tinctive character, sorption being nearly completed at infinitesimal pressures.

Equilibria are fully established with great rapidity and thereafter remain constant and unchanged within a few per cent. for periods of many years provided the system is kept sealed. On the other hand, if this charcoal, not exposed to vapor, is merely kept in a stoppered bottle, it loses a large percentage of its activity as determined by sorption of iodine (without previous treatment).

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

The Influence of Concentration on the Compressions of Aqueous Solutions of Certain Sulfates and a Note on the Representation of the Compressions of Aqueous Solutions as a Function of Pressure[1]

BY R. E. GIBSON

Experimental measurements of the effect of hydrostatic pressure on the volumes of solutions of different concentrations form an essential part of the data necessary for the calculation of the effect of pressure on the chemical potentials of the components and hence on phase equilibria involving these solutions. Three systems have already been studied,[2] and details concerning the determination of the experimental data and the computations have been described.

The apparatus for the determination of the compressions of solutions by the piston-displacement method[2a,3] at high pressures is not well adapted to measurements at low pressures, *i. e.*, up to 1000 bars. As the compressibility of all liquids diminishes rapidly with pressure, the relative volume change produced by the first thousand bars is extremely large, often being one-fifth to one-quarter of the total volume change produced by ten thousand bars, and should therefore be measured with as great precision as possible. The work described in this paper was undertaken to supply data on the compressions of solutions of different concentrations produced by a rise of pressure from atmospheric to one thousand bars, and at the same time to make as wide a survey as possible of the general effect of the nature and concentration of the solute on the compressions of aqueous solutions.

It is steadily being realized that any theory likely to be of useful application to actual solutions must account for all the properties of these solutions not only under average laboratory conditions but also over any desired range of temperature and pressure. Furthermore, it is becoming apparent that in a complicated system such as an aqueous salt solution specific effects or effects characteristic of the chemical nature of the solute play a large part in determining the observed behavior of the solution. The importance of such effects may best be estimated empirically by the study of as wide a variety of substances as possible. From these points of view I shall discuss the regularities exhibited in the behavior of twelve sulfate solutions under pressure.

Experimental

The apparatus for measuring the compressions of the solutions is shown diagrammatically in Fig. 1. The pressure was generated by forcing oil from a Tammann press into heavy-walled cylinders or bombs of vanadium steel, and was measured by an electrical resistance gage. During an experiment the bombs were immersed in a well-stirred thermostat maintained at 25 ± 0.02°. Pyrex glass piezometers of capacities between 10 and 14 cc. were used for measuring the volume changes of the solutions. These piezometers differed only in size from those already described by Adams,[4] who has also described in detail the experimental technique, and the methods of computing the compressions from the observed quantities. The results in this paper are all based on the known compressions of Pyrex glass and mercury, which were taken as 0.00303 and 0.00399, respectively, at 1000 bars.

Several precautions, necessary if results reproducible within the precision of the pressure measurements are to be obtained, may be emphasized here. It is essential to prevent any permanent drop in the temperature of the liquid in the piezometer after the mouth of the reëntrant tube is sealed with mercury. Errors due to the formation of air bubbles while the solution is coming to the temperature of the thermostat may be eliminated by preparing the solutions from boiled distilled water and storing them prior to

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(1) The substance of this paper was presented at the Washington Meeting of the American Chemical Society, March, 1933.

(2) (a) Adams, THIS JOURNAL, **53**, 3769 (1931); (b) Adams, *ibid.*, **54**, 2229 (1932); (c) Adams and Gibson, *ibid.*, **54**, 4520 (1932).

(3) Adams, Williamson and Johnston, *ibid.*, **41**, 12 (1919); Parsons and Cook, *Proc. Roy. Soc.* (London), **85**, 332-349 (1911); Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 1 (1913).

(4) Adams, Ref. 2a, pp. 3773-3776.

use at 25°. The heat treatment of the glass piezometers appears to have considerable influence on the reproducibility of the results. With a piezometer which had been annealed by Mr. L. H. Adams at 550° for fifteen minutes and used by him at high pressures, I obtained excellent results, but with untreated piezometers the results sometimes varied over a range of 10 parts in 500 or ten times the estimated error in the pressure reading. The results given in this article were all obtained with two piezometers both of which consistently gave values for the compression of water at 1000 bars which were reproducible within 1 part in 400. One of these piezometers had been heated slowly to 580° in an electric furnace, kept at that temperature for ten minutes, and then slowly cooled to 520°, after which its temperature had been allowed to fall rapidly. The other had been held at 490° for ten days.[5] In both cases the reproducibility of the results was substantially improved by the annealing of the piezometer. It seems plausible to suppose, and indeed experiments indicate,[6] that strained glass behaves anisotropically under pressure and a distortion of the piezometer may take place, thereby giving an anomalous change in volume. The pressure apparatus was so designed that two bombs could be connected in parallel and two compressions measured simultaneously. In this way valuable checks on the sources of error could be made. It was especially valuable in establishing confidence in the reproducibility of the pressure gage.

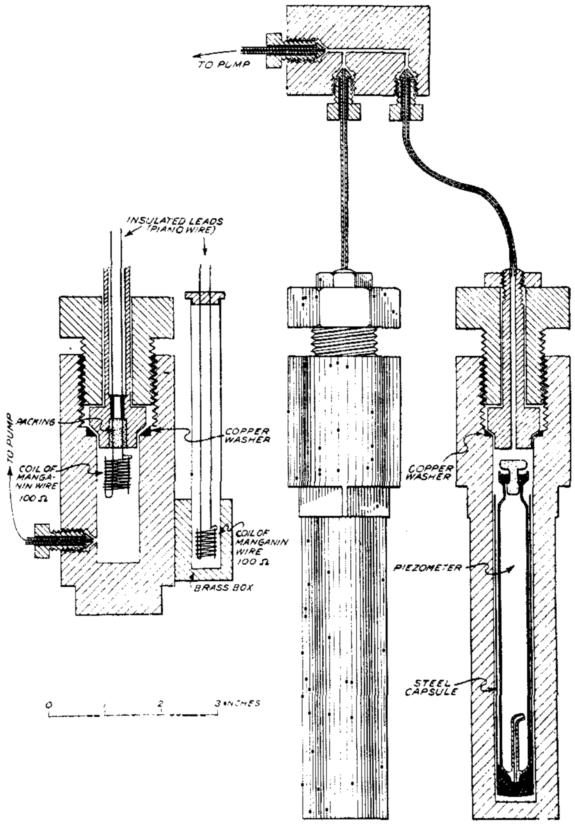

Fig. 1.—Diagrammatic sketch of apparatus for measuring the compression of liquids showing details of piezometer, bombs, pressure gage and connections.

