Fig. 1). In each experiment, 20 ml. of the 0.1% water solution of diphenylbenzidine sulfonic acid was treated with 50 ml. of 1.5 *N* sulfuric acid and 2.0 ml. of 0.01 *N* potassium dichromate in 1.0 *N* sulfuric acid. The potential of the mixture rose gradually during the establishment of equilibrium over a period of twenty to thirty minutes, at the end of which time 5.0 ml. of C. P. 48% hydrofluoric acid was added, and the back titration begun with 0.01 *N* ferrous solution in 1.0 *N* sulfuric acid. Thus the sulfuric acid concentration was approximately 1.0 *N* and constant throughout the titration. The system was allowed to come to equilibrium after the addition of each drop of reducing solution, the whole experiment requiring several hours.

It will be seen from an examination of the data in Table I that the experimental values agree quite well with those calculated on the assumption that the green compound is a semiquinone; they disagree with those calculated for a meriquinone. In the upper part of the curves, the observed values are higher than the calculated ones for a semiquinone, which is what we would expect if there were some overlapping of the first and second stages of the oxidation. Hence, the evidence points quite definitely to the existence of a semiquinone as an intermediate product in the oxidation of benzidine derivatives, rather than to a meriquinone.

TABLE I

(1.47×10^{-5} mole of diphenylbenzidine sulfonic acid in 70 ml. of 1.0 *N* sulfuric acid, and 2 ml. of 0.01 *N* $K_2Cr_2O_7$ in 1.0 *N* sulfuric acid; 5 ml. of 48% C. P. hydrofluoric acid added after thirty minutes, and back titration begun with 0.01 *N* ferrous solution in 1.0 *N* sulfuric acid; potentials referred to satd. calomel electrode.)

% oxidized	Volume, ml.	E. m. f., v.		
		Obsd.	Calcd. as meriquinone	Calcd. as semiquinone
18.2	78.2	0.3649	0.3793	0.3658
27.3	78.1	.3793	.3876	.3794
36.4	78.0	.3905	.3948	.3904
45.5	77.9	.4005	.4017	.4003
54.6	77.8	.4093	.4088	.4097
63.6	77.7	.4195	.4166	.4196
72.7	77.6	.4331	.4258	.4306
81.8	77.5	.4555	.4379	.4442

$E_{S.Q.} = 0.405 + 0.06 \log (X/(100 - X))$, where X equals percentage of D. B. oxidized. $E_{M.Q.} = 0.294 + 0.03 \log [M.Q.]/[D.B.]^2$.

As regards the second stage of the oxidation (from green to violet), the experimental results were much less satisfactory. First, the oxidation potential of the potassium dichromate was not high enough to ensure complete conversion of the green intermediate product to the violet holoquinoid form, and, second, more energetic oxidizing agents caused a marked decomposition of the latter, accompanied by drifting potentials. The result was that the quantity of the violet form found varied from experiment to experiment, and only rarely approximated to that consistently found for the green. However, even though the experimental conditions were so unfavorable, the observed potentials always lay closer to the values calculated on the basis of the semiquinone theory than to those required by the semiquinone theory.

Summary

Diphenylbenzidine decasulfonic acid has been oxidized to the corresponding green and violet forms, and the subsequent reduction studied electrometrically. The green form was very stable, the violet considerably less so, and both were reasonably soluble in water and dilute acid solutions. The form of the titration curves indicated that the green intermediate product was a semiquinone, not a meriquinone.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON, AND THE GEORGE WASHINGTON UNIVERSITY]

The Apparent Volumes and Thermal Expansions of Certain Salts in Aqueous Solution between 20 and 40°[1]

BY R. E. GIBSON AND JOHN F. KINCAID

In the course of a study of the correlation of the compressions with other thermodynamic properties of solutions we found it necessary to obtain reliable values of the thermal expansions. For a few aqueous salt solutions these quantities could be computed from measurements already published but the general result of a careful survey was the discovery of an almost complete absence of reliable systematic data. Interest in thermal expansions is enhanced by the researches of Gucker,[2] who found that when the apparent molal expansibilities of electrolytes in aqueous solutions are plotted against the square root of the volume concentration straight lines are obtained, but that the slopes of these lines depend markedly on the individual characters of the salts and are negative instead of positive as an extrapolation of the interionic attraction theory would require. It seemed desirable, therefore, to determine some expansions

[1] Part of this work is taken from a thesis presented by John F. Kincaid to the George Washington University in partial fulfilment of the requirements for the degree of Master of Arts.

[2] F. T. Gucker, Jr., THIS JOURNAL, **56**, 1017 (1934).

of solutions experimentally so that data on a fair number of typical salts might be available. Accordingly we shall present and discuss in this article the thermal expansions between 20 and 40° of aqueous solutions of barium chloride, potassium bromide, sodium iodide, potassium nitrate and lithium bromide, together with the specific volumes of solutions of the three last-named salts.

