. The quantity c_2 refers to grams per cc. at 25° and 1 bar pressure. Equation (3) does not fit the results for lithium chloride over the entire range, there being large and real departures in the most concentrated solutions. Barium thiocyanate solutions present an even more extreme case, a graphical examination revealing that it was not worth while even attempting to apply equation (3) to the results. The curious behavior of these solutions is visible in Fig. 3.

The coefficients a' and a, given in the second columns of Tables II and III, respectively, are both numerically equal to the increase with pressure (per 1000 bars) of the partial volume of the salts in the infinitely dilute solutions. It is evident that equations (2) and (3) do not extrapolate to quite the same value for this quantity even though there is little to choose between the equations as far as representation of the experimental data is concerned. Whether a' or a gives the closer approximation to $-\Delta_P v_2$ at infinite dilution is a matter which can only be decided either by much more accurate measurements at lower concentrations or by a sound theoretical reason

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[10] Gucker, THIS JOURNAL, **55**, 2713 (1933).

[10a] This equation may also be written in a form more suitable to giving the correct weight to all the observations in any curve-fitting process, *viz.*

$$-(k - x_1k_w) = ac_2 + bc_2^{3/2}$$

[11] Ref. 2a, Eqns. 3 and 4.

[12] Gucker, *J. Phys. Chem.*, **38**, 307 (1934); Gibson, *ibid.*, p. 319.

for preferring equation (2) to equation (3) or *vice versa.*

TABLE III

COEFFICIENTS IN THE EQUATIONS REPRESENTING THE APPARENT COMPRESSION, THE APPARENT MOLAL COMPRESSION, AND THE APPARENT EQUIVALENT COMPRESSION OF THE SOLUTES AS FUNCTIONS OF THE SQUARE ROOT OF THE VOLUME CONCENTRATION

Solute	$a \times 10^4$	$-b \times 10^4$	M_2a	$-\frac{M_2^{3/2}}{\sqrt{1000}}b$	$\frac{M_2}{z}a$	$-\left(\frac{M_2}{z}\right)^{3/2}\frac{b}{\sqrt{1000}}$
NaCl	612.0	510.5	3.577	0.721	3.577	0.721
KCl	446.5	454.3	3.329	.924	3.329	.924
LiCl[a]	715.7	793.0	3.034	.692	3.034	.692
$BaCl_2$	413.2	258.6	8.607	2.459	4.303	.869
$CeCl_3$	535.2	356.9	13.20	4.372	4.40	.841
NaBr	307.3	217.7	3.162	0.719	3.162	.719
KBr	212.4	172.8	2.528	.710	2.528	.710
CsBr	88.40	70.12	1.880	.688	1.880	.688
LiI	97.30	74.10	1.303	.363	1.303	.363
KI	82.5	60.00	1.369	.41	1.369	.41
KCNS	172.3	201.7	1.674	.611	1.674	.611
KNO_3	225.8	215.7	2.283	.694	2.283	.694
K_2CrO_4	537.7	427.2	10.44	1.726	5.22	.610
Na_2CO_3	1206.0	1112.7	12.78	3.840	6.39	1.358
CH_3COOH	−83.7	370.17	−0.502	0.544	−0.502	0.544

[a] Equation fails to represent data above $x_2 = 0.30$.

Comparison of the Effects of Different Salts on the Compression of Water.—Richards and Chadwell[13] concluded (from a limited number of observations) that in dilute solutions equal numbers of molecules of solute lower the compressibility of water by the same amount and we found[2a] for solutions of unhydrolyzed sulfates that solutions of the same molality had approximately the same bulk compressions. We are now able to extend this result in a modified form to solutions of other salts. Figure 2 shows that when the bulk compression,[14] k, is plotted against the concentration function $1/2C_2[\nu_C z_C + \nu_A z_A^2]$ (ν_C and ν_A being the numbers of cations and anions into which a molecule dissociates and z_C and z_A the valences of the cations and anions), the points for practically all the series of solutions fall within a relatively narrow belt on the diagram.