Calibration of Pressure Gage.—The electrical resistance pressure gage differed somewhat in detail from those already in use. The coil of wire whose change in resistance with pressure was measured consisted of a *single* layer of No. 38 double silk covered manganin wire of 100 ohms resistance, wrapped on a light hollow cylinder of waxed paper. The coil was coated lightly with shellac, baked at 140° for twelve hours and then seasoned under a pressure of eight thousand atmospheres. The ends were hard soldered to fine platinum wires which in turn were brazed to piano wire leads that ran through an insulating packing. The gage assembly is shown in Fig. 1. The gage coil, an exactly similar coil placed in thermal contact with the gage block but not under pressure, and two standard 100-ohm coils were arranged to form a Wheatstone bridge through which a constant current was maintained. The e. m. f. across the galvanometer circuit measured the resistance change in the gage coil.[7]

The electrical pressure gage was calibrated at intervals of 150 bars up to 1400 bars directly against a dead-weight piston gage. Two calibrations were made. Directly thereafter, the pressures at which solid and liquid benzene were in equilibrium at definite temperatures between 20 and 30° were carefully observed in order that a fairly reliable pressure scale between 500 and 1000 bars might be established. A sample of pure benzene which had come in sealed tubes from Timmerman's laboratory at the Bureau International des Étalons Physico-chimique in Brussels was used. The freezing pressure could be estimated with a precision of 1 bar, but uncertainties in the zero of the gage introduced a possible error not exceeding 2 bars. At the conclusion of these experiments the pressure gage was again checked against the dead-weight gage. No significant change in the calibration was found between 1 bar and 1400 bars. Equation (1) gives an adequate representation of the melting curve of benzene between 500 and 1000 bars

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

where P is pressure in bars and t the temperature in degrees centigrade. This equation gives 1.1 bars for the freezing pressure of benzene at 5.58° (the ordinary melting temperature at room pressure) and so may be applied with some confidence between 1 and 500 bars also. It would, however, be unwise to use the equation above 1000 bars without further investigation.

The freezing temperature of benzene at 1000 kg./sq. cm. (981 bars) as computed by equation (1) is 31.95°. This figure may be compared with 31.75, 30.2 and 32.5°, values obtained by Tammann,[8] Puschin and Grebenschtschikow,[9] and Bridgman,[10] respectively, for the freezing temperature

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(5) I am indebted to Mr. G. W. Morey of this Laboratory for suggesting and carrying out this second method of heat treatment.

(6) Bridgman, *Proc. Am. Acad. Arts Sci.*, **44**, 269 (1909); *Am. J. Sci.*, **10**, 359 (1924). Bridgman's measurements of linear compressibility indicate anisotropic behavior in both natural and artificial glasses.

(7) For further details see Adams, Williamson and Johnston, Ref. 3.

(8) Tammann, "Aggregatzustände," Leopold Voss, Leipzig, 1923, p. 100.

(9) Puschin and Grebenschtschikow, *Z. physik. Chem.*, **113**, 57 (1924).

(10) Bridgman, *Phys. Rev.*, **3**, 172 (1914).

of samples of benzene at this pressure. Expressed in terms of the freezing pressure at a given temperature the discrepancies among these results look much larger, and emphasize the necessity of extreme purity of sample and control of temperature in the establishment of a pressure scale by means of a melting curve.

Materials.—Except where specially mentioned, the solutions were each made up directly from weighed amounts of anhydrous salt and water. The solid *sulfates* of *sodium, magnesium, cadmium,* and *ammonium* were prepared by the recrystallization from aqueous solution of J. T. Baker C. P. analyzed preparations and subsequently dehydrated by vacuum desiccation and ignition. *Lithium sulfate* was prepared by evaporation of a solution of J. T. Baker C. P. lithium carbonate in C. P. analyzed sulfuric acid. The salt was recrystallized twice from aqueous solution and dried by ignition at 400°. C. P. cesium hydroxide from the Foote Mineral Company was dissolved in C. P. analyzed sulfuric acid. When this solution was evaporated *cesium sulfate* crystallized as the monohydrate. The salt was recrystallized twice from aqueous solution, dried in an air oven, and ignited at 500°. The crystals were found, on being examined with a petrographic microscope, to be remarkably free from voids or impurities. The various *zinc sulfate* solutions were made by quantitative dilution of a stock solution prepared from the pure recrystallized heptahydrate and water. The compositions of the stock solution and of the other solutions were checked by evaporation of a weighed amount of solution to dryness in presence of excess of sulfuric acid. The solid was weighed as zinc sulfate and also, after ignition, as zinc oxide. J. T. Baker C. P. analyzed copper sulfate pentahydrate was used without further treatment in the preparation of the *copper sulfate* solutions. Pure *beryllium sulfate* was obtained as follows. A solution in hydrochloric acid of C. P. beryllium carbonate from the Welsbach Company was treated with a boiling 10% solution of sodium bicarbonate to free the beryllium from aluminum and iron.[11] The beryllium was then precipitated as hydroxide by the addition of ammonia. The hydroxide was dissolved in ammonium carbonate solution and the basic carbonate was precipitated by the passage of steam through the filtered solution.[12] This process was repeated. The basic carbonate was dissolved in excess of sulfuric acid and added to alcohol whence beryllium sulfate tetrahydrate was thrown down. After ignition to remove ammonium salts, the compound was dissolved in warm aqueous sulfuric acid and the tetrahydrate, after precipitation by alcohol, was washed thoroughly with alcohol and ether and dried in a vacuum desiccator. Analysis by ignition showed that the preparation contained 14.14% BeO. The formula $BeSO_4 \cdot 4H_2O$ requires 14.13%. From a solution of cerium nitrate obtained from the Foote Mineral Company in 1917, the carbonate was precipitated by the addition of sodium bicarbonate. It was washed thoroughly and dissolved in sulfuric acid. The sulfate hydrate was recrystallized three times from boiling water, and converted to anhydrous *cerium sulfate* by ignition at 400–450°. All the solutions of *sulfuric acid* were made directly from J. T. Baker C. P. analyzed sulfuric acid.

Results.—The experimental results are summarized in Table I. Except in the cases of zinc sulfate and sulfuric acid the compressions are given at even intervals of the weight fraction of the salt. In all cases the necessary interpolations were made over very short intervals, never exceeding 0.0003 for k, as the solutions were made up as

TABLE I

THE BULK AND SPECIFIC COMPRESSIONS AND SPECIFIC VOLUMES OF AQUEOUS SOLUTIONS OF SULFATES. EXPERIMENTAL RESULTS OVER A PRESSURE RANGE FROM 1 TO 1000 BARS