Experimental.—Two pycnometers were used in the determination of the specific volumes of the solutions at 25°. They were both of the same design, one being the pycnometer which has been in use in the Geophysical Laboratory for over fifteen years[3] and the other a copy recently made. The volume of the first pycnometer has remained the same, 55.0368 ml. at 25°, for many years; the volume of the second was determined at intervals during the work by weighing its water content. In all, six measurements were made, the mean value being 52.5994 ml. with an average departure from the mean of 2×10^{-4} ml. The thermostats were held at $25.00 \pm 0.01°$, the temperature being measured with the 10 junction copper–constantan thermoelement already described[4] and a Wolff potentiometer.

The expansions were measured with a dilatometer which, together with the technique, has already been described.[4] The volume of the dilatometer at 25° was redetermined and found to be 47.52 ml. and the capillary was very completely calibrated with weighed threads of mercury. The temperature of the dilatometer thermostat was measured on the Wolff potentiometer with a 5-junction copper-constantan thermoelement, calibrated at the inversion point of sodium sulfate decahydrate (32.384°, 6463 microvolts). The departure from Adams' table[5] at this point was 1.5 microvolts. Temperatures were therefore converted from microvolts to degrees with the aid of this table and a deviation curve. From the change in height of the meniscus of the liquid in the dilatometer capillary, a knowledge of the stem temperature, the expansion of the glass, the cross section of the capillary, the volume of the dilatometer, and the specific volume of the solution, it was possible to compute directly $\Delta_T v$, the change in specific volume of the solution for any finite change of temperature. Readings were taken at even intervals of 2.5°.

Materials.—Each solution was made up separately from weighed amounts of anhydrous salt and distilled water. *Potassium bromide, potassium nitrate, sodium iodide* and *barium chloride* were all obtained from the J. T. Baker C. P. analyzed preparations. *Potassium bromide* and *nitrate* were recrystallized in the ordinary way from water and dried in an oven for several days. Three solutions of approximately 10% were made up with the commercial and the recrystallized potassium nitrate. When interpolation to the same concentration was made, the densities of these solutions departed on an average 0.2×10^{-5} from the mean value. *Sodium iodide* was crystallized from water at a temperature above the decomposition point of the dihydrate, from absolute methanol solution, and was also used without recrystallization. In all cases the solid was powdered and heated for several days around 200°. The solutions were made up and stored in an atmosphere of nitrogen. The densities of concentrated solutions were independent of the sample and it was judged that the salt as obtained commercially was sufficiently pure. *Barium chloride* dihydrate was dehydrated in an Abderhalden apparatus and also in an air oven. No decomposition of the chloride was observed. J. T. Baker C. P. analyzed lithium carbonate and hydrobromic acid were used in the preparation of *lithium bromide*. The former was washed many times with hot distilled water, dissolved in the acid and the alkaline solution was boiled down, filtered, acidified and allowed to deposit crystals of the dihydrate. These were filtered by suction and recrystallized. Two portions were recrystallized five times. The dihydrate was then dried in a vacuum desiccator over phosphorus pentoxide where it was converted to a mixture of the monohydrate and the anhydrous salt. It is of interest to note that, whereas lithium bromide dihydrate loses water at an exceedingly slow rate, if at all, when placed *in vacuo* over "Anhydrone," it loses water rapidly under the same conditions over phosphorus pentoxide. The final dehydration was carried out in the flasks in which the actual solutions were made up. The salt was heated to constant weight in a high vacuum at 100–120° with phosphorus pentoxide absorbing the evolved water. Anhydrous lithium bromide and lithium bromide dihydrate are both extremely hygroscopic.

Two solutions of approximately 10% lithium

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(3) R. E. Hall, *J. Wash. Acad. Sci.*, **14**, 167 (1924).

(4) R. E. Gibson, *J. Phys. Chem.*, **31**, 496 (1927).

(5) "International Critical Tables," Vol. I, p. 58.

bromide and two of approximately 40% lithium bromide were made from entirely different samples and their specific volumes compared. They were consistent to 1 × 10^{-5} and we feel that the purity of the solid lithium bromide justifies specific volumes given to five decimal places.

The experimental results are recorded in the first two tables.[6] Table I gives the specific volumes at 25° and is self-explanatory. Table II gives the changes in specific volume resulting from a temperature change from 25.00° to the temperature indicated together with the corresponding change in apparent volume and the residuals which indicate the consistency of the results and the fit of the equation used to represent the data.