Furthermore, the results which do not fall in the narrow belt are correlated with the presence of hydrogen or lithium ions in the solution, and are in harmony with the suggestion of Bernal and Fowler,[15] based on Raman spectra observations, that these ions tend to promote in water the more compressible "quartz-like" structure, or, in the older terminology, the more highly polymerized water molecules. The concentration function used differs from the ionic strength of Lewis and Randall in that the formal concentration of the cation is multiplied by the first instead of the second power of the valence. The procedure is arbitrary and is justified only by the empirical result that the graph enables one to make an approximate estimate of the bulk compression of any solution with an error not exceeding 10% from a knowledge of its concentration and the nature of the solute.

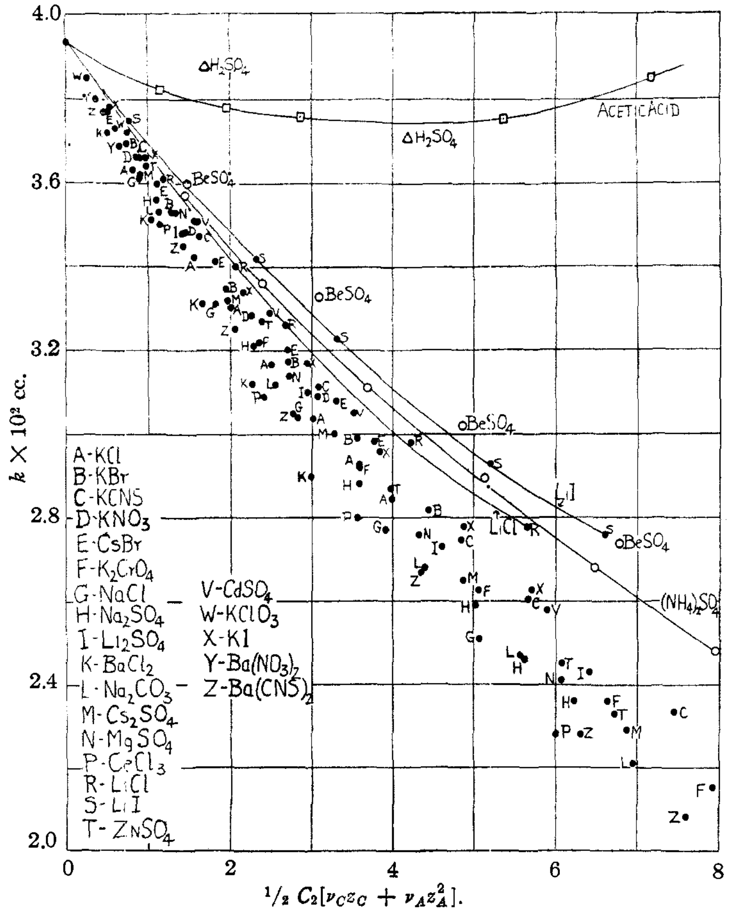

Fig. 2.—The bulk compression of different salt solutions as a function of the "modified ionic strength." In the computation of the "modified ionic strength" the concentration of the cation is multiplied by the first power of its valence.

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[13] Richards and Chadwell, THIS JOURNAL, **47**, 2299 (1925).

[14] Richards' compressibility was really the bulk compression between 100 and 300 bars divided by the pressure increase.