Wt. fraction of salt x_2	Molality m	$m^{1/2}$	Bulk compression $k \times 10^4$	Sp. vol. v	Sp. compr. $\Delta_p v \times 10^4$	$\frac{\Delta_p v}{x_1} \times 10^4$	ψ_2
		Li_2SO_4					
0	0	0	$393._5$	1.0029	$394._6$	$394._6$	
0.05	0.479	0.692	$348._4$	0.9613	$334._9$	$352._5$	0.486
.10	1.011	1.005	$309._7$	.9218	$285._5$	$317._2$	.482
.15	1.605	1.266	$272._5$	.8847	$241._1$	$283._7$	.502
.20	2.274	1.507	$241._5$	.8493*	$205._1$	$256._4$	.491
.25	3.032	1.741	$213._2$	.8154*	$173._8$	$231._7$	.488
		Na_2SO_4					
0	0	0	$393._5$	1.0029	$394._6$	$394._6$	
0.05	0.371	0.609	$356._2$	0.9594	$341._8$	$359._7$	0.392
.10	.782	.884	321	.9182	295	328	.405
.15	1.242	1.113	288	.8788	253	297	.416
.20	1.760	1.327	259	.8410	218	272	.413
.22	1.985	1.407	$245._9$	.8264	$203._4$	$260._5$	.420
.24	2.223	1.493	236	.8119	192	252	.420
		Cs_2SO_4					
0	0	0	$393._5$	1.0029	$394._6$	$394._6$	
0.1	0.307	0.554	$362._5$	0.9212	$333._9$	$371._0$	0.266
.2	.691	.831	$332._3$	.8405	$279._3$	$349._1$	.263
.3	1.185	1.088	$300._2$	.7593*	$227._9$	$325._6$	.258
.4	1.843	1.356	$265._3$	.6809*	$180._6$	$301._0$	.258
.5	2.765	1.662	$229._3$	.6041*	$138._2$	$276._4$	.258
			$228._6$				
		$MgSO_4$					
0	0	0	$393._5$	1.0029	$394._6$	$394._6$	
0.05	0.437	0.661	$352._9$	0.9540	$336._7$	$354._4$	0.326
.10	.923	0.961	$313._5$	.9077	$284._6$	$316._2$	.344
.15	1.466	1.212	$276._2$	.8634	$238._5$	$280._6$	.360
.20	2.077	1.442	$241._1$	.8211	$198._0$	$247._5$	.370
.25	2.769	1.664	$210._0$	.7805	$163._9$	$218._5$	.372
		$ZnSO_4$					
0	0	0	$393._5$	1.0029	$394._6$	$394._6$	
0.0497	0.324	0.569	$363._8$	0.9530*	$346._7$	$364._8$	
.1148	.803	.896	$326._6$	.8902*	$290._7$	$328._4$	
.1782	1.345	1.160	$287._4$	.8312*	$238._9$	$290._7$	
.2504	2.069	1.439	$245._2$	.7665*	$187._9$	$248._8$	
.2708	2.302	1.517	$232._7$	.7487*	$174._2$	$238._9$	
		$CdSO_4$					
0	0	0	$393._5$	1.0029	$394._6$	$394._6$	
0.10	0.533	0.730	$351._4$	0.9090	$319._5$	$354._9$	0.202
.15	.847	.920	$328._7$	.8633	$283._9$	$333._8$	.213
.20	1.199	1.095	$305._4$	.8185*	$249._9$	$312._1$	.220
.30	2.056	1.434	$257._6$	.7308	$188._5$	$268._9$	.228
.40	3.198	1.789	$211._7$	.6555	$139._1$	$231._2$	.253
		$BeSO_4$					
0	0	0	$393._5$	1.0029	$394._6$		
0.05	0.501	0.707	$362._5$	0.9601*	$348._1$	$366._4$	0.350
.10	1.057	1.029	$333._2$	.9188*	$306._2$	$340._2$	.361
.15	1.679	1.296	$302._2$	.8793*	$265._8$	$312._7$	.375
.20	2.379	1.543	$274._3$	.8410*	$230._8$	$288._5$	.378
.25	3.172	1.780	$248._6$	.8060*	$200._4$	$267._2$	.389

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(11) Parsons and Barnes, THIS JOURNAL, **28**, 1589 (1906).

(12) Sidgwick and Lewis, *J. Chem. Soc.*, 1289 (1926).

(13) "International Critical Tables," Vol. III.

TABLE I (*Concluded*)

Wt. fraction of salt x_2	Molality m	$m^{1/2}$	Bulk compression $k \times 10^4$	Sp. vol. v	Sp. compr. $\Delta_P v \times 10^4$	$\frac{\Delta_P v}{x_1} \times 10^4$	ψ_2
		$(NH_4)_2SO_4$					
0	0	0	393.5	1.0029	394.6	394.6	
0.0620	0.500	0.707	357.0	0.9675	345.4	368.2	
.10	.841	.917	336.4	.9471	318.6	354.0	0.587
.14	1.232	1.110	315.8	.9267	292.7	340.3	
.15	1.335	1.155	310.5	.9217	286.2	336.7	.595
			310.9		286.6	337.2	
.20	1.892	1.375	289.9	.8980	260.3	325.4	.593
.25	2.522	1.588	267.7	.8756	234.4	312.5	.598
.30	3.243	1.801	247.6	.8546	211.6	302.2	.603
			248.2		212.1	303.0	
.35	4.075	2.019	231.6	.8347	193.3	297.4	.601
.40	5.045	2.246	214.5	.8159	175.0	291.7	.601
		$CuSO_4$					
0	0	0	393.5				
0.10	0.696	0.834	338.9	0.9046	306.6	340.7	
.15	1.106	1.052	311.5	.8587*	267.5	314.7	
		$Ce_2(SO_4)_3$					
0	0	0	393.5	1.0029			
0.05	0.093	0.305	376.0	....			
.08	.153	.391	366.5	0.9267*	339.6	369.1	
		H_2SO_4					
0	0		393.5	1.0029	394.6	394.6	
0.0536[a]	0.578		387.8	0.9686	375.6	396.9	
.1266[a]	1.478		370.4	.9239	342.2	391.6	
.2667[a]	3.708		331.7	.8415	279.1	380.6	
.3301[a]	5.024		315.1	.8066	254.2	379.5	
.5952[a]	14.992		268.4	.6717	180.3	445.4	
.7767[a]	35.46		245.5	.5898	144.8	648.5	
.7898[a]	38.31		246.1	.5847	143.9	684.6	
.8635[a]	64.5		240	.5603	139.5	...	
.9277[a]	130.8		267	.5490	146.6	...	

[a] Concentrations computed from density determinations.

* Determined experimentally by Gibson.

close to even weight fractions as possible. Reliable values of the specific volumes of a number of the solutions were not available and so were determined experimentally by a pycnometer method at 25°. These new values of the specific volumes are denoted by an asterisk adjacent to the appropriate figure in Table I. The other specific volumes were taken directly from the "International Critical Tables."[13] From the experimental data, the bulk compression, or simply the compression, k, which is defined as the change in the volume of 1 cc. of solution produced by a definite increase of external pressure was obtained immediately. For the purposes of discussion it is convenient to introduce another quantity, the *specific compression*, which is the decrease in volume produced when 1 g. of a phase is subjected to a rise of pressure from atmospheric to 1000 bars. The specific compression is indicated by prefixing the operator, $-\Delta_P$, to the appropriate volume symbol. Thus $-\Delta_P v$ is the decrease in volume per gram of solution, $-\Delta_P v_w$, that of 1 g. of water, and $-\Delta_P v_s$, that of 1 g. of solid solute. At frequent intervals check determinations of the compression of water were made, and the values of k for the solutions are all based on the assumption that k for water is 0.03935 for the interval 1 to 1000 bars. The consistency of the results may be illustrated by the figures for ammonium sulfate solutions. In each determination the solution was made directly from weighed amounts of salt and water and the compressions differed by amounts not exceeding ±0.00005 from the mean.