TABLE I

SPECIFIC AND APPARENT VOLUMES AT 25.00°. EXPERIMENTAL RESULTS AND CALCULATIONS

100 x_2	v	ϕ_2	Deviation ($v_{\text{obsd.}} - v_{\text{calcd.}}$) × 10^5 Eq. 1	Eq. 3
		Potassium Nitrate		
0.000	1.00293	(0.377)		
5.361	0.97032	0.3947	1.2	1.3
9.963	.94295	$.4008_8$	−0.4	−0.3
10.132	.94195	$.4011_1$	− .2	− .1
10.300	.94096	$.4012_6$	− .7	− .7
15.243	.91207	$.4068_8$	− .6	− .6
15.289	.91181	$.4069_6$	− .2	− .2
20.423	.88227	$.4121_3$	.6	.6
25.355	.85429	$.4166_8$	.5	.0
		Sodium Iodide		
				Eq. 2
0.000	1.00293	(0.234_1)		
5.378	0.96189	.2399		− 0.2
6.017	.95704	.2403		+ .4
9.287	.93224	$.2417_4$		− .7
10.016	.92673	$.2421_0$		− .3
16.172	.88026	$.2443_7$		− 1.9
19.740	.85346	$.2457_4$		+ 0.6
24.718	.81617	$.2473_5$		+ 1.2
32.047	.76148	$.2495_1$		− 0.6
34.424	.74389	$.2504_4$		+ 7.2
37.636	.72002	$.2512_2$		+ 1.1
43.431	.67718	$.2528_8$		− 1.3
44.546	.66904	$.2534_0$		+ 7.0
48.176	.64225	$.2542_6$		− 4.3
49.707	.63106	$.2548_0$		− 1.0
50.483	.62539	$.2550_8$		+ 0.5
60.020[a]	.55580	$.2579_6$		−15.6
		Lithium Bromide		
0.000	1.00293			
4.989	0.96724_0	0.2874_2		
10.518	$.92816_3$	$.2920_3$		
10.633	$.92735_6$	$.2921_5$		
14.758	.89850	$.2953_0$		
15.007	.89678	$.2956_0$		
19.947	.86240	$.2983_9$		
25.221	.82590	$.3010_2$		
36.962	.74494	$.3049_3$		
39.375	.72822	$.3052_4$		
39.918	.72443	$.3052_5$		
44.980	.68910	$.3052_2$		
54.980	.61797	$.3027_5$		
60.551	.57782	$.3008_5$		

[a] Not used in fitting equation.

TABLE II

THE EXPANSIONS AND APPARENT EXPANSIONS OF AQUEOUS SOLUTIONS OF CERTAIN SALTS

Temp., °C.	$\Delta_T v \times 10^5$	$\Delta_T \phi_2 \times 10^5$	Deviation ($\Delta_T v_{\text{obsd.}} - \Delta_T v_{\text{calcd.}}$) × 10^5
	Potassium Bromide		
	$x_2 = 0$		
20.00	−116.4		
22.50	− 61.4		
25.00	0.0		
27.50	+ 67.5		
30.00	140.8		
32.50	219.8		
35.00	304.1		
37.50	393.6		
40.00	488.0		
	$x_2 = 0.05721$	$v(25°) = 0.96237$[a]	
20.00	−131.4	−379	−0.1
22.50	− 68.0	−177	+ .3
25.00	0.0	0	.0
27.50	+ 72.7	+159	− .4
30.00	150.9	318	+ .1
32.50	233.3	456	+ .1
35.00	319.8	579	+ .2
37.50	410.1	682	− .1
40.00	504.5	776	.0
	$x_2 = 0.10465$	$v(25°) = 0.92922$[a]	
20.00	−141.0	−352	−0.2
22.50	− 72.6	−168	+ .2
25.00	0.0	0	+ .2
27.50	+ 76.2	+151	− .2
30.00	157.3	298	+ .2
32.50	241.4	426	+ .1
35.00	328.6	538	− .4
37.50	420.1	647	+ .1
40.00	514.2	739	+ .1
	$x_2 = 0.20357$	$v(25°) = 0.8611_2$[b] $(0.8611_0$[a]$)$	
20.00	−153.3	−297.7	−0.3
22.50	− 77.9	−142.5	+ .3
25.00	0.0	0.0	+ .3
27.50	+ 80.2	+129.7	− .3
30.00	163.9	254.5	+ .1

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[6] The symbols used in this paper are as follows. The subscripts 1 and 2 refer to the water and salt in solution, respectively, the subscripts w and s stand for pure water and pure solid salt, respectively. The symbol Δ_T indicates the increase with temperature of the quantity to which it is prefixed. The weight fraction is represented by x, the grams per cc. by c, the moles per liter by C, the specific volume by v, the apparent volume by ϕ, the temperature in °C. by t. $\phi_T = (\mathrm{d}\phi_2/\mathrm{d}T)_P$ and M is the molecular weight. The apparent volume is defined by the relation $v = x_2\phi_2 + x_1v_w$.