[15] Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

The quantities A or A/r_2 give a much better insight into the influence of the salt on the compression of water than does k, whose physicochemical significance is obscure. The figures in columns 4 and 5 of Table III are the coefficients in an equation, derived from equation (3), which expresses $M_2(A/r_2)$, the apparent *molal* compression of the salt, as a linear function of the square root of the *molal* concentration (moles per liter). These figures enable one to compare the relative effects produced by the different salts. The same relations are seen in Fig. 3 where A is plotted against the molality. The effect of a salt on the specific compression of water increases with the charge and decreases with the radius of the salt ions. Several empirical attempts were made to take into account quantitatively these two physical properties of the solute but nothing of special interest resulted. One attempt is illustrated in the last two columns of Table III which give the coefficients in the equation expressing the increase in the apparent *equivalent* compression as a function of the square root of the concentration expressed in gram equivalents per liter. It will be seen that although the apparent equivalent compressions in infinite dilution still differ appreciably, the slopes for the different chloride solutions are brought very close together. Another attempt is illustrated by comparing Fig. 3 with Fig. 4 where the function A is plotted against the ionic strength. Here, again, the curves are brought closer together, but still significant differences remain which cannot be entirely compensated for by inverse proportionality to the ionic radius.

The curves for lithium chloride and lithium iodide solutions in Fig. 3 occupy an unexpected position, being close to the corresponding salts of potassium instead of leading the alkali metal series. The same order is seen in the results at 25° of Lanman and Mair[16] and in those at 35° recently published by Scott, Obenhaus and Wilson,[17] if these latter data are replotted against a molecular concentration. All these investigators worked at pressures between 100 and 300 bars. The anomalous behavior of the lithium salts is presumably connected with the effect of the lithium ions on the structure of water.[15] It may even be that the hydration of the lithium ions really consists of the formation of water complexes of open structure, coördinated around the small lithium ions.

The slopes of the curves in Fig. 3 give directly the increase with pressure of the partial molal volumes of the salt. As usual at low pressure, this quantity is positive in most cases, but it does become negative in concentrated solutions of potassium iodide, potassium thiocyanate, and cesium bromide, a phenomenon which has hitherto been observed only at very high pressures.

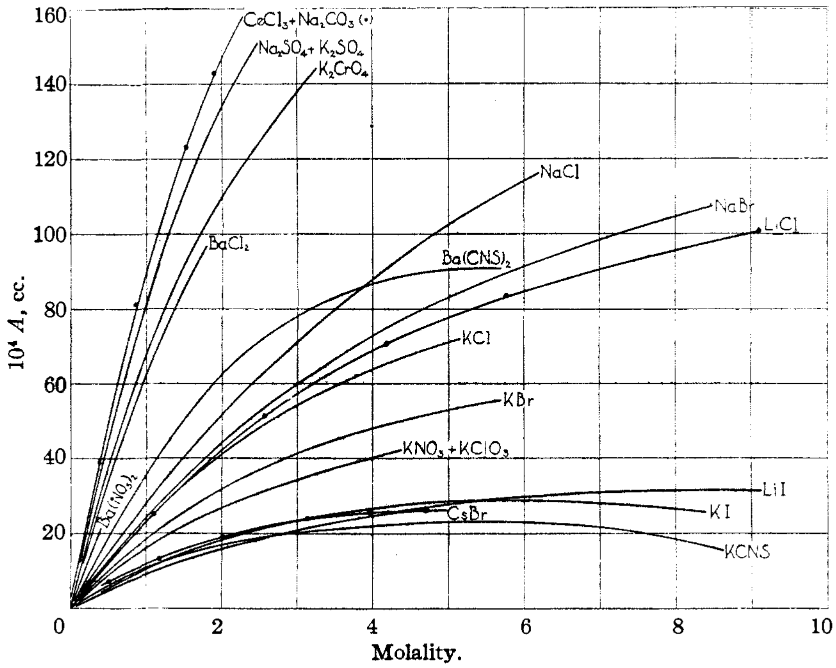

Fig. 3.—The deviation function A ($= \Delta_P v/x_1 - \Delta_P v_w$) as a function of the molality for aqueous solutions of different salts.

The Effective Pressure, P_e.—On the assumption of Tammann's hypothesis[18] that water in an aqueous solution behaves like water under a pressure greater than the external pressure, it is possible to modify an equation expressing the volume of water as a function of pressure to obtain a volume–pressure equation for an aqueous solution

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[16] Lanman and Mair, THIS JOURNAL, **56**, 390 (1934).