Discussion of Results

Bulk Compression–Concentration Curves.—When the bulk compressions of the different solutions were plotted against the mass of *sulfate* per unit mass or volume of solution or against the molality m, it was found that the curves for the solutions of the sulfates of lithium, sodium, potassium,[14] cesium, magnesium, zinc, cadmium and copper fell very close to each other on the diagram. Curves of k *vs.* m are shown in Fig. 2. It will be seen that the solutions of the eight sulfates mentioned above, which we shall for convenience call the "normal" sulfate solutions, all fall within a very narrow belt, bounded by the

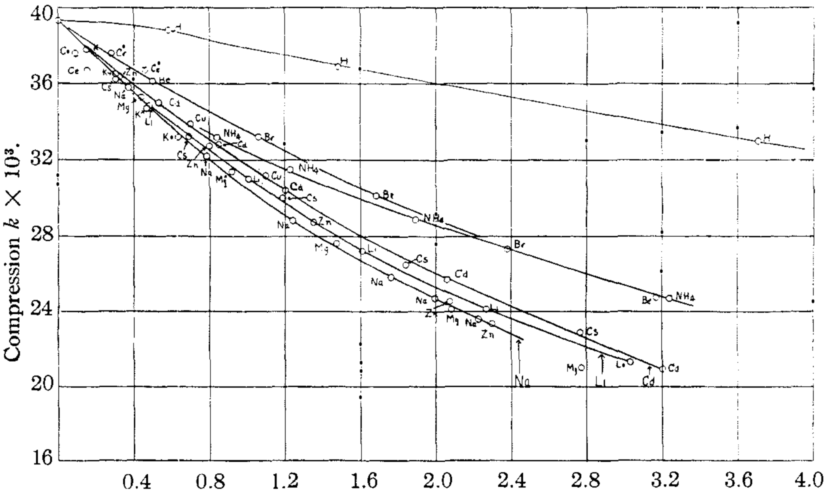

Fig. 2.—The volume compressions of sulfate solutions as functions of the molality.

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[14] Adams, Ref. 2b, p. 2230.

curve for sodium sulfate solutions on the one side and the curve for cadmium sulfate solutions on the other. Indeed, if a curve drawn midway between the sodium and cadmium sulfate curves were taken as expressing the compressions of these eight solutions as a function of the molality, the maximum errors introduced at molalities of 0.5, 1.0, 2.0 and 3.0 would be $\pm 3 \times 10^{-4}$, $\pm 6 \times 10^{-4}$, $\pm 6 \times 10^{-4}$ and $\pm 10 \times 10^{-4}$, respectively. The maximum error in the concentrated solutions represents about 5% of the quantity measured. It is, however, several times the experimental error.

The solutions of cerium, ammonium, beryllium and hydrogen sulfates have compressions which do not lie in this narrow region. The effect of sulfuric acid on the compression of water was found to be surprisingly small; indeed it required 2.7 moles of sulfuric acid to produce the same lowering of the compression as produced by 0.5 mole of sodium sulfate. The solutions of cerium, beryllium and ammonium sulfate which are known to be considerably hydrolyzed in solution occupy intermediate positions between the "normal" solutions and the acid, a phenomenon which will be discussed later. In Fig. 2 there are two sets of points for $Ce_2(SO_4)_3$, one set labeled Ce corresponding to the molality of salt, the other labeled Ce' corresponding to a molal concentration expressed as moles of SO_4 per kilogram of water. This latter set of points classes $Ce_2(SO_4)_3$ with the more hydrolyzed sulfates and is therefore more consistent with the rest of the diagram.

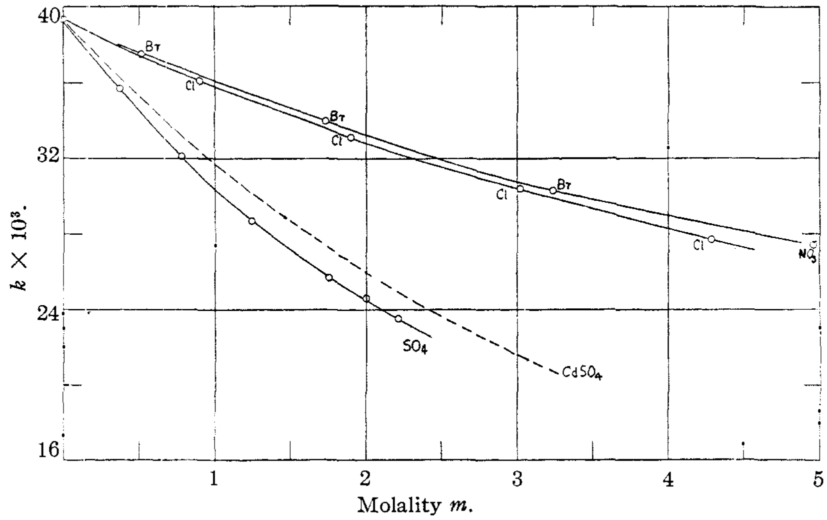

Fig. 3.—A comparison of the volume compression of different salts of sodium as functions of the molality. The "normal" sulfates all lie between the curves labeled SO_4 and $CdSO_4$.

In Fig. 3 we have plotted the bulk compression–molality curves of solutions of those salts of sodium for which compression data at 1000 bars are available. The diagram illustrates the general magnitude of the effect of sodium sulfate on the compression of water as compared with that of sodium chloride, sodium bromide or sodium nitrate. The effect of changing the anion associated with the sodium ion is of a different order of magnitude from the effect of changing the cation associated with the sulfate. It is reasonable to conclude from Figs. 2 and 3 that for solutions of sulfates that are not strongly hydrolyzed the bulk compressions are functions of the amount of sulfate per unit mass of water and to a first approximation at least are independent of the nature of the cation.

