Summary

The solubilities of citric and tartaric acids in water have been determined at 10° intervals (including 25°) over the range of temperature 0–100°.

The solubility curve for citric acid consists of two straight line curves which intersect at 35.8°; below this transition temperature citric acid monohydrate exists, while above anhydrous citric acid is the stable phase.

The solubility curve for tartaric acid is a straight line representing solutions in equilibrium with the anhydrous form of the acid.

BROOKLYN, N. Y. RECEIVED JUNE 23, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTH DAKOTA AGRICULTURAL COLLEGE]

The Partial Molal Volumes of Potassium Chloride, Potassium Bromide and Potassium Sulfate in Sodium Chloride Solutions

BY HENRY E. WIRTH

Since the discovery by Masson[1] that the apparent molal volume of a dissolved salt is a linear function of the square root of the volume concentration, several investigators[2,3] have made exhaustive tests of the applicability of this relationship. It was found valid for a number of salts over a surprisingly large concentration range. Root[4] derived from Masson's rule a simple equation relating density and volume concentration which has found wide application.

Redlich and Rosenfeld[5] derived from the Debye–Hückel theory a linear relationship between the square root of the volume concentration and the partial molal volume of a dissolved salt. This gave a partial theoretical basis to Masson's rule as the apparent molal volume is closely related to the partial molal volume. The expression obtained was

$$\overline{V}_2 = \overline{V}_2^0 + q\omega^{3/2} c^{1/2} \qquad (1)$$

$\overline{V}_2$ is the partial molal volume of the salt in a solution of concentration c; $\overline{V}_2^0$ is the partial molal volume at infinite dilution; q is a complex factor involving the temperature, compressibility, the type of electrolyte, the dielectric constant and its change with pressure; and ω is one-half the summation of the number of ions times the square of the valence of the ion. When considering a solution containing two or more electrolytes the last term in Eq. 1 becomes $q'(\Sigma\omega c)^{1/2}$.

The factor $\Sigma\omega c$ corresponds to the ionic strength on a volume basis, so that the partial molal volume of a salt in solution should be a linear function of the square root of the volume ionic strength. This relationship was tested by determining the partial molal volumes of potassium chloride, potassium bromide and potassium sulfate in sodium chloride solutions of different concentrations.

Methods

Preparation of Solutions.—The salts used were either Baker Analyzed or Mallinckrodt Reagent quality and were not further purified. Salts to be weighed were dried at 350–400°. Solutions for the density determinations were prepared by adding a weighed amount of the dried salt (potassium chloride, potassium bromide or potassium sulfate) to a weighed amount of water or sodium chloride solution. The volume concentration of the added salt could then be calculated using the observed density. Enough sodium chloride solution for each series was prepared and its concentration determined from the density. This concentration was corrected for the change caused by the addition of another salt. The concentrations reported are expressed as moles per liter of solution.

The sodium chloride solutions used were approximately 0.04, 0.16, 0.36, 0.64 and 1.0 normal. To each of these solutions was added sufficient potassium chloride, potassium bromide or potassium sulfate to make the volume ionic strength of the added salt approximately 0.04, 0.16, 0.36 and 0.64. Solutions in water of the latter salts of volume ionic strength 0.04, 0.16, 0.36, 0.64 and 1.0 were also prepared.

Density Determination.—The density of each of the above solutions was determined by means of the sinker method. The solutions whose densities were to be measured were placed in heavily silver plated copper cans immersed in a thermostat at 25°. Metallic containers were used to decrease the time required to attain temperature equilibrium. The temperature was maintained constant to ±0.001°. The sinker was suspended in the solution by means of a fine platinum wire which was coated with platinum black where it passed through the liquid surface. This wire could be fastened to a pan of a balance which was supported over the thermostat.

Differences in density were calculated directly using the equation

$$d_3 - d_2 = (m_2 - m_3)/v \qquad (2)$$

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

[2] Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

[3] Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

[4] Root, THIS JOURNAL, **55**, 850 (1933).

[5] Redlich and Rosenfeld, *Z. physik. Chem.*, **A155**, 65 (1931).

where d_2 is the density of the sodium chloride solution, d_3 is the density of the solution of sodium chloride plus the added salt, m_2 and m_3 are the weights required to balance the sinker when immersed in the respective solutions and v is the volume of the sinker. When using this equation it is necessary to know the volume of the sinker only to the accuracy desired for the density differences.

In practice two sinkers were used so that duplicate determinations could be made successively.

Three hundred-cc. floats were used, and as m_2 and m_3 were determined to 0.1 mg. the method was sensitive to differences of 0.8 parts per million in the density. The accuracy as determined by duplicate measurements on identical solutions was about 2 parts per million with a maximum deviation of 5 parts per million.