TABLE II (*Continued*)

Temp., °C.	$\Delta_T v \times 10^5$	$\Delta_T \phi_2 \times 10^5$	Deviation $(\Delta_T v_{\text{obsd.}} - \Delta_T v_{\text{calcd.}}) \times 10^5$
32.50	250.0	367.9	+0.1
35.00	338.0	470.6	− .0
37.50	427.9	562.0	− .5
40.00	521.0	649.9	+ .3
$x_2 = 0.29858$ $v(25^\circ) = 0.7968_0$[a]			
20.00	−156.8	−251.9	−0.3
22.50	− 79.2	−120.9	+ .3
25.00	0.0	0.0	+ .1
27.50	+ 81.3	+113.9	+ .2
30.00	164.8	221.0	+ .5
32.50	248.9	317.2	− .1
35.00	334.5	405.9	− .7
37.50	422.3	489.7	− .5
40.00	512.1	568.7	+ .8
$x_2 = 0.38908$ $v(25^\circ) = 0.7365_5$[a]			
20.00	−154.1	−213.3	−0.1
22.50	− 77.3	−102.3	+ .2
25.00	0.0	0.0	− .3
27.50	+ 79.6	+ 98.7	+ .2
30.00	159.8	189.7	+ .2
32.50	240.8	273.7	.0
35.00	322.4	351.1	− .4
37.50	405.7	424.6	+ .3
Potassium Nitrate			
$x_2 = 0.05361$			
20.00	−144.9	− 647	−0.2
22.50	− 74.7	− 310	− .2
25.00	0.0	0	.0
27.50	+ 79.8	+ 297	− .1
30.00	164.7	586	+ .4
32.50	252.9	838	− .3
35.00	346.7	1099	+ .4
37.50	442.7	1309	− .8
40.00	544.7	1546	+ .4
$x_2 = 0.10300$			
20.00	−163.2	− 571	−0.3
22.50	− 83.0	− 271	+ .5
25.00	0.0	0	− .3
27.50	+ 88.3	+ 270	+ .1
30.00	180.1	522	.3
32.50	274.8	753	− .4
35.00	373.2	975	− .3
37.50	475.0	1183	− .3
40.00	580.1	1383	+ .3
$x_2 = 0.15289$			
20.00	−176.8	− 511.5	0.0
22.50	− 90.7	− 253.1	− .3
25.00	0.0	0.0	+ .3
27.50	+ 93.4	+ 236.8	+ .3
30.00	189.9	461.8	+ .2
32.50	289.1	673.0	− .1
35.00	391.1	873.2	− .4
37.50	496.0	1063.5	− .3
40.00	604.0	1246.7	+ .4
$x_2 = 0.20423$			
20.00	−185.9	−456.8	−0.2
22.50	− 94.1	−221.3	+ .3
25.00	0.0	0.0	+ .3
27.50	+ 96.4	209.1	− .2
30.00	195.7	409.8	− .2
32.50	297.7	601.3	+ .1
35.00	401.0	778.5	− .3
37.50	507.3	950.4	+ .3
$x_2 = 0.25355$			
22.50	− 95.5	−196.0	+0.3
25.00	0.0	0.0	− .4
27.50	+ 98.7	+190.5	− .3
30.00	200.1	374.7	+ .5
32.50	302.4	545.5	− .1
35.00	407.0	709.9	− .1
37.50	513.3	865.7	.0
Sodium Iodide			
$x_2 = 0.06017$			
20.00	−136.1	− 444	+0.1
22.50	− 70.7	− 216	.0
25.00	0.0	0	.0
27.50	+ 74.9	+ 191	− .7
30.00	156.3	399	+ .5
32.50	240.6	565	.0
35.00	329.8	731	+ .3
37.50	422.2	869	− .3
40.00	519.1	1006	.0
$x_2 = 0.09287$			
20.00	−145.5	−430	−0.1
22.50	− 74.5	−202	+ .4
25.00	0.0	0	+ .3
27.50	79.5	+197	− .3
30.00	163.8	389	+ .5
32.50	251.3	559	+ .3
35.00	341.9	711	− .3
37.50	436.5	856	− .4
40.00	535.3	997	+ .3
$x_2 = 0.16172$			
20.00	−162.7	−402.5	+0.1
22.50	− 83.1	−195.4	.0
25.00	0.0	0.0	+ .1
27.50	+ 86.3	+183.6	− .1
30.00	175.7	356.8	+ .1
32.50	268.1	518.2	+ .4
35.00	362.5	665.3	− .1
37.50	459.6	802.0	− .1
$x_2 = 0.24718$			
20.00	−177.1	−362.1	−0.2
22.50	− 89.2	−174.0	+ .4
25.00	0.0	0.0	− .1
27.50	+ 92.3	167.9	+ .2
30.00	186.0	323.6	− .1
32.50	282.1	471.7	+ .1
35.00	379.1	607.6	− .4
37.50	478.8	738.3	+ .3
$x_2 = 0.32047$			
20.00	−183.7	−326.4	−0.2
22.50	− 91.9	−156.6	+ .5

TABLE II (*Continued*)