The physico-chemical significance of the compression results is more apparent from a consideration of the function A which is defined as

$$A = -(\Delta_P v_w - \Delta_P v/x_1)$$

where x_1 is the weight fraction of water in the solution. It will be seen that the function *A is approximately the difference between the specific compression of pure water and the specific compression of water in any solution* and represents the effect of the appropriate amount of solute on the specific compression of water.[15] In Fig. 4, A is shown as a function of the molality, a logical type of graph since both of the quantities plotted are referred to unit mass of water. Here again the sulfates of hydrogen, ammonium, beryllium and cerium fall outside the narrow zone which com-

(15) It is assumed that the contribution made by the solute to the compression of an amount of solution containing 1 g. of water, *viz.*, $-[(x_2/x_1)\Delta_P v_s]$ is negligibly small. This assumption is justifiable for salt solutions up to moderate concentrations (20–30%) at low pressures, since $(\Delta_P v_s)$ is very small in comparison with $\Delta_P v_w$. In very concentrated solutions, however, the difference between the specific compression of water in the pure state and in solution is more accurately expressed by $(A - (x_2/x_1)\Delta_P v_s)$, but for most of the salts mentioned in this paper $\Delta_P v_s$ is as yet not known. When mixtures of liquids whose compressions are nearly the same are treated the procedure followed in this paper requires modification. A knowledge of the compression of both pure components is then essential.

prises the other sulfates. The values of A for cesium sulfate solutions are smaller than would be expected from the behavior of the other alkali metals. These cesium sulfate solutions contained as high as fifty per cent. of salt, and cesium is the most compressible of all the metals. It might, therefore, be supposed that the error made in neglecting the compression of the solute is abnormally high in this case and hence the values of A are too low. It must be remarked, however, that no reasonable assumption of the value of the compression of cesium sulfate is large enough to bring the curve for the cesium sulfate solutions up to those for the other alkali sulfates.

The slopes of the curves in Fig. 4 are directly proportional to $M_2 \Delta_P v_2$, the changes in the partial molal volumes of the salts under a rise of pressure from atmospheric to 1000 bars. The dotted curve in this diagram is introduced for purposes of comparison and represents the behavior of sodium chloride solutions.

Analytical Representation of A as a Function of the Concentration.—It has been demonstrated for aqueous solutions that the *apparent* (or *apparent molal*) *volume* of the solute is a linear function of the square root of the volume concentration[16] over a wide range of concentration. Other *apparent* properties such as the *apparent heat capacity*[17] and the *apparent*[18] *compressibility* also follow the square root law. Except in the most concentrated solutions the molality, or the weight ratio (x_2/x_1), may be used instead of the volume concentration. If, therefore, the apparent *specific compression* of the solute, $\Delta_P \phi_2$, defined by the relation

$$\Delta_P v = x_1 \Delta_P v_w + x_2 \Delta_P \phi_2$$

is a linear function of the square root of the molality,[18a] it follows that A may be expressed as

$$A = am + bm^{3/2} \qquad (2)$$

For all the solutions studied in this paper equation (2) was found to represent A as a function of concentration within the error of experiment. The results of the computations are given in Table II, the coefficients a and b being listed in the second and third columns, and the mean difference without regard to sign between the observed and calculated values being given in the fourth column.

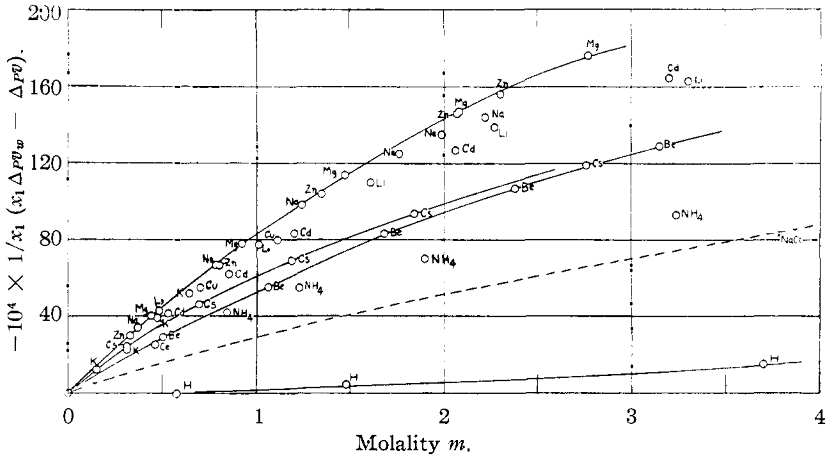

Fig. 4.—The deviation function A $(= \Delta_P v/x_1 - \Delta_P v_w)$ plotted against the molal concentration.

TABLE II

REPRESENTATION OF THE DEVIATION FUNCTION A BY MEANS OF THE EQUATION $A = am + bm^{3/2}$ FOR DIFFERENT SOLUTIONS

Solute	$a \times 10^4$	$-b \times 10^4$	Av. dev. without regard to sign $\times 10^4$
Na_2SO_4	115.0	33.9	0.5
$MgSO_4$	114.5	30.4	.4
Li_2SO_4	109.5	32.1	.4
K_2SO_4	104	29	...
$ZnSO_4$	104.5	24.0	.6
$CuSO_4$	99	26	...
$CdSO_4$	94.9	24.3	1.0
Cs_2SO_4	89.1	28.0	0.4
$BeSO_4$	69.6	16.3	.8
$(NH_4)_2SO_4$	68.1	22	.6[a]
NaCl	35	6.6	
NaBr	30	6.1	

[a] Omitting point at 40%.

The increase with pressure of the partial molal volume of the salt, $M_2 \Delta_P v_2$, may be calculated from equation (3)

$$M_2 \Delta_P v_2 = 1000(\mathrm{d}A/\mathrm{d}m) \text{ or} \qquad (3)$$

$$M_2 \Delta_P v_2 = 1000 \left[a + \frac{3}{2} bm^{1/2}\right] \qquad (4)$$

The accuracy with which equation (2) represents the data leads to the conclusion that equation (4) furnishes simply and exactly a very important

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(16) The literature is cited and a large number of examples are given by Geffcken, *Z. physik. Chem.*, **155A**, 1 (1931).

(17) Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

(18) Gucker, THIS JOURNAL, **55**, 2709 (1933).

(18a) Adams, Ref. 2b, p. 2233, first demonstrated that $\Delta_P \phi_2$ and $\Delta_P v_2$ are linear functions of $(x_2/x_1)^{1/2}$ and hence of $m^{1/2}$ for aqueous solutions of potassium sulfate and sodium chloride under pressure.

step between compression measurements and the changes of chemical potential with pressure.

By definition, A is the difference between the specific compression of pure water and that of water in a given solution on the assumption that the contribution of the salt to the compression of the solution is negligible.[15] The derivative dA/dm is the effect per mole of the solute on the specific compression of the water in a solution of any concentration. The coefficient, a, representing the initial slope of the curve of A plotted against the molality, is, therefore, the lowering of the specific compression of water when one mole of salt is added to an infinitely large amount of water. It will be seen that for solutions of Na_2SO_4, $MgSO_4$, Li_2SO_4, K_2SO_4, $ZnSO_4$, $CuSO_4$ and $CdSO_4$ the values of a lie within the relatively narrow interval between 0.0095 and 0.0115. For Cs_2SO_4, a is slightly less, 0.0089, while for the hydrolyzed salts, $BeSO_4$ and $(NH_4)_2SO_4$, the value of a drops to approximately 0.007. The coefficients in equation (2) for solutions of sodium chloride and sodium bromide are included for purposes of comparison and are of an entirely different order, a being only 0.003 for sodium bromide. The same regularities and differences are observed in the variation of the coefficient b with the nature of the solute.