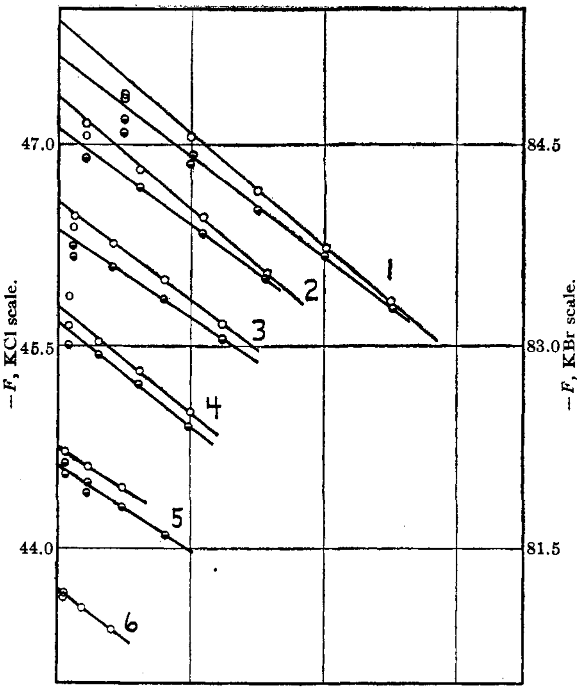

Fig. 1.— $-F$ *vs.* increase in the square root of the volume ionic strength for potassium chloride (○) and potassium bromide (⊖): curve 1, water solution; curves 2, 3, 4, 5 and 6 are for 0.04, 0.16, 0.36, 0.62 and 0.97 normal sodium chloride solutions, respectively; temperature, 25°.

Calculation of Results.—In general the methods of Gucker[6] were used with those modifications necessary due to the presence of a third component.

The apparent molal volume (Φ_3) of a salt in a solution containing another salt may be defined by

$$\Phi_3 = [V - (n_1\overline{V}_1^0 + n_2\Phi_2)]/n_3 \qquad (3)$$

where V is the total volume of solution containing n_1 moles of solvent and n_2 and n_3 moles of solutes, $\overline{V}_1^0$ is the volume occupied by a mole of pure solvent, and Φ_2 is the apparent molal volume of the second component in a solution containing n_1 moles of solvent and n_2 moles of solute only.

The quantity $F_3 = -(d_3-d_2)/c_3$ was found to be a linear function of the square root of the volume ionic strength, $\mu_v = \omega_2c_2 + \omega_3c_3$. The experimental data were therefore represented by equations of the form $d_3 - d_2 = ac_3 - bc_3(\mu_v^{1/2} - c_2^{0\,1/2})$ where the term $(\mu_v^{1/2} - c_2^{0\,1/2})$ represents the increase in volume ionic strength due to the addition of n_3 moles of the third component.

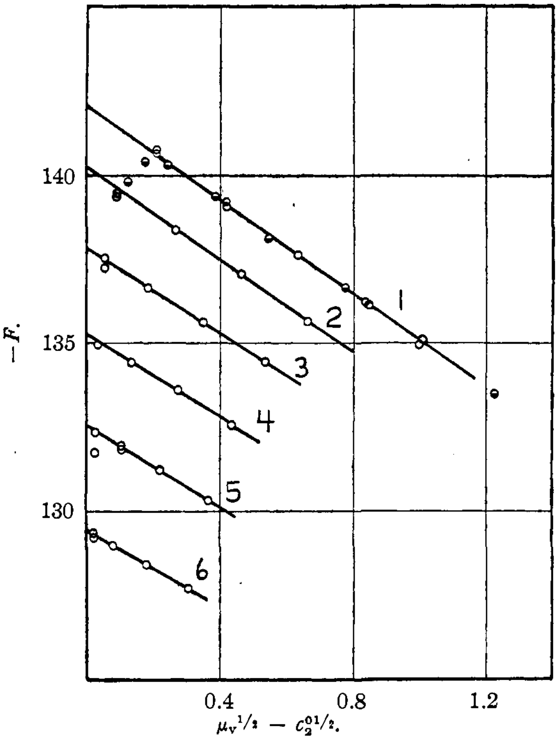

Fig. 2.— $-F$ *vs.* increase in the square root of the volume ionic strength for potassium sulfate; curve 1, water solution; curves 2, 3, 4, 5 and 6 are for 0.04, 0.16, 0.35, 0.62 and 0.97 normal sodium chloride solutions, respectively; ⊖, Jones and Ray; temperature, 25°.