[17] Scott, Obenhaus and Wilson, *J. Phys. Chem.*, **38**, 931 (1934).

[18] Tammann, "Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," Leipzig, 1907, p. 36.

merely by the addition of a constant, P_e, and a small term which gives an approximation to the compression of the salt in the solution. It should be remarked that this procedure is only applicable to cases where the compressibility of the solute is small in comparison with that of water. The utility of the effective pressure as a means of predicting the behavior of solutions under high pressure has already been demonstrated[2b] in the cases where data are available, and in the same article the formula for computing P_e from compression data is also given.

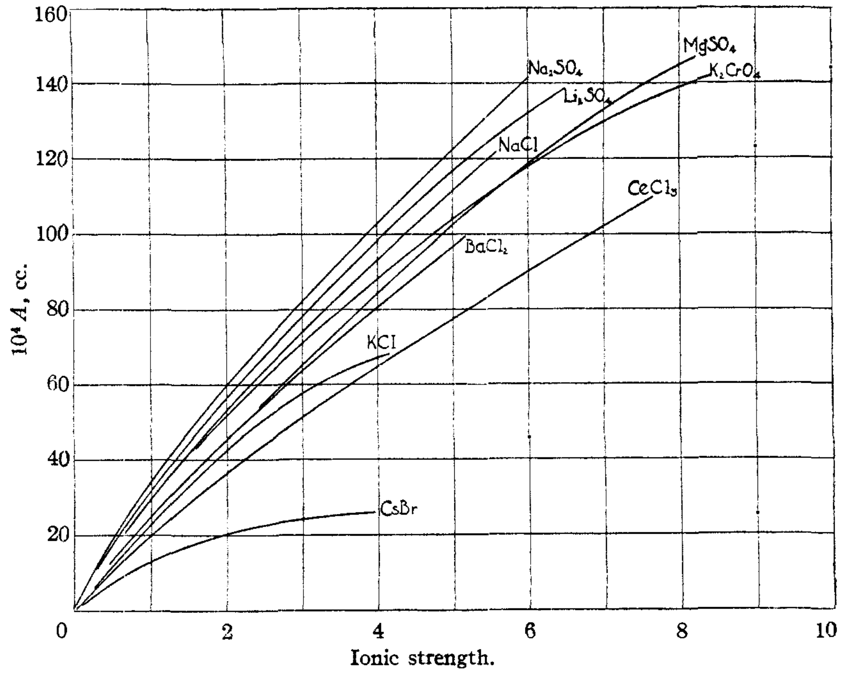

Fig. 4.—The deviation function A as a function of the ionic strength.

For all the aqueous solutions of salts studied up to date it has been found that P_e is a linear function of the product of the concentration of salt and water in the solution.

The relation

$$P_e = L \times C_1C_2 \qquad (4)$$

where L is a constant for each solute, holds over the whole range of concentration, as may be seen in Fig. 5. A number of the straight lines do not pass directly through the origin but in all cases the zero error is small. If V is the volume of solution containing n_1 molecules of salt and n_2 molecules of water, then $P_e = (n_1n_2/V^2) \times L$. As P_e may be regarded as a cohesive pressure set up by the interaction between the unlike molecules in the solution, this latter relation brings out a striking analogy between P_e in aqueous solutions and the cohesive pressure in gases which gives rise to the a/v^2 term in van der Waals' equation of state. If equation (4) has any significance then P_e is a function of the pressure. In our previous work[2b] we have neglected this dependence of P_e on the pressure, an approximation which is not serious because of the relatively small compressibilities of the liquids studied, but which may be important in cases where the compressibilities are large.