Richards and Chadwell[19] concluded from measurements of the compressibilities between 100 and 300 bars of aqueous solutions of ether, methyl acetate and urethan that, in dilute solutions, equimolar solutions have approximately the same compressibilities. Moreover, they analyzed the various physico-chemical factors leading to the change of compressibility of water with addition of solute and concluded that at least three agencies are active: (a) depolymerization of the water by the solute, (b) internal pressures set up by intermolecular forces, (c) the compressibility of the solute itself. They interpreted their experimental evidence as indicating that in dilute solutions the effect due to the polymerization of the water predominated and that for the solutions they examined the depolymerization was approximately proportional to the number of moles of solute added. The evidence bearing on the polymerization of water,[20] although in many respects indirect, has been strengthened in the last few years, especially through observations of Raman spectra,[21] and the inference is reasonable that liquid water is to some extent polymerized, and that increase of pressure, temperature or concentration of solute tends to reduce the proportion of the heavier molecules. The analysis which has just been made of the results in Table II shows that the *molal lowering of the specific compression of water* (dA/dm) is approximately the same for all the "normal" sulfate solutions (with the possible exception of cesium sulfate), thereby extending the findings of Richards and Chadwell, but it also shows that even in dilute solutions dA/dm does depend on the nature of the *anion*. The same conclusions might be reached by inspection of Figs. 2, 3 and 4. Continuing Richards and Chadwell's argument, therefore, we may suggest that it is the anion portion of a salt that is most effective in changing the degree of association of the water, and that in dilute solutions equal numbers of moles of sulfate reduce the polymerization of the water by the same amount. A wider survey of the effect of pressure on aqueous solutions is in progress and further generalization must await the experimental results.

The large difference between the effects of sulfuric acid and of its salts on the compression of water and the intermediate behavior of the partially hydrolyzed sulfates of beryllium and ammonium is at first sight surprising, but is paralleled in other lyotropic properties of solutions such as the effect of salts and acids on the surface tension of water[22] or the adsorption of these substances from aqueous solutions,[23] and was also observed by Röntgen and Schneider[22] in their determination of compressibilities at low pressure. Indeed, the results of Röntgen and Schneider indicate that chlorides, iodides, nitrates, and their respective acids show the same phenomena. The concept of hydration of ions does not account for these effects. By ordinary criteria[24] the hydrogen ion is less hydrated than the metal ions, it is true, but the lithium and cesium ions represent almost the extremes of the degrees of hydration, and yet the difference between the effects of lithium sulfate and cesium sulfate on the compression of water is of only secondary importance, a fact which is in itself of some significance. Furthermore, the hypothesis of differences in surface activ-

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

[20] The main literature on the subject is cited by Richards and Chadwell.

[21] Investigations of this kind have been summarized by Hibben *Chem. Rev.*, in press.

[22] Röntgen and Schneider, *Ann. Physik*, **29**, 209 (1886).

[23] Rona and Michaelis, *Biochem. Z.*, **94**, 245 (1919).

[24] Remy, *Z. physik. Chem.*, **89**, 467 (1915).

ity between acids and salts which is invoked to explain the different surface tension and adsorption effects is not applicable to compressions. Differences in degree of ionization also seem inadequate to account for the differences between the acids and salts on the compression of water. The explanation may be found in the hypothesis that hydrogen ions tend to inhibit the depolymerization of water and even to promote polymerization, thus working against the anion which undoubtedly causes depolymerization. It is suggestive that carbonates and hydroxides in general exert per mole the greatest effect on the compression of water. On the other hand, Raman spectra[21] of solutions of sulfuric acid and acid sulfates indicate differences in structure from solutions of normal sulfates, but, up to the present, no interpretation of these data throwing light on the effect of sulfates on the properties of water has been made.

In the preceding discussion the effect of the anion portion of the solute has been emphasized. It must not be concluded, however, that the cation portion is without specific influence on the compression of water. The families of curves indicate minor differences in the behavior of the various "normal" sulfates, cesium sulfate especially diverging from the rest, and within the narrow limits of these divergences a lyotropic series for the cations may be detected.

Gilbaut[25] found that his measurements of the compressibilities of aqueous solutions up to 300 atmospheres could be expressed with a maximum discrepancy of 1 part in 300 by the relation

$$\rho \log (\mu/\mu_0) = -KX_2' \tag{5}$$

In equation (5) μ is the "molecular compressibility coefficient" of the solution, μ_0 the "molecular compressibility coefficient" of pure water, X_2' the mole fraction of solute computed on the assumption that the molecular weight of the solute is one-half of the conventional formula weight and ρ is the density of the solution. The "molecular compressibility coefficient" is the change in volume per unit pressure of that volume of solution which contains in all 5.551 gram molecules of solvent and solute. Gilbaut's experimental work was of a high order of precision. It was found, however, that Gilbaut's formula (equation 5) does not apply in its simple form to the compressions of sulfate solutions at 1000 bars.

The Specific Compression of Water as a Function of Pressure.—In 1888 Tait[26] proposed the following relation for the compressibility of water as a function of pressure

$$\frac{dv}{dP} = \frac{C}{B + P} \tag{6}$$

where C and B are constants. In the integrated form this equation becomes

$$-\Delta_P v = C \ln (B + P) + \mathit{constant} \tag{7}$$

It was found that the recent and carefully measured values of the compression of water given by Adams[27] could be represented very exactly by Tait's equation. The coefficients in equation (8) were obtained by adapting equation (6) to fit the mean compressibilities of water, $(\Delta v/\Delta_P)$, between 500 and 1000 bars and between 3000 and 4000 bars. The deviations between observed and calculated values of $\Delta_P v$ divided by the observed value of $\Delta_P v$ and multiplied by 10^2, *i. e.*, the "deviations per cent." for equation (8) are shown in the second column of Table III. Equation (8) not only fits the data fairly well at high pressures but also gives as the compressibility of water at atmospheric pressure 45.5×10^{-6} reciprocal bars, which compares well with the best experimental values at 25°, namely, 45.16[28] and 45.90[29]

$$-\Delta_P v = 0.3071 \log (2.923 + P) - 0.1430 \tag{8}$$

$$-\Delta_P v = 0.2925 \log (2.7 + P) - 0.1262^{30} \tag{8'}$$

TABLE III

PERCENTAGE DEVIATIONS BETWEEN THE OBSERVED VALUES OF $\Delta_P v$ AND THOSE CALCULATED BY EQUATIONS 8, 8', 9' AND 12

Deviations in per cent., $\dfrac{\Delta_P v \text{ (obs.)} - \Delta_P v \text{ (calcd.)}}{\Delta_P v \text{ (obs.)}} \times 10^2$

Press. in kilobars	H_2O Eqn. 8	H_2O Eqn. 8'	10% NaCl Eqn. 9'	25% NaCl Eqn. 9'	25% NaCl Eqn. 12	10% K_2SO_4 Eqn. 9'
0	0	0	0	0	0	0
1	0.3	−1.5	−1.9	−3.3	−3.3	−2.2
2	.7	−0.5	−0.9	−2.3	−3.3	−1.1
3	.6	− .1	− .5	−1.3	−2.2	−1.0
4	.4	.1	− .6	−1.1	−1.9	−1.0
5	.3	.3	− .1	−0.8	−1.3	−0.9
6	.1	.2	.1	− .1	−0.8	− .6
7	− .2	.1	.0	− .1	− .7	− .7
8	− .4	.1	.0	.1	− .4	− .8
9	− .6	.1	.0	.3	− .3	− .8
10	− .7	.2	.1	.6	.2	− .5

Equation (8'), suggested by Mr. L. H. Adams, differs slightly from equation (8) in the coef-

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(25) Gilbaut, *Z. physik. Chem.*, **24**, 385 (1897).