Temp., °C.	$\Delta_T v \times 10^5$	$\Delta_T \phi \times 10^5$	Deviation ($\Delta_T v_{\text{obsd.}} - \Delta_T v_{\text{calcd.}}$) $\times 10^5$
25.00	0.0	0.0	−0.5
27.50	+ 94.9	+152.9	+ .2
30.00	190.1	294.6	.0
32.50	286.6	428.1	− .2
35.00	384.2	554.2	+ .1
	x_2 = 0.43431		
20.00	−182.9	−269.9	0.0
22.50	− 92.4	−132.9	− .2
25.00	0.0	0.0	+ .2
27.50	+ 92.9	+125.9	+ .2
30.00	186.2	245.4	− .1
32.50	280.4	359.4	− .3
35.00	375.6	468.8	+ .1
	x_2 = 0.60020		
20.00	−157.3	−184.6	+0.1
22.50	− 78.9	− 90.6	.0
25.00	0.0	0.0	− .1
27.50	+ 79.7	+ 87.8	+ .3
30.00	159.0	171.1	− .1
32.50	239.0	251.7	.0
	Barium Chloride		
	x_2 = 0.05251 $v(25°)$ = 0.9571$_4$^{c}		
20.00	−128.3	−343	−0.1
22.50	− 66.7	−162	+0.1
25.00	0.0	0	− .1
27.50	+ 71.3	+139	− .3
30.00	148.0	278	+ .2
32.50	228.7	388	.0
35.00	313.5	484	.0
37.50	402.3	560	− .3
40.00	495.6	632	+ .2
	x_2 = 0.10121 $v(25°)$ = 0.91540^c		
20.00	−138.1	−331	−0.1
22.50	− 71.1	−157	+ .1
25.00	0.0	0	− .1
27.50	+ 74.9	+140	.0
30.00	153.6	268	+ .2
32.50	235.6	375	− .1
35.00	320.9	470	− .1
37.50	409.3	548	− .2
40.00	500.8	615	+ .2
	x_2 = 0.15322 $v(25°)$ = 0.87126^c or 0.87128^b		
20.00	−145.5	−306	0.0
22.50	− 74.4	−146	− .1
25.00	0.0	0	+ .1
27.50	+ 77.7	+134	+ .2
30.00	157.8	252	+ .2
32.50	240.2	353	− .3
35.00	325.5	444	− .1
37.50	412.9	520	− .1
40.00	502.7	584	+ .2
	x_2 = 0.20102 $v(25°)$ = 0.83129^c		
20.00	−149.3	−280.1	−0.4
22.50	− 75.3	−130.3	+ .6
25.00	0.0	0.0	−0.1
27.50	+ 78.0	+119.9	+ .1
30.00	158.3	227.8	− .4
32.50	241.9	329.8	+ .6
35.00	325.8	411.9	− .2
37.50	411.8	484.0	− .5
40.00	500.5	550.2	+ .4
	x_2 = 0.25934 $v(25°)$ = 0.78302^c		
20.00	−151.8	−252.9	−0.3
22.50	− 76.4	−119.1	+ .4
25.00	0.0	0.0	+ .1
27.50	+ 78.9	+111.4	+ .2
30.00	158.8	210.1	− .1
32.50	241.0	301.5	+ .3
35.00	323.3	378.3	− .3
37.50	407.2	446.1	− .6
40.00	493.3	508.6	+ .5
	Lithium Bromide		
	x_2 = 0.04989		
20.00	−121.1	−210.5	−0.1
22.50	− 62.9	− 92.2	+ .2
25.00	0.0	0.0	− .1
27.50	+ 68.2	+ 82.2	− .1
30.00	141.4	152.3	.0
32.50	219.2	208.5	+ .1
35.00	301.2	246.6	+ .1
37.50	387.9	278.6	+ .2
40.00	477.8	282.6	− .1
	x_2 = 0.10633		
20.00	−125.1	−198.4	−0.3
22.50	− 64.4	− 89.3	+ .3
25.00	0.0	0.0	+ .1
27.50	+ 68.6	+ 78.1	+ .1
30.00	141.0	143.0	.0
32.50	217.1	194.7	− .3
35.00	296.7	234.2	− .3
37.50	380.0	266.2	.0
40.00	466.3	284.0	+ .3
	x_2 = 0.15007		
20.00	−126.2	−181.9	−0.3
22.50	− 64.5	− 82.0	+ .4
25.00	0.0	0.0	.0
27.50	+ 68.5	+ 74.0	+ .1
30.00	140.2	136.6	+ .2
32.50	214.7	185.9	− .1
35.00	292.1	223.9	− .5
37.50	373.0	256.5	+ .1
40.00	456.1	275.2	+ .2
	x_2 = 0.19947		
20.00	−126.6	−167.4	−0.2
22.50	− 64.7	− 77.7	+ .1
25.00	0.0	0.0	+ .1
27.50	+ 67.7	+ 68.7	+ .2
30.00	137.8	125.8	.0
32.50	210.3	172.0	− .3
35.00	285.6	211.6	+ .1
37.50	362.6	238.1	− .1
40.00	442.0	257.2	+ .2