The practical use of P_e may be further demonstrated. If equation (1) in the previous paper[2b] be differentiated with respect to pressure, we obtain as an expression for the isothermal compressibility of a solution at any pressure and 25°

$$\beta \equiv -\frac{1}{(V)_{P=0}}\left(\frac{\mathrm{d}V}{\mathrm{d}P}\right)_T = \rho\left[\frac{0.13337x_1}{2.923 + P_e + P} - x_2\frac{\mathrm{d}v_s}{\mathrm{d}P}\right] \qquad (5)$$

By means of this equation values of β at atmospheric pressure were computed for four series of

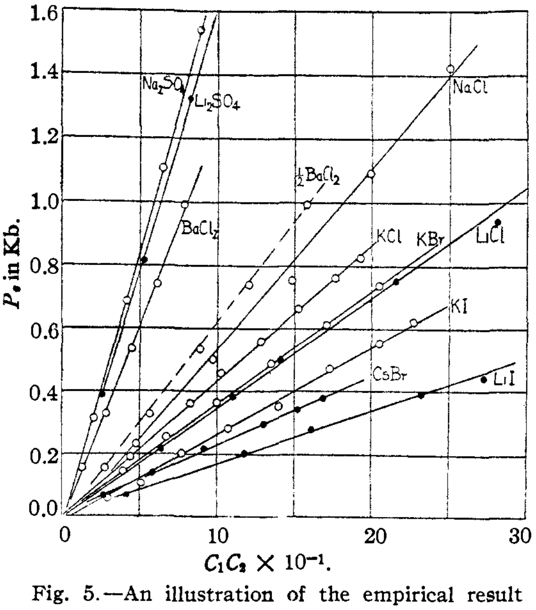

Fig. 5.—An illustration of the empirical result that the effective pressure is directly proportional to the concentration of water and of salt in aqueous solutions.

TABLE IV

A COMPARISON OF THE ISOTHERMAL COMPRESSIBILITIES OF SALT SOLUTIONS AT 25° AND 1 BAR AS CALCULATED FROM COMPRESSIONS AT 1000 BARS AND AS DETERMINED BY FREYER FROM THE VELOCITY OF SOUND IN SOLUTIONS. THE VALUES OF β ARE IN RECIPROCAL BARS

$100x_2$	$\beta \times 10^6$ from compressions at 1000 bars	$\beta \times 10^6$ from sound velocities at 1 bar
	KCl	
6.0	41.8	41.7
10.0	39.5	39.4
16.0	36.3	36.2
20.0	34.3	34.2
24.0	32.4	32.4
	KBr	
6.0	43.2	43.5
10.0	41.7	41.9
20.0	38.1	38.4
30.0	34.6	34.8
40.0	31.1	31.4
	KI	
6.0	44.3	44.3
16.0	41.7	41.7
30.0	37.8	38.0
45.0	33.4	33.7
	NaCl	
6.0	40.6	40.4
10.0	37.6	37.5
16.0	33.2	33.4
20.0	30.7	31.0
24.0	28.4	28.8

salt solutions, P_e being calculated from the compression data at 1000 bars and interpolated to the appropriate concentration by equation (4). The results are compared in Table IV with isothermal compressibilities computed by Freyer[19] from his measurements of sound velocities in these solutions at atmospheric pressure. Freyer's original results were given at 20° and an attempt was made to correct them to 25° by use of his tables of changes in the adiabatic compressibility with temperature (given for only one concentration of each salt) and the data of Hubbard and Loomis[20] on the effect of temperature on the compressibility of water. The agreement between the two sets of values is noteworthy, especially when it is remembered that for each solution the calculated compressibility at 1 bar depends on a single compression measurement made at 1000 bars.

Assuming that the water in a given solution occupies the same volume as it would in the pure state under an external pressure equal to P_e, one may compute the volume, ψ_2, which one gram of the salt appears to occupy in the solution.[21] For the salts discussed here ψ_2 is again practically independent of the concentration and of a magnitude approximately equal to that expected for the pure liquefied salts. The results are shown diagrammatically in Fig. 6, where $(\psi_2 - v_s)/v_s$ is plotted against the concentration. The behavior of lithium chloride is different from that of the other salts in that ψ_2 is excessively large in dilute solutions and decreases as the concentration increases. Lithium iodide does not behave like LiCl but does show a relatively large value of $(\psi_2 - v_s)/v_s$.