This form of the equation was selected since, as pointed out by Gibson,[7] less weight is given to the quantity F. The constants a and b were determined by the method of least squares. a is the value of $-F_3^0$ in the sodium chloride solution containing no other salt and b is $\partial F_3/\partial\mu_v^{1/2}$. Φ_3^0 was calculated from the relation $\Phi_3^0 = (F_3^0 + M_3)/d_2$, where M_3 is the molecular weight of the added salt. Values of Φ_3 at other concentrations were then obtained using the slope $\partial\Phi_3/\partial\mu_v^{1/2} = (\partial F_3/\partial\mu_v^{1/2})/d_2$.

If n_1 and n_2 are kept constant and only n_3 varied

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(6) Gucker, *J. Phys. Chem.*, **38**, 307 (1934).

(7) Gibson, *ibid.*, **38**, 319 (1934).

as was done in this work the equation derived by Gucker[6]

$$\bar{V}_3 = \Phi_3 + \frac{c_3(1000 - c_3\Phi_3)(\partial\Phi_3/\partial c_3)}{(1000 + c_3^2(\partial\Phi_3/\partial c_3))} \qquad (4)$$

may be used to calculate the partial molal volume. Using $\mu_v^{1/2}$ as the variable the equation becomes

$$\bar{V}_3 = \Phi_3 + \frac{c_3[\omega_2(\partial c_2/\partial c_3) + \omega_3](1000 - c_3\Phi_3)(\partial\Phi_3/\partial\mu_v^{1/2})}{2000\mu_v^{1/2} + c_3^2[\omega_2(\partial c_2/\partial c_3) + \omega_3](\partial\Phi_3/\partial\mu_v^{1/2})} \qquad (5)$$

Throughout this article the subscript 1 refers to the solvent, 2 to the sodium chloride or sodium chloride solution and 3 to the added salt (potassium chloride, potassium bromide or potassium sulfate) or its solution. The superscript 0 refers to infinite dilution ($c_3 = 0$).

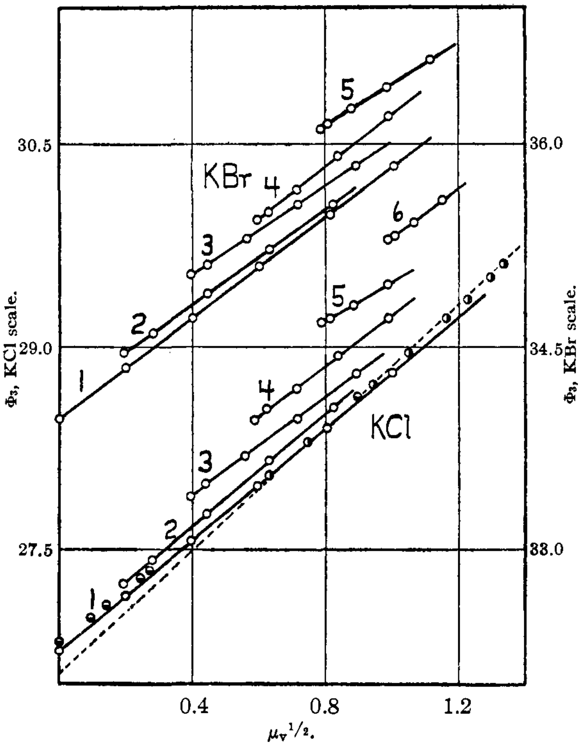

Fig. 3.—Apparent molal volume *vs.* square root of the volume ionic strength for potassium chloride and potassium bromide in water (curve 1) and in sodium chloride solutions (curves 2, 3, 4, 5 and 6): ⊖, Geffcken and Price; ◑, Kruis; — — — calculated from equation of Jones and Ray; temperature, 25°.

Results

The experimental values for the densities of potassium chloride, potassium bromide and potassium sulfate in water solution are expressed by equations of the form suggested by Root.[4]

For KCl: $d^{25}_4 = 0.997074 + 0.047896c - 0.002069c^{3/2}$
For KBr: $d^{25}_4 = 0.997074 + 0.085141c - 0.001842c^{3/2}$
For K_2SO_4: $d^{25}_4 = 0.997074 + 0.142068c - 0.006987c\mu_v^{1/2}$

The apparent molal volumes (Table I, Figs. 3 and 4) were calculated from the constants in these equations. The value 26.74 ml. found for the limiting apparent molal volume of potassium chloride is slightly less than that (26.81 ml.) reported by Geffcken and Price.[8] However, the equation given by Jones and Ray[9] leads to the value 26.57 ml. for Φ_3^0 and to values of the apparent molal volume at higher concentrations that are in essential agreement with the results obtained by Kruis[10] (Fig. 3).