(26) "Report on Some of the Physical Properties of Water," 1888, p. 47. Quoted by G. Tammann in "Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," Leipzig, 1907, p. 38.

(27) Adams, Ref. 2a, p. 3780.

(28) Hubbard and Loomis, *Phil. Mag.*, **5**, 1177 (1928).

(29) Pooler, *Phys. Rev.*, **35**, 832 (1930).

(30) In these equations the unit of pressure is the kilobar.

ficients and fits the data remarkably well at the higher pressures, as may be seen from the third column in Table III, although it is not quite so good in the lower range.

The Specific Compressions of Solutions as a Function of Pressure.—By the application of a principle enunciated by Tammann,[31] namely, that a given amount of water in a solution behaves as the same amount of pure water under a constant pressure greater than atmospheric, Tait's equation may be applied to any particular solution in the form

$$-\Delta_P v/x_1 = 0.3071 \log \frac{2.923 + P_e + P}{2.923 + P_e} - (x_2/x_1)\,\Delta_P v_s, \text{ or} \quad (9)$$

$$-\Delta_P v/x_1 = 0.2925 \log \frac{2.7 + P_e + P}{2.7 + P_e} - (x_2/x_1)\,\Delta_P v_s \quad (9')$$

In these equations $\Delta_P v$ is the increase in volume of 1 g. of solution when its pressure is raised P kilobars above atmospheric, x_2 and x_1 the weight fractions of solute and solvent and $-\Delta_P v_s$ the specific compression of the pure solute. The quantity P_e may be treated either as a constant to be determined empirically from the compression data or as the increase in the internal pressure of the water consequent to the addition of solute, and determinable from specific volume data at room pressure. Except at high pressures and concentrations the quantity $-(x_2/x_1)\,\Delta_P v_s$ is practically insignificant.

Equation (9) or (9′) may be used in several ways. If $\Delta_P v$, x_1 and P are known, P_e, the difference between the internal pressure of the water in the solution and that of pure water, may be computed and hence ψ_1, the volume of 1 g. of water under a pressure of P_e kilobars, may be found. From the equation

$$v = x_1\psi_1 + x_2\psi_2 \quad (10)$$

the volume, ψ_2, which 1 g. of solute contributes to the solution on the assumption of Tammann's principle, may be computed. Values of ψ_2 computed from the specific compressions to 1 kilobar and the specific volumes of the sulfate solutions at 1 bar are given in the last column of Table I. In these computations the term $(x_2/x_1)\,\Delta_P v_s$ was neglected.

The converse calculation may also be made and leads to results of considerable significance in a study of the effect of pressure on solutions. If it is assumed that the solute merely melts on going into solution and expands about 10%, a value may be assigned to ψ_2. From the specific volume data at atmospheric pressure, ψ_1, and hence P_e, the pressure necessary to reduce the specific volume of water to ψ_1, may then be calculated by equations (10) and (8). When P_e is substituted in eqn. (9), $\Delta_P v/x_1$ follows readily, as $-(x_2/x_1)\,\Delta_P v_s$ may be neglected or, except in the most concentrated solutions, may be determined closely enough from the compressibility of the pure solute. Such calculations were carried out for all the sulfate solutions mentioned here and in all cases the calculated values of $\Delta_P v$ at 1000 bars agreed with those observed to within 4% of $\Delta_P v$. Table III illustrates the application of equations (9) and (9′) to several solutions for which reliable high-pressure data are at hand.[32] In columns 4 and 5 percentage deviations are given for sodium chloride solutions, ψ_2 being taken as 0.509 and $\Delta_P v_s$ being computed from the compressibility of solid sodium chloride. In column 7 the results of the application of equation (9′) to potassium sulfate solutions are shown, ψ_2 being 0.413. Before the results were corrected by the factor, $(x_2/x_1)\,\Delta_P v_s$, the deviations did not exceed 1%. In all cases $(B + P_e)$ was computed from the specific volumes of solutions at atmospheric pressure by means of equation (9), the equation which fits best at low pressures. The agreement between the observed and calculated values of $\Delta_P v$ is strikingly good even up to ten kilobars, and it must be emphasized that no measurements of the compressions of solutions were involved in the establishment of the appropriate constants in equations (9) and (9′), and hence in the calculation of the compressions. Adams[33] found that equation (11) expressed the specific compression of water as a function of pressure with a high degree of precision over a range of 10 kilobars

$$-\Delta_P v = 0.01641\,P - 0.000343\,P^2 + 0.06820\,(1 - e^{-0.42P}) \quad (11)$$

When Tammann's hypothesis is applied, this equation may be used for aqueous solutions in the form

$$-\Delta_P v = x_1[0.01641P - 0.000343P(2P_e + P) + 0.06820\,e^{-0.42P_e}\,(1 - e^{-0.42P})] - x_2\,\Delta_P v_s \quad (12)$$

The application of this equation to a 25% solution of sodium chloride is shown in the sixth column of Table III. The equation may not be applied as readily as Tait's.

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[31] Tammann, *op. cit.*, p. 36.

[32] Adams, Ref. 2a, p. 3783 (NaCl); Adams, Ref. 2b, p. 2230 (K_2SO_4).

[33] Adams, Ref. 2a, p. 3784.

Tammann demonstrated the validity of his principle by the fragmentary data on the compressions of solutions at low pressures that were available in 1907. The systematic observations up to the highest pressures under which liquid aqueous solutions exist show that Tammann's principle may be used to compute the compressions of aqueous solutions up to 10,000 bars merely from a knowledge of the behavior of water under pressure and of the specific volumes of the solutions at room pressure, together with an assumption (not very critical) of the volume of the solute in the solution.

The parameter P_e by which the volume–pressure relation for pure water is modified to give the volume–pressure relations for an aqueous solution deserves some attention. It may be called the change in the internal pressure of the water produced by the solute, just as the constant B in equation (7) may be regarded as the internal pressure of the water; it is, on Tammann's hypothesis, the hydrostatic pressure which changes the properties of water to the same extent as a given concentration of solute does. Figure 5 illustrates the numerical values obtained for P_e, the variation of P_e with the molality of the solution and the effect of the nature of the solute on the internal pressure–concentration curves.