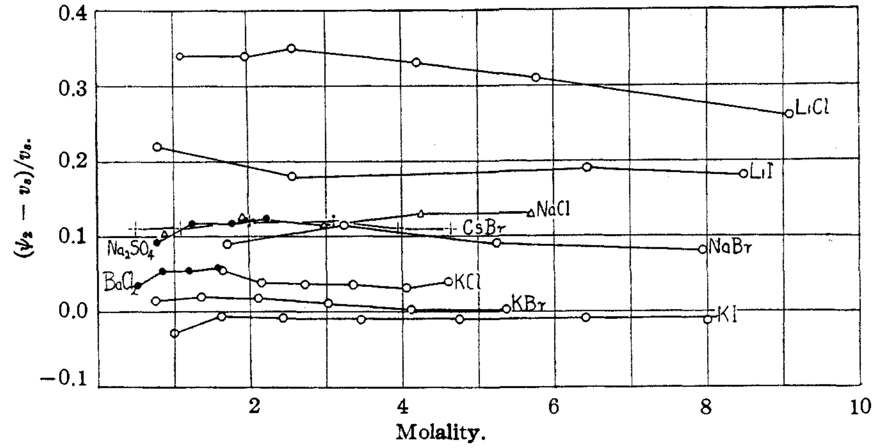

Fig. 6.—The variation with concentration of the fractional increase in volume of the salts on dissolving in aqueous solutions on the assumption of Tammann's hypothesis.

Solutions of Acetic Acid.—Acetic acid differs from the other solutes considered here in that it is a liquid and a weak electrolyte. In Fig. 7, $M_2 \Delta_P \phi_2$, the increase with pressure of the apparent molal volume of the acid, is plotted against the square root of the volume concentration and the same functions are plotted for KCl, KBr and LiCl. For solutions containing from 0 to 40% of acetic acid $M_2 \Delta_P \phi_2$ is a linear function of $C_2^{1/2}$ but for solutions of higher concentration this relation breaks down. It will be seen from the diagram, however, that the range of *molal* concen-

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[19] Freyer, THIS JOURNAL, **53**, 1313 (1931).

[20] Hubbard and Loomis, *Phil. Mag.*, **5**, 1177 (1928).

[21] Gibson, Ref. 2a, p. 12.

tration over which the linear relation holds is greater for acetic acid than for any of the salts except lithium chloride and for this salt the linear relation fails to represent the data at the higher concentrations. Unlike the salts, acetic acid has a negative value of $M_2 \Delta_P \phi_2$ at zero concentration, but the differences between the molal compressions of the pure solute and the apparent molal compressions at zero concentration are of the same magnitude. For acetic acid $M_2(\Delta_P v_a - \Delta_P \phi_2)$ is -3.11 cc. per mole, while $M_2(\Delta_P v_s - \Delta_P \phi_2)$ for KCl is -3.76, and for KBr, -2.9 cc. per mole. The slopes of the lines are also approximately the same. We conclude, therefore, that as regards the influence of concentration on the apparent molal compression (or the effect per mole of the solute on the compression of water) there is little difference between the behavior of strong electrolytes and that of the weak electrolyte acetic acid. Gucker[22] has called attention to the fact that some non-electrolytes exhibit a linear relation between the apparent molal compressibility and the square root of the concentration, and Tammann[23] has concluded that the attractive forces between weak electrolytes and non-electrolytes (whose internal pressures exceed that of water) and water do not differ essentially from those of strong electrolytes. The conclusion seems inevitable that the square-root law which holds so well empirically cannot have its theoretical explanation in the theory of interionic attraction as at present developed.