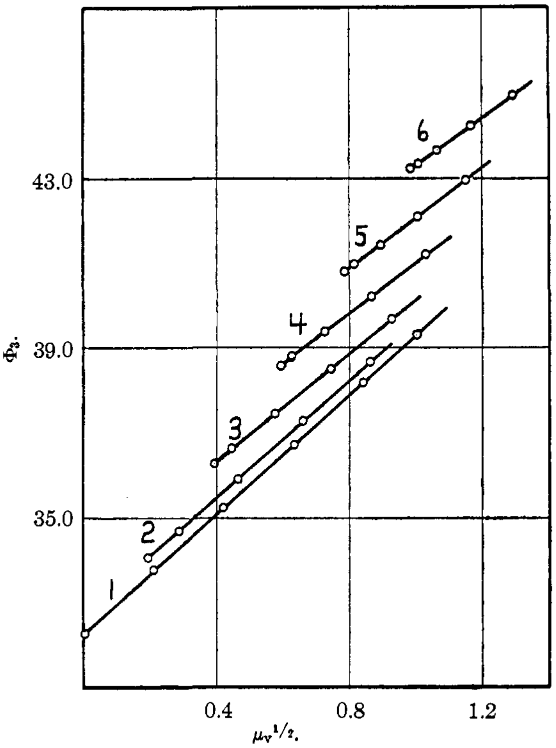

Fig. 4.—Apparent molal volume *vs.* square root of the volume ionic strength for potassium sulfate in water (curve 1) and in solutions of sodium chloride (curves 2, 3, 4, 5 and 6); temperature, 25°.

The discrepancy between the three sets of values may be due to differences in temperature or to impurities in the salts used. In either case the results reported here are comparable as the temperature was maintained at the same constant value and the same lots of salts were used except in the one instance noted below.

The value of the limiting apparent molal vol-

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(8) Geffcken and Price. *Z. physik. Chem.*, **B26**, 81 (1934).
(9) Jones and Ray. THIS JOURNAL, **59**, 187 (1937).
(10) Kruis. *Z. physik. Chem.*, **B34**, 1 (1936).

TABLE I

APPARENT AND PARTIAL MOLAL VOLUMES OF POTASSIUM CHLORIDE, POTASSIUM BROMIDE AND POTASSIUM SULFATE IN WATER SOLUTION

c_3	$\mu_v^{1/2}$	$(d_3 - d_1)1000$	$-F_3$	Φ_3	$\overline{V}_3$
Potassium Chloride					
0	0	0	(47.90)	26.74	26.74
0.03985	0.1996_3	1.888	47.38	27.15	27.36
.03950	$.1987_5$	1.869	47.31		
.15838	$.3979_7$	7.455	47.07	27.56	27.97
.15906	$.3988_3$	7.482	47.04		
.35623	$.5968_5$	16.620	46.66	27.97	28.59
.36072	$.6006_0$	16.828	46.65		
.64525	$.8032_7$	29.839	46.24_4	28.40	29.22
.64621	$.8038_7$	29.883	46.24_3		
.99498	$.9974_9$	45.602	45.83_2	28.81	29.81
.99662	$.9983_1$	45.671	45.82_6		
Potassium Bromide					
0	0	0	(85.14)	33.97	33.97
0.03983	0.1995_7	3.373	84.68	34.34	34.52
.04048	$.2012_0$	3.424	84.58		
.16112	$.4014_0$	13.602	84.42	34.71	35.08
.15986	$.3998_2$	13.484	84.35		
.36555	$.6046_1$	30.719	84.04	35.09	35.64
.35846	$.5987_2$	30.116	84.01		
.65991	$.8123_5$	55.212	83.66_6	35.47	36.20
.62782	$.7923_5$	52.536	83.68_0		
1.00809	1.0040_4	83.970	83.29_6	35.83	36.72
1.00555	1.0027_7	83.747	83.28_5		
Potassium Sulfate					
0	0	0	(142.07)	32.28	32.28
0.01483_3	0.2109_5	2.088	140.7_7	33.76	34.50
$.01479_5$	$.2106_8$	2.081	140.6_5		
$.05864_3$	$.4194_4$	8.164	139.2_2	35.22	36.69
.059107	$.4211_0$	8.221	139.0_9		
.13534	$.6371_9$	18.628	137.64	36.75	38.99
.13292	$.6314_7$	18.296	137.65		
.23815	$.8452_5$	32.427	136.16	38.21	41.14
.23219	$.8346_1$	31.632	136.23		
.33290	$.9993_4$	44.934	134.98	39.29	42.74
.33874	1.0080_8	45.775	135.13		

ume of potassium bromide in water (33.97 ml.) is about 0.8% higher than that obtained from the results of Geffcken and Price[8] for potassium chloride, sodium bromide and sodium chloride by the following calculation: $\Phi^0_{KBr} = \Phi^0_{KCl} + \Phi^0_{NaBr} - \Phi^0_{NaCl} = 26.81 + 23.48 - 16.60 = 33.69$ ml. This latter value is in agreement with the less accurately determined value of 33.56 ml. calculated from the results of Jones and Bickford.[11] Similarly, the value of Φ^0_3 for potassium sulfate in water as calculated from the results of these authors for sodium sulfate, potassium chloride and sodium chloride is 31.94 ml. as compared with 32.28 ml. found in the present work. The data of Jones and Ray[9] are in excellent agreement with those reported here (see Fig. 2) and give 32.36 ml. as the limiting apparent molal volume of potassium sulfate in water solution.