Table II (*Concluded*)

Temp., °C.	$\Delta_T v \times 10^5$	$\Delta_T \phi_2 \times 10^5$	Deviation ($\Delta_T v_{\text{obsd.}} - \Delta_T v_{\text{calcd.}}$) $\times 10^5$
	x_2 = 0.25221		
20.00	−126.8	−157.8	−0.3
22.50	− 64.4	− 73.4	− .1
25.00	0.0	0.0	+ .2
27.50	+ 66.6	+ 63.8	+ .2
30.00	135.0	117.8	.0
32.50	205.4	162.6	− .2
35.00	277.3	197.8	− .4
37.50	351.3	226.0	− .1
40.00	426.7	245.0	+ .3
	x_2 = 0.36962		
20.00	−123.8	−136.4	−0.3
22.50	− 62.5	− 64.4	+ .2
25.00	0.0	0.0	+ .4
27.50	+ 62.8	+ 54.7	− .2
30.00	127.5	104.7	+ .1
32.50	192.6	146.1	− .1
35.00	258.2	179.9	.0
37.50	325.1	208.3	.0
40.00	392.4	229.4	+ .3
	x_2 = 0.39375		
20.00	−123.0	−133.1	−0.4
22.50	− 61.7	− 62.2	+ .3
25.00	0.0	0.0	+ .2
27.50	+ 62.7	+ 55.4	+ .1
30.00	126.2	103.6	+ .1
32.50	190.1	144.3	− .5
35.00	255.0	179.3	− .3
37.50	320.5	208.0	.0
40.00	386.3	229.6	+ .2
	x_2 = 0.39918		
20.00	−122.9	−132.8	−0.4
22.50	− 61.8	− 62.4	+ .2
25.00	0.0	0.0	+ .4
27.50	+ 62.4	+ 54.6	+ .2
30.00	125.4	102.2	− .1
32.50	189.3	143.3	− .2
35.00	253.7	177.9	− .3
37.50	318.7	205.9	− .2
40.00	384.4	228.5	+ .4
	x_2 = 0.44980		
20.00	−120.2	−124.9	−0.3
22.50	− 60.2	− 58.7	+ .3
25.00	0.0	0.0	+ .1
27.50	+ 61.1	+ 53.4	+ .3
30.00	122.3	99.6	− .2
32.50	184.3	141.0	− .1
35.00	246.4	175.9	− .3
37.50	308.9	205.2	− .2
40.00	371.9	229.9	+ .4
	x_2 = 0.54980		
20.00	−116.4	−116.4	−0.1
22.50	− 58.2	− 55.7	+ .1
25.00	0.0	0.0	− .1
27.50	+ 58.8	+ 51.7	+0.1
30.00	117.3	98.0	− .2
32.50	176.5	141.0	+ .1
35,00	235.1	178.6	− .2
37.50	293.9	212.3	− .1
40.00	352.6	241.7	+ .1

[a] Specific volumes from the data of Hölemann and Kohner, *Z. physik. Chem.*, **B13**, 344 (1931), interpolated to the desired concentrations by the equations $\phi_2 = 0.28099 + 0.05287x_2^{1/2}/x_1^{1/4}$ and $\phi_2 = 0.28186 + 0.05012c_2^{1/2}$. [b] Our measurement. [c] Specific volumes interpolated by the equation $\phi_2 = 0.11441 + 0.06964c_2^{1/2}$, from the data of Kohner (*Z. physik. Chem.*, **B1**, 447 (1928); Palitsch, *ibid.*, **A138**, 390 (1928); Shibata and Hölemann, *ibid.*, **B13**, 351 (1931)).

Discussion of Results

Apparent Volumes.—The apparent volumes of potassium nitrate in aqueous solutions at 25° are expressible within experimental error over the whole concentration range as a linear function of the square root of the volume concentration, equation (1).

$$\phi_2 = 0.37763 + 0.07164c_2^{1/2} \qquad (1)$$

This same well-known and useful form of equation also represents the apparent volumes of sodium iodide very well in solutions up to 40% but then fails badly. We found that a linear function of the square root of the geometric mean of the weight fraction and the weight ratio, that is, $x_2^{1/2}/x_1^{1/4}$, equation (2), fitted the data over the whole range of concentration much better than the ordinary square root of the volume concentration formula.

$$\phi_2 = 0.23407 + 0.02479x_2^{1/2}/x_1^{1/4} \qquad (2)$$

$$\phi_2 = .37745 + .07242x_2^{1/2}/x_1^{1/4} \qquad (3)$$

Only the point at 60% NaI shows any large departure from the straight line. It should be mentioned that our values of the specific volumes of sodium iodide solutions are the results of two entirely independent measurements made with different samples of salt in different laboratories. The results for potassium nitrate were also well fitted by equation (3), but for certain other salts formulas of the type of equation (2) were not as good as those of the type of equation (1). It must be admitted that no theoretical basis is known as yet for the remarkable way in which the apparent volumes in concentrated solutions are represented by linear functions of the square root of some quantity expressing the concentration, but the practical value of such functions in the handling and checking of data is enormous. The choice of a concentration variable depends on the particular case and is at present justified only by the length of the concentration range over which the linear function fits the data. We have now examples in which each of the variables, x_2, c_2 and $x_2/x_1^{1/2}$, in turn is to be preferred to the other two.