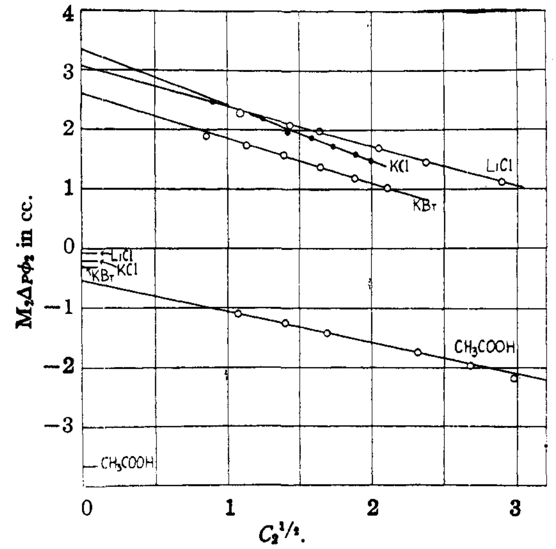

Fig. 7.—The apparent molal compressions of three salts and acetic acid as a function of the square root of the volume concentration.

The apparent compression of water, $\Delta_P \phi_1$, in acetic acid solutions was computed on the assumption that the compression of pure acetic acid is 0.0614 cc. per gram, the value obtained by extrapolation from our data. Figure 8 shows the plot of $\Delta_P \phi_1$ against the square root of the concentration of water (open circles). The linear relation does not hold at all at the acetic acid end, but it does hold at the water end and the extrapolation of the straight line to pure water gives 0.0390 as $\Delta_P \phi_1$ for pure water, which is in reasonable agreement with the observed specific compression, *viz.*, 0.0395.

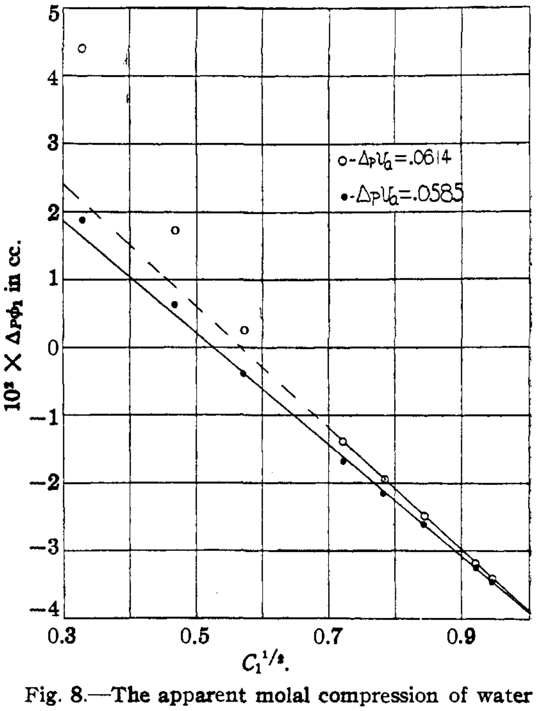

Fig. 8.—The apparent molal compression of water in acetic acid solutions as a function of the square root of the volume concentration of the water.

At the acetic acid end $\Delta_P \phi_1$ is very sensitive to the value chosen for the compression of pure acetic acid, and although the compressions of these solutions have been measured up to 99.5% acid, some doubt may be entertained concerning the extrapolated value. When 0.0585 cc. per gram is used as the compression of acetic acid the lower curve in Fig. 8 is obtained which is roughly a straight line from pure water to 90% acid. It must be emphasized, however, that there is no justification for thinking that the compression of the pure acid is as low as 0.0585, and that the

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[22] Gucker, *Chem. Rev.*, **13**, 128 (1933).