The equations representing the experimental results for potassium chloride in sodium chloride solutions are:

0.04 *N* NaCl:

$$d_3 - d_2 = 0.04735c_3 - 0.00209c_3(\mu_v^{1/2} - 0.1962)$$

0.15 *N* NaCl:

$$d_3 - d_2 = 0.04657c_3 - 0.00183c_3(\mu_v^{1/2} - 0.3935)$$

0.35 *N* NaCl:

$$d_3 - d_2 = 0.04578c_3 - 0.00191c_3(\mu_v^{1/2} - 0.5890)$$

0.62 *N* NaCl:

$$d_3 - d_2 = 0.04473c_3 - 0.00144c_3(\mu_v^{1/2} - 0.7871)$$

0.97 *N* NaCl:

$$d_3 - d_2 = 0.04370c_3 - 0.00184c_3(\mu_v^{1/2} - 0.9859)$$

TABLE II

APPARENT AND PARTIAL MOLAL VOLUMES OF POTASSIUM CHLORIDE IN SODIUM CHLORIDE SOLUTIONS

c_2	c_3	$\mu_v^{1/2}$	$\frac{(d_3 - d_2)}{1000}$	$-F_3$	Φ_3	$\overline{V}_3$
$c_2^0 = 0.03849$, $d_2 = 0.998672$						
0.03849	0	0.1961_9	0	(47.35)	27.24	27.24
.03845	0.03967	$.2794_9$	1.867	47.06	27.42	27.56
.03845	.03979	$.2797_0$	1.876	47.15		
.03832	.15904	$.4442_5$	7.445	46.81	27.76	28.14
.03832	.15922	$.4444_6$	7.449	46.78		
.03810	.36074	$.6315_4$	16.759	46.46	28.15	28.74
.03810	.35642	$.6281_1$	16.557	46.45		
.03779	.63849	$.8223_6$	29.393	46.04	28.55	29.35
$c_2^0 = 0.1548$, $d_2 = 1.003447$						
0.1548	0	0.3934_7	0	(46.57)	27.89	27.89
.1547	0.03937	$.4404_8$	1.826	46.38	27.98	28.06
.1547	.03996	$.4411_5$	1.857	46.47		
.1541	.15870	$.5593_1$	7.341	46.26	28.19	28.45
.1541	.15868	$.5592_9$	7.339	46.25		
.1533	.35562	$.7133_5$	16.356	45.99	28.47	28.92
.1533	.35538	$.7131_8$	16.341	45.98		
.1520	.64044	$.8901_8$	29.241	45.66	28.80	29.44
$c_2^0 = 0.3469$, $d_2 = 1.011226$						
0.3469	0	0.5889_8	0	(45.78)	28.46	28.46
.3465	0.03958	$.6213_6$	1.806	45.63	28.52	28.58
.3465	.04005	$.6217_3$	1.837	45.87		
.3453	.16003	$.7108_7$	7.285	45.52	28.69	28.89
.3453	.15980	$.7107_1$	7.276	45.53		
.3433	.35840	$.8376_8$	16.237	45.30	28.93	29.32
.3434	.35430	$.8352_6$	16.056	45.32		
.3404	.63804	$.9891_8$	28.720	45.01	29.21	29.80
$c_2^0 = 0.6196$, $d_2 = 1.022113$						
0.6196	0	0.7871_3	0	(44.73)	29.18	29.18
.6189	0.03956	$.8114_4$	1.769	44.72	29.21	29.24
.6189	.03970	$.8115_4$	1.775	44.71		
.6167	.15980	$.8811_9$	7.131	44.62	29.31	29.43
.6167	.15947	$.8810_0$	7.107	44.57		
.6131	.35790	$.9853_7$	15.908	44.45	29.46	29.70
$c_2^0 = 0.9719$, $d_2 = 1.035984$						
0.9719	0	0.9858_5	0	(43.70)	29.79	29.79
.9708	0.03972	1.0052_2	1.734	43.66	29.82	29.84
.9707	.03960	1.0051_6	1.727	43.61		
.9673	.15906	1.0612_8	6.927	43.55	29.92	30.05
.9673	.15867	1.0611_1	6.913	43.57		
.9614	.35906	1.1491_1	15.581	43.39	30.08	30.34