Baxter and Wallace[7] and Geffcken[8] have determined the specific volumes of solutions of sodium iodide at 25°. Our results are in fair agreement with theirs and slightly more consistent.

As has been shown already,[9–11] the square root law breaks down completely for lithium bromide solutions, the apparent volumes passing through a maximum, and our results indicate (see Fig. 1) that even in moderately dilute solutions (5–20%) ϕ_2 does not vary linearly with $c_2^{1/2}$. Special attention was paid to these solutions because of the numerous breaks on the apparent volume–concentration curves at 35° and 200 bars reported by Scott and his associates[10,11] and on similar curves for data at 20° described by Hüttig and Kükenthal.[12] We determined a large number of specific volumes at 25°. The apparent volumes computed from these results varied quite smoothly with the concentration, and when the expansion data were applied we found that the apparent volumes at 35° behaved likewise. These curves are given in Fig. 1. On the same diagram we have plotted the apparent volumes at 35° recalculated from Scott's density data.[10,11] It will be seen that the two sets of results agree quite well in the more concentrated region except for three points which hardly seem consistent with Scott's own data. The conclusion is therefore drawn that the apparent volumes at atmospheric pressure may be represented as a smooth curve when plotted against the concentration and that the assumption of a series of breaks is not necessary. At lower concentrations our results differ markedly from Scott's. We cannot explain this, but we note that in this region our volumes at 25° agree with those of Baxter and Wallace[7] and that the error in thermal expansion from 25 to 35° would have to be of the order of 100% to account for the difference between our values and Scott's. We have also used the expansions to obtain apparent volumes of lithium bromide at 20° and compared these with the apparent volumes computed from Hüttig and Kükenthal's work. The discrepancy is enormous, the curves run parallel but are displaced by an amount which cannot be explained by minor errors in temperature or calibration of weights. As there is certainly not an error of several hundred per cent. in our expansion data we can say that Hüttig and Kükenthal's work disagrees with that of Scott, Baxter and Wallace, and ourselves. Hüttig and Keller[13] published densities of lithium bromide solutions also at 20°. The apparent volumes at 20° calculated from these results lie close to our values for the apparent volumes at 35°.

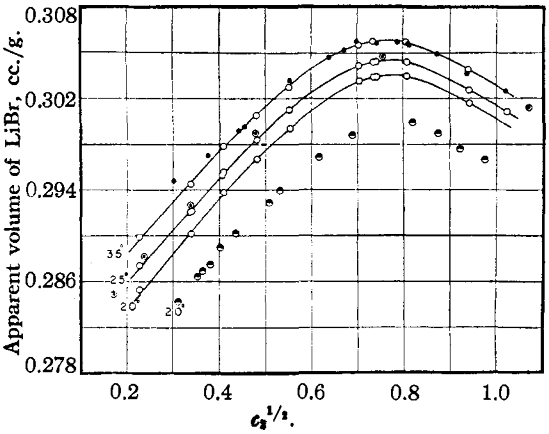

Fig. 1.—The apparent volumes of lithium bromide at different temperatures as functions of the square root of the concentration in grams of lithium bromide per cc. of solution. The results given in this paper are compared with values computed from the work already published. ●, Scott; ◉, Baxter and Wallace; ○, Gibson and Kincaid; ◒, Hüttig and Kükenthal.

Apparent Expansions and Expansibilities.—The apparent expansion $\Delta_T\phi_2$ is the finite change in the apparent volume of the salt corresponding to a finite change in temperature. By the method of least squares quadratic equations of the form

$$\Delta_T\phi_2 = A + B(t - 30) + C(t - 30)^2$$

were fitted to the expansion data for each solution. The values of A, B and C are given in Table III and the fit of the equations may be judged from the residuals in the last column of Table II. When these equations are differentiated, the temperature coefficient of ϕ_2, *viz.*, ϕ_T, is obtainable at any temperature between 20 and 40°. It may be noted that $M_2\phi_T$ is the same as Gucker's[2] (pp. 1018–19) $\Phi(E_2)$. In Fig. 2 we have plotted $M_2\phi_T$ at 25 and at 35° against $C_2^{1/2}$ for the different solutions. The curves for potas-

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(7) G. P. Baxter and C. C. Wallace, THIS JOURNAL, **38**, 70 (1916).

(8) W. Geffcken, *Z. physik. Chem.*, **5B**, 91 (1929).