[23] Tammann, *Z. anorg. allgem. Chem.*, **174**, 231 (1928).

lower curve merely illustrates the changes produced in $\Delta_P\phi_1$ by the different values taken for the compression of the pure acid. It may also be mentioned that it does not follow directly that $\Delta_P\phi_1$ is a linear function of $C_1^{1/2}$ if $\Delta_P\phi_2$ is a linear function of $C_2^{1/2}$.

Departures of the Compression of Solutions of Acetic Acid from the Simple Law of Mixtures. —On account of the high compressibility of acetic acid there is no simple way of computing P_e for its aqueous solutions from compression data. In some respects P_e may be taken as a measure of the departures from ideal behavior of the solution, and in its place the following relation was examined for acetic acid solutions

$$(x_1k_1 + x_2k_2 - \Delta_Pv)/\Delta_Pv = k_3c_1c_2 \qquad (6)$$

This equation will express the relative departures from the simple law of mixtures for compressions as a linear function of the product of the concentrations of water and acid, if k_1 is the specific compression of pure water and k_2 the specific compression of the pure acid. When the equation was fitted to the compression data, k_1, k_2 and k_3 were treated as unknown parameters and the values obtained for them were 0.03907, 0.05778 and 1.0061, respectively. It will be noticed that the values of k_1 and k_2 agree reasonably well with the specific compressions of pure water and pure acid. Furthermore, the equation expressed the data very well from pure water to 95% acetic acid, the root mean square deviation being 0.00025.

Equation (6), with k_1 being equal to the compression of pure water and k_2 equal to the compression of solid salt, was also applied to eight of the salt solutions described in this paper. Within one per cent. the relative departures from the simple law of mixtures were linear functions of the product of the concentrations of water and salt.

A similar type of relation was found by Biron[24] to hold for the departures from ideal behavior measured by the volume changes accompanying the mixing of liquids. He used the formula $\Delta V/V = kN_1N_2$ where $\Delta V/V$ is the relative expansion on mixing and N_1 and N_2 are the mole fractions of the components. Hildebrand and Carter[25] have confirmed this relation for some liquid mixtures. As Avogadro's law does not hold for liquids, it is thought that the number of moles per unit volume is a better unit than the mole fraction, especially when the components of the solution differ widely in molecular volumes.

Summary

Experimental measurements of the compressions to 1000 bars of various solutions of sixteen salts (mostly those of potassium) and of acetic acid have been made over the whole concentration range. An equation expressing the apparent compression of the salt as a linear function of the square root of the volume concentration is the most generally useful way of representing the results within the error of experiment, although, in a number of cases, the weight ratio or the molality may be used instead of the volume concentration. The effects of different salts on the compression of water increase with the charge on the solute ions and decrease with the ionic radius, but examination showed that it is probable that some other properties of the solute besides these two are also active in determining the behavior of the solution under pressure. The effective pressure of the salts in the solution is directly proportional to the product of the concentration of water and salt. It is also shown that the equation for the volume of a solution as a function of the pressure, based on the hypothesis of the effective pressure, gives values for the compressibility of solutions at 1 bar which are in accord with those obtained from sound velocity measurements even though the effective pressure is determined from data at 1000 bars.

For acetic acid solutions the bulk compression–concentration curve passes through a minimum but as far as the apparent molal compression–concentration relations are concerned there is little difference between the acid and any strong electrolyte. The apparent compression of water in acetic acid solutions is a linear function of the square root of the concentration only at the water end. The relative departures from the simple law of mixtures of the compressions of acetic acid solutions and of salt solutions vary linearly with the product of the concentrations of salt and water in the solutions. The freezing curve of benzene, expressed as a quadratic equation in a previous paper, and used to determine the pressure scale between 500 and 1000 bars, is slightly modified as a result of improvements in technique.

WASHINGTON, D. C. RECEIVED NOVEMBER 15, 1934

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[24] Biron, *J. Russ. Phys.-Chem. Soc.*, **41**, 569 (1909).

[25] Hildebrand and Carter, THIS JOURNAL, **54**, 3595 (1932).