The apparent molal volumes calculated from the constants in these equations are uniformly

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[11] Jones and Bickford, THIS JOURNAL, **56**, 605 (1934).

greater than those in water solution (Fig. 3). The equation $\overline{V}_3 = 26.735 + 3.086\mu_V^{1/2}$ which represents the partial molal volumes of potassium chloride in water solution can also be used to calculate the partial molal volumes in sodium chloride solutions. Omitting the values of $\overline{V}_3^0$ $(c_3 = 0)$ which depend on the method used to extrapolate to infinite dilution the average deviation between the observed and calculated values is 0.03$_6$ ml. The maximum deviation which occurs three times is 0.07$_5$ ml. This is within the experimental error which, although difficult to estimate, averages about 0.04 ml.

The equations representing the experimental data for potassium bromide in sodium chloride solutions are

0.04 *N* NaCl:

$$d_3 - d_2 = 0.08460c_3 - 0.00174c_3(\mu_V^{1/2} - 0.1977)$$

0.16 *N* NaCl:

$$d_3 - d_2 = 0.08386c_3 - 0.00164c_3(\mu_V^{1/2} - 0.3966)$$

0.35 *N* NaCl:

$$d_3 - d_2 = 0.08319c_3 - 0.00196c_3(\mu_V^{1/2} - 0.5918)$$

0.62 *N* NaCl:

$$d_3 - d_2 = 0.08211c_3 - 0.00157c_3(\mu_V^{1/2} - 0.7855)$$

The values found in 0.97 *N* sodium chloride solution were inconsistent with the rest of the results obtained so are not represented by an equation or presented in the figures. As the potassium bromide used in this single series was from a different source the discarding of these data appears to be justified.

TABLE III

APPARENT AND PARTIAL MOLAL VOLUMES OF POTASSIUM BROMIDE IN SODIUM CHLORIDE SOLUTIONS

c_2	c_3	$\mu_V^{1/2}$	$\frac{(d_3-d_2)}{1000}$	$-F_3$	Φ_3	$\overline{V}_3$
			$c_2^0 = 0.03907$, $d_2 = 0.998696$			
0.03907	0	0.1976$_6$	0	(84.60)	34.46	34.46
.03902	0.03998	.2810$_6$	3.374	84.39	34.60	34.73
.03902	.04003	.2811$_5$	3.378	84.39		
.03885	.15982	.4457$_2$	13.455	84.19	34.89	35.20
.03885	.15952	.4453$_9$	13.426	84.16		
.03857	.36075	.6319$_2$	30.254	83.86	35.22	35.71
.03858	.35718	.6290$_9$	29.943	83.83		
.03819	.63524	.8206$_3$	53.051	83.51	35.55	36.21
			$c_2^0 = 0.1573$, $d_2 = 1.003549$			
0.1573	0	0.3966$_4$	0	(83.86)	35.03	35.03
.1571	0.03997	.4439$_3$	3.347	83.74	35.10	35.18
.1571	.04012	.4440$_9$	3.356	83.65		
.1564	.15946	.5620$_5$	13.331	83.60	35.30	35.53
.1564	.15965	.5622$_1$	13.342	83.57		
.1553	.36000	.7178$_5$	30.006	83.35	35.55	35.92
.1553	.35651	.7154$_3$	29.709	83.33		
.1537	.63956	.8906$_6$	53.114	83.05	35.83	36.40
			$c_2^0 = 0.3502$, $d_2 = 1.011359$			
0.3502	0	0.5917$_8$	0	(83.19)	35.43	35.43
.3497	0.03971	.6240$_3$	3.296	83.00	35.49	35.55
.3497	.03978	.6240$_8$	3.301	82.98		
.3482	.15940	.7124$_7$	13.219	82.93	35.66	35.87
.3482	.15891	.7121$_2$	13.177	82.92		
.3457	.35949	.8397$_4$	29.732	82.71	35.91	36.31
.3457	.35668	.8380$_9$	29.503	82.72		
.3421	.63693	.9894$_8$	52.485	82.40	36.20	36.80
			$c_2^0 = 0.6170$, $d_2 = 1.022007$			
0.6170	0	0.7854$_9$	0	(82.11)	36.11	36.11
.6161	0.03950	.8097$_0$	3.241	82.05	36.15	36.19
.6161	.03985	.8099$_2$	3.273	82.13		
.6134	.15915	.8789$_7$	13.036	81.91	36.26	36.39
.6135	.15969	.8792$_9$	13.092	81.98		
.6089	.35969	.9841$_8$	29.422	81.80	36.42	36.60
.6090	.35685	.9827$_7$	29.191	81.80		
.6026	.63854	1.1140$_5$	52.097	81.59	36.62	37.04
			$c_2^0 = 0.9716$, $d_2 = 1.035972$			
0.9716	0	0.9857$_0$	0	(80.4)	37.2 (?)	37.2 (?)
.9702	0.03939	1.0047$_6$	3.161	80.25		
.9702	.03980	1.0049$_6$	3.193	80.23		
.9658	.15936	1.0607$_0$	12.775	80.16		
.9585	.36027	1.1483$_7$	28.904	80.23		
.9586	.35705	1.1470$_1$	28.636	80.20		
.9484	.63474	1.2582$_3$	50.819	80.06		