(9) W. Geffcken, *ibid.*, **155A**, 18 (1931).

(10) A. F. Scott, V. M. Obenhaus and R. W. Wilson, *J. Phys. Chem.*, **38**, 931 (1934).

(11) A. F. Scott and G. L. Bridger, *ibid.*, **39**, 1031 (1935).

(12) G. F. Hüttig and H. Kükenthal, *Z. Elektrochem.*, **34**, 14 (1928).

(13) G. F. Hüttig and M. Keller, *ibid.*, **31**, 390 (1925).

sium nitrate and potassium bromide at 25° are straight lines confirming Gucker's observations, but the curves for these salts at 35° and for the other three salts both at 25 and 35° are distinctly not linear, running in such a way that one may expect a maximum somewhere between the lowest concentration we investigated and the origin. The general shape of these curves is sigmoid, and an examination of Figs. 2 and 3 in Gucker's paper shows that the same is true of the data he examined. It seems probable that in all cases the initial slopes of the apparent expansion–concentration curves are positive in very dilute solution but that they quickly pass through zero and become negative. At higher concentrations the curves have regions of inflection which may be so drawn out that for all practical purposes the curves may be regarded as linear.

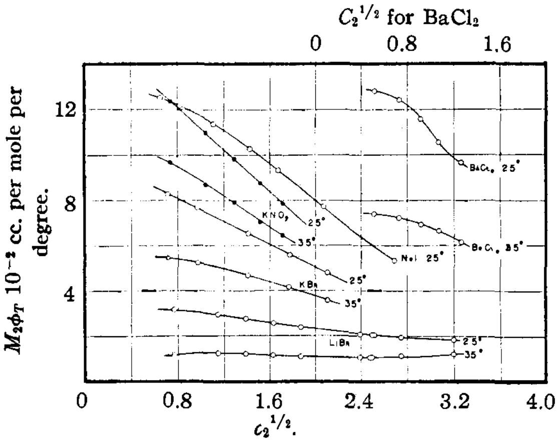

Fig. 2.—The apparent molal expansibilities of salts in aqueous solution at 25 and 35° as functions of the square root of the concentration expressed in moles per liter.

TABLE III

COEFFICIENTS IN THE EQUATIONS REPRESENTING THE APPARENT EXPANSIONS AS FUNCTIONS OF THE TEMPERATURE

$$\Delta_T\phi_2 = A + B(t - 30°) + C(t - 30°)^2$$

$100\ x_2$	$A \times 10^5$	$B \times 10^5$	$C \times 10^5$
	Potassium Bromide		
5.721	317.2	57.68	−1.176
10.465	295.6	54.40	−1.018
20.357	254.2	47.22	−0.782
29.858	219.2	40.87	− .613
38.908	189.2	35.12	− .510
	Potassium Nitrate		
5.361	579.3	109.12	−1.323
10.300	518.6	97.41	−1.129
15.289	460.4	87.77	−0.942
20.423	410.6	78.15	− .845
25.355	372.9	70.86	− .684
	Sodium Iodide		
6.017	390.6	72.61	−1.105
9.287	384.2	71.11	−1.016
16.172	356.5	66.52	−0.943
24.718	324.0	60.85	− .766
32.047	294.6	55.25	− .681
43.431	245.7	46.91	− .466
60.020	171.2	32.88	− ,271
	Barium Chloride		
5.251	273.9	48.55	−1.302
10.121	266.0	47.16	−1.244
15.322	250.6	44.44	−1.120
20.102	229.8	41.32	−0.946
25.934	210.6	37.92	− .831
	Lithium Bromide		
4.989	153.1	24.70	−1.148
10.633	142.8	23.87	−0.994
15.007	135.6	22.69	− .885
19.947	125.6	21.15	− .806
25.221	117.8	20.03	− .742
36.962	104.4	18.22	− .579
39.375	103.4	18.06	− .549
39.918	102.4	17.97	− .545
44.980	100.0	17.67	− .476
54.980	98.4	17.89	− .358

Although the curve of $M_2\phi_T$ at 25° against $C_2^{1/2}$ is not linear for lithium bromide in aqueous solutions there seems to be no indication of any breaks.

Summary

We have measured the thermal expansions from 20 to 40° of aqueous solutions of barium chloride, potassium bromide, potassium nitrate, sodium iodide and lithium bromide over the entire range of concentration and also the specific volumes at 25° of the solutions of the three last-named salts. From these results apparent volumes, apparent expansions and apparent expansibilities were computed and where possible expressed analytically by simple formulas as functions of temperature and concentration. We have suggested a new concentration variable which sometimes replaces c_2 to advantage in the square root formulas. It seems from our results that the linear relation between apparent expansibilities and the square root of the concentration is fortuitous and not to be expected in general, the complete curve being sigmoid. We find no evidence requiring breaks in the curves of the apparent volumes or the apparent expansions of lithium bromide against the concentration at atmospheric pressure.

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