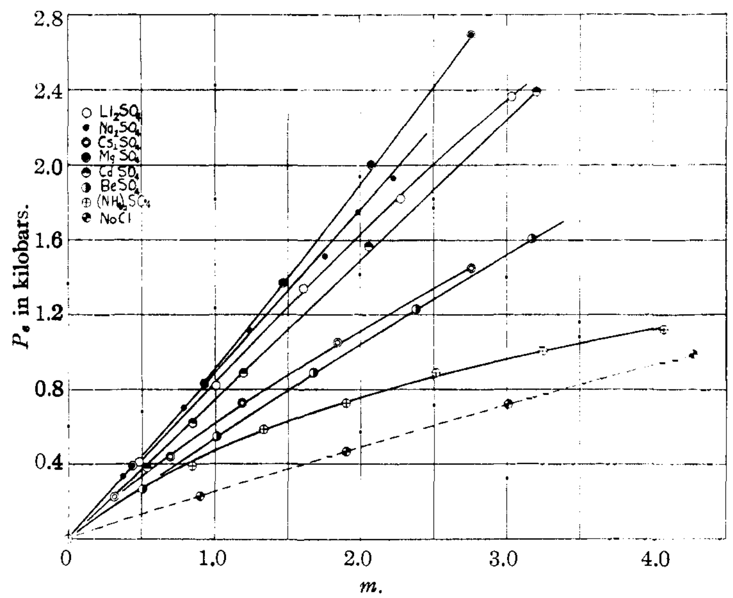

Fig. 5.—The change in the "internal pressure" of the water as a function of the molal concentration of the solute.

Specific Volumes of Salts in Aqueous Solutions.—The figures in the last column of Table I are interesting. They indicate that the effective volumes of the salts in the solutions, computed from the compression data on the basis of Tammann's hypothesis, are practically independent of the concentration and of magnitudes close to the expected volumes of the pure liquefied salts. The relative independence of these volumes of concentration contrasts strongly with the variation with concentration of the *partial* or *apparent* volumes. Conversely, if the salt is assumed to melt with a slight increase in volume (10%) and to retain its volume unchanged on mixing with the solvent, the apparent volume of the water may be computed and this leads directly to a calculation of the compression of the solution which is exceedingly close to that observed by direct experiment. It seems, therefore, that the quantity ψ_2 has a very good claim to the title of the "actual volume occupied by the solute in the solution." Indeed, ψ_2 appears to have more physical significance than either the purely formal *partial* or *partial molal volumes* or the *apparent volumes*, the latter being computed on what is admittedly a very arbitrary basis.

These applications of Tait's equation and Tammann's hypothesis point very strongly to the conclusion that from the practical standpoint it is more plausible and profitable to regard the properties of an aqueous solution as those of water modified by the presence of a solute, rather than to look upon the solution as a dispersion of solute molecules or ions in a relatively inert medium or a medium whose properties, *e. g.*, dielectric constant, are incapable of direct measurement.

Bancroft and Davis[34] suggested a method for determining "the volume in solution of the components of the solution," the quantity ψ_2 in the present paper, by the application of the formula connecting the osmotic and vapor pressures of the solution. Perman and Urry[35] have also discussed and used the relation. A rigorous analysis of the vapor pressure–osmotic pressure relation shows, however, that the volume of the solvent which enters into the equation is merely the thermodynamic partial molal volume, which is a purely formal quantity. Bancroft and Davis' equation,

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[34] Bancroft and Davis, *J. Phys. Chem.*, **32**, 1 (1928).

[35] Perman and Urry, *Proc. Roy. Soc.* (London), **A126**, 44 (1930).

if applied exactly, could at best give only the partial volumes of the components, which may be more easily derived from density and compressibility data.

I am very much indebted to Mr. L. H. Adams for his many valuable suggestions made in the course of this work, and to Dr. E. G. Zies for his help in the purification of the materials.

Summary

Experimental measurements of the compressions to 1000 bars of various solutions of eleven sulfates have been made over the whole range of concentration, and the results indicate that, for those sulfates which are not greatly hydrolyzed in solution, the bulk compressions of solutions of the same molality are approximately the same. A deviation function, A, giving the difference between the specific compression of pure water and water in any solution, has been examined and found to be expressible within the error of experiment by the equation $A = am + bm^{3/2}$. A short discussion of the influence of the nature of the solute on the coefficients of this equation and of the general effects of solute on the compression of water is given. The equation for A is particularly useful for the calculation of the changes in the partial volumes of the components from the specific compression of the solutions.

The most recent results for the compression of water may be expressed with useful accuracy as a function of pressure by a two-constant equation proposed by Tait, and when this equation is modified by the introduction of a constant representing the change of the internal pressure of the water produced by the addition of solute, a procedure suggested by an hypothesis of Tammann, the resulting formula represents very accurately the volume-pressure relations in salt solutions. Indeed, it is possible to compute with an error of less than 4% the compression of a salt solution up to 10,000 bars without a single measurement of the compressibility of a solution.

In certain cases new experimental values of the specific volumes of the salt solutions are given.

The pressures at which very pure benzene freezes at definite temperatures between 20 and 30° have been measured and the results are given as the quadratic equation (1). It is suggested that this equation may be used in the establishment of a pressure scale between 500 and 1000 bars.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY, SCHOOL OF PUBLIC HEALTH, HARVARD UNIVERSITY]

The Effect of Acetic Acid upon Traces of Lead Chromate

BY LAWRENCE T. FAIRHALL AND KEIJI AKATSUKA

In estimating small amounts of lead in biological material by means of the chromate method,[1] the lead chromate is precipitated in a solution slightly acidified with acetic acid, *i. e.*, 1 drop excess of glacial acetic acid to 50 cc. of solution. As little as 0.01 mg. of lead in 50 cc. of such a solution gives a clearly visible Tyndall beam when thus precipitated. When, however, the quantity of acetic acid is largely increased no Tyndall effect is apparent even though the amount of lead is as much as 0.1 mg. Similarly from a very slightly acidified solution, 0.1 mg. of lead as chromate is clearly visible on the filter paper as a light yellow precipitate, while from a 2% acetic acid solution no precipitation can be seen and furthermore with the average quantitative filter paper and large amounts of lead there is loss of lead chromate. In spite of results showing that acetic acid does not interfere with the quantitative determination of lead as chromate,[2] it is not surprising that occasional tests have been reported as negative when based upon visual evidence.

The following experiments, however, show that lead chromate is not appreciably soluble in acetic acid. The apparent disappearance of a trace of lead chromate when precipitated in an excess of acetic acid is at once accounted for if it is centrifuged and examined microscopically. Figure 1 shows the typical amicron material aggregated in clumps as usually obtained in neutral or slightly acid solution. Figures 2 and 3 show the type of precipitate formed in 2 and 50% acetic acid, respectively. In the latter it is evident that the initial condensation of solid from the highly dis-

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(1) Fairhall, *J. Ind. Hyg.*, **4**, 9 (1922).

(2) Patten, *J. Assn. Off. Agr. Chem.*, **4**, 217 (1920).