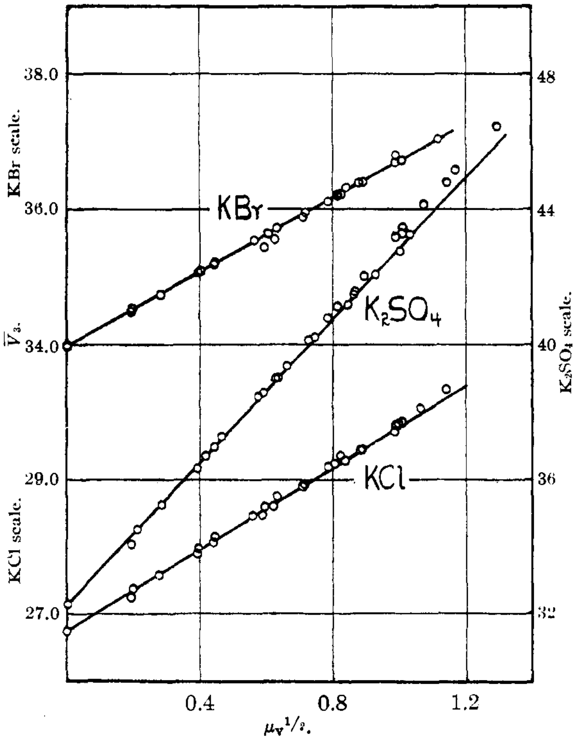

Fig. 5.—Partial molal volume *vs.* square root of the volume ionic strength for potassium chloride, potassium bromide and potassium sulfate in water and in solutions of sodium chloride; temperature, 25°.

The equation $\overline{V}_3 = 33.970 + 2.736\mu_V^{1/2}$ which represents the partial molal volumes of potassium bromide in water solution also represents the values in sodium chloride solution with an average deviation of 0.03$_0$ ml. The maximum deviation which occurs twice was 0.12 ml. Again the values of the partial molal volumes at zero concentration of potassium bromide were discarded in making the comparison although they are plotted in Fig. 5.

The experimental results for potassium sulfate in sodium chloride solutions are represented by

0.04 N NaCl:

$$d_3 - d_2 = 0.14025c_3 - 0.00691c_3(\mu_v^{1/2} - 0.1974)$$

0.15 N NaCl:

$$d_3 - d_2 = 0.13783c_3 - 0.00631c_3(\mu_v^{1/2} - 0.3926)$$

0.35 N NaCl:

$$d_3 - d_2 = 0.13526c_3 - 0.00610c_3(\mu_v^{1/2} - 0.5925)$$

0.62 N NaCl:

$$d_3 - d_2 = 0.13257c_3 - 0.00612c_3(\mu_v^{1/2} - 0.7868)$$

0.97 N NaCl:

$$d_3 - d_2 = 0.12951c_3 - 0.00589c_3(\mu_v^{1/2} - 0.9868)$$

The partial molal volumes calculated from these results cannot be expressed accurately by the equation $\overline{V}_3 = 32.28 + 10.46\mu_v^{1/2}$ which represents the partial molal volume of potassium sulfate in water solution. The addition of a third term (0.40 μ_v) permits the calculation of the partial molal volumes in sodium chloride solution with an average deviation from the experimental values of 0.08_8 ml. The maximum deviation of 0.30 ml. was found once. As the partial molal volumes of potassium sulfate depend on the difference between larger quantities than do the partial molal volumes of potassium chloride and potassium bromide the above average deviation is within the probable experimental error of the determination. Below a volume ionic strength of 0.25 the two term equation adequately represents the experimental values.

TABLE IV

APPARENT AND PARTIAL MOLAL VOLUMES OF POTASSIUM SULFATE IN SODIUM CHLORIDE SOLUTIONS

c_2	c_3	$\mu_v^{1/2}$	$\frac{(d_3 - d_2)}{1000}$	$-F_3$	Φ_3	$\overline{V}_3$
$c_2^0 = 0.03895$, $d_2 = 0.998691$						
0.03895	0	0.1973_6	0	(140.25)	34.05	34.05
.03893	0.01462_5	$.2877_6$	2.040	139.4_9	34.68	35.21
.03893	$.01468_5$	$.2880_7$	2.047	139.3_9		
.03887	$.05997_8$	$.4677_7$	8.300	138.3_8	35.92	37.25
.03887	$.05828_8$	$.4623_1$	8.066	138.3_8		
.03876	.13312	$.6619_1$	18.248	137.08	37.27	39.34
.03876	.13169	$.6586_7$	18.051	147.07		
.03860	.23522	$.8627_1$	31.909	135.66	38.66	41.46
$c_2^0 = 0.1541$, $d_2 = 1.003419$						
0.1541	0	0.3925_9	0	(137.83)	36.30	36.30
.1540	0.01478_3	$.4454_2$	2.033	137.5_2	36.63	36.94
.1540	$.01481_4$	$.4455_1$	2.033	137.2_4		
.1538	$.06000_3$	$.5777_5$	8.200	136.6_6	37.46	38.44
.1538	$.05894_3$	$.5750_0$	8.055	136.6_6		
.1533	.13400	$.7452_1$	18.173	135.62	38.52	40.20
.1533	.13237	$.7419_2$	17.955	135.64		
.1527	.23482	$.9274_4$	31.707	134.45	39.66	42.03
$c_2^0 = 0.3511$, $d_2 = 1.011393$						
0.3511	0	0.5925_4	0	(135.26)	38.56	38.56
.3509	0.01483_8	$.6288_2$	2.003	134.9_9	38.78	38.99
.3509	$.01484_4$	$.6288_3$	2.003	134.9_4		
.3502	$.06020_3$	$.7285_8$	8.093	134.4_3	39.38	40.12
.3503	$.05927_7$	$.7267_4$	7.968	134.4_2		
.3492	.13311	$.8651_9$	17.782	133.59	40.20	41.58
.3492	.13259	$.8642_9$	17.716	133.62		
.3477	.23764	1.0298_5	31.509	132.59	41.20	43.25
$c_2^0 = 0.6191$, $d_2 = 1.022094$						
0.6191	0	0.7868_3	0	(132.57)	40.79	40.79
.6187	0.01508_2	$.8148_4$	1.996	132.3_4	40.95	41.12
.6187	$.01504_6$	$.8147_6$	1.982	131.7_3		
.6176	$.05883_7$	$.8911_2$	7.765	131.9_7	41.41	42.00
.6176	$.05914_0$	$.8916_2$	7.796	131.8_2		
.6156	.13363	1.0082_2	17.540	131.26	42.11	43.28
.6156	.13296	1.0072_3	17.447	131.22		
.6128	.23711	1.1507_0	30.904	130.34	42.97	44.78
$c_2^0 = 0.9737$, $d_2 = 1.036052$						
0.9737	0	0.9867_6	0	(129.51)	43.19	43.19
.9731	0.01496_3	1.0089_4	1.936	129.3_9	43.31	43.44
.9731	$.01487_0$	1.0088_0	1.922	129.2_5		
.9712	$.05885_7$	1.0713_4	7.594	129.0_2	43.67	44.13
.9712	$.05892_7$	1.0714_3	7.600	128.9_7		
.9680	.13183	1.1677_0	16.936	128.47	44.22	45.16
.9680	.13246	1.1684_9	17.012	128.43		
.9634	.23612	1.2929_6	30.154	127.71	44.93	46.45

The observed departures from linearity found at the higher concentrations for the partial molal volumes of potassium sulfate are not unexpected since potassium sulfate is of an entirely different valence type than sodium chloride and there is no common ion. The agreement actually obtained is however ample justification for the use of the volume ionic strength as the variable rather than the total volume concentration or total normality.

The above results can be a confirmation of the Debye–Hückel theory only in so far as the selection of the variable is concerned since the concentrations employed were relatively large. The value of the slope $\partial\overline{V}_3/\partial\mu_v^{1/2}$ as predicted by the theory is a constant depending only on the type of electrolyte and is attained only at high dilution.[12] In the present work, in two cases it has been found that the experimentally determined slope for a single electrolyte in water solution also applies to solutions containing an additional electrolyte.

Summary

The apparent and partial molal volumes of potassium chloride, potassium bromide and potassium sulfate in water and in solutions of sodium chloride have been determined for certain concentrations up to a volume ionic strength of unity. The determinations were made at a temperature of 25°.

The partial molal volumes of potassium chloride and potassium bromide depend only on the total volume ionic strength of the solution.

The partial molal volume of potassium sulfate depends on the volume ionic strength in dilute solutions but in more concentrated solutions of sodium chloride it is larger than the value in water solution.

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[12] Redlich and Rosenfeld, *Z. Elektrochem.*, **37**, 705 (1931).