[CONTRIBUTION FROM THE SCHOOL OF CHEMICAL TECHNOLOGY, NORTH DAKOTA AGRICULTURAL COLLEGE]

Apparent and Partial Molal Volumes of Sodium Chloride and Hydrochloric Acid in Mixed Solutions[1]

BY HENRY E. WIRTH[2]

In a previous paper[3] it was shown that the partial molal volumes of potassium chloride, potassium bromide and potassium sulfate in sodium chloride solutions depend on the total volume ionic strength. The slopes of the partial molal volume–square root of concentration curves for these salts in aqueous solutions are near the values predicted by the Debye–Hückel theory.[4] A few electrolytes (*i. e.*, hydrochloric acid, lithium chloride and nitric acid) give slopes that are less than the theoretical value.[5] The effect of hydrochloric acid on the partial molal volumes of sodium chloride, and the effect of sodium chloride on the partial molal volumes of hydrochloric acid have therefore been investigated.

Methods.—In general the same apparatus and methods were employed. Pyrex tubes were substituted for the silver plated containers previously used as the latter were attacked by acid solutions.

C. P. grade chemicals were used without attempt at further purification.

The partial molal volumes of sodium chloride were determined in water and in approximately 0.04, 0.16, 0.36, 1.0, 2.18 and 4.23 *N* hydrochloric acid solutions. Enough hydrochloric acid solution for each series was prepared and the concentration determined by base titration as described below for the stock acid solution. As a check the concentrations were also calculated from the determined densities. Weighed amounts of sodium chloride were added to weighed portions of the acid solution to give the solutions used in the density determinations.

The partial molal volumes of hydrochloric acid were determined in water and in approximately 0.04, 0.16, 0.36, 1.0 and 2.25 *N* sodium chloride solutions. To meet the requirement that the ratio of moles of water to moles of sodium chloride remain constant throughout a given series, weighed stock acid solution was added to a weighed amount of water and to this solution was added an amount of sodium chloride calculated from the total water present.

The stock acid solution was analyzed by adding a weighed excess of approximately 0.25 *N* carbonate-free base to a sample and titrating the excess with approximately 0.01 *N* acid in a carbon dioxide-free atmosphere. Phenolphthalein was used as the indicator. The base was standardized against potassium acid phthalate. The average of six analyses was 0.2197_5 g. of hydrochloric acid per g. of solution (average deviation 0.0000_5). The average of five determinations using the weight Volhard method for chloride was 0.2196_0 (average deviation 0.0000_2).

Results[6]

The experimental values of the density for the solutions studied are presented in Tables I, II and III. Each series of results was represented by an equation of the form

$$-F_3 = a + b(\mu_V^{1/2} - C_2^{0\,1/2}) + c(\mu_V^{1/2} - C_2^{0\,1/2})^2 \qquad (1)$$

The values for the constants *a*, *b* and *c* are given in Table IV. The apparent and partial molal volumes were calculated from this equation using the methods previously employed.[3] Values of the apparent and partial molal volumes are given in Tables I, II and III for the actual concentrations studied. Tables V[1] and VI[1] present values of $\overline{V}_3$ for various even concentrations.

It is possible to compare the values of the apparent molal volumes of the solutes in aqueous solutions with values which have previously appeared in the literature. In Fig. 1 values of Φ_3 for sodium chloride at 25° as determined in the present study are compared with those reported by Kruis.[7] The apparent molal volume at infinite dilution ($\overline{V}_3^0$) found by Kruis is 16.60_5 as compared with 16.67_0. This difference arises in

---

[1] Tables V, VI, VII and VIII referred to in this paper may be obtained from the American Documentation Institute, 2101 Constitution Ave., Washington, D. C., by remitting 24¢ for microfilm or 60¢ for photoprints.

[2] Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio.

[3] H. E. Wirth, THIS JOURNAL, **59**, 2549 (1937).

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

[5] F. T. Gucker, Jr., *Chem. Rev.*, **8**, 111 (1933).

[6] The symbols used have the following significance:

d_1, d_2, d_3 = Density of water, of solution containing one solute and of solution containg two solutes, resp.

M_1, M_2, M_3 = Molecular weight of water, of first solute and of second solute, resp.

n_1, n_2, n_3 = Moles of water, moles of first solute and moles of second solute, resp. In a given series the ratio n_1/n_2 was maintained constant while n_3 varied.

C_2, C_3 = Volume concentration of first and second solute, resp., expressed as moles per liter of solution.

V = Volume of solution containing $n_1 + n_2 + n_3$ moles.

$\overline{V}_1 = \partial V/\partial n_1, \overline{V}_2 = \partial V/\partial n_2, \overline{V}_3 = \partial V/\partial n_3$. Partial molal volumes of water, of first solute and of second solute, resp.

$\overline{V}_1^0$ = Molal volume of pure water.

$\overline{V}_3^0$ = Partial molal volume of second solute when $C_3 = 0$, $C_2 = C_2^0$.

Φ_3 = $[V - (n_1\overline{V}_1^0 + n_2\Phi_2)]/n_3$. Apparent molal volume of second solute, where Φ_2 is the apparent molal volume of the first solute in a solution containing n_1 moles of solvent and n_2 moles of solute only.

F_3 = $1000(d_2 - d_3)/C_3$.

μ_V = $\omega_2C_2 + \omega_3C_3$. Volume ionic strength, where ω is one-half the summation of the number of ions times the square of the valence of the ion.

[7] A. Kruis, *Z. physik. Chem.*, **B34**, 1 (1936).

TABLE I

APPARENT AND PARTIAL MOLAL VOLUMES OF SODIUM CHLORIDE AND HYDROCHLORIC ACID IN WATER SOLUTION (25°)

C_3	$\mu_v^{1/2}$	$(d_3 - d_1)1000$	$-F_3$	Φ_3	$\bar{V}_3$
		Sodium Chloride			
0	0	0	(41.83_3)	16.67_0	16.67_0
0.03986	0.1997	1.654	41.50	17.00	17.17
.03986	.1997	1.655	41.52		
$.1591_1$	.3989	6.547	41.15	17.35	17.70
$.1591_1$	.3989	6.546	41.14		
$.3567_3$	.5973	14.552	40.79_2	17.71	18.26
$.3567_3$	.5973	14.553	40.79_6		
$.9792_0$	.9895	39.205	40.03_7	18.48	19.47
$.9791_8$	.9895	39.201	40.03_5		
2.251_2	1.5004	87.653	38.93_7	19.57	21.19
2.251_2	1.5004	87.668	38.94_3	19.57[a]	21.11[a]
5.411_5	2.3263	200.88	37.12_1	21.39[a]	23.68[a]

[a] Calculated from equation: $\Phi_3 = 16.435 + 2.010\, C_3^{1/2} + 0.052\, C_3$

C_3	$\mu_v^{1/2}$	$(d_3 - d_1)1000$	$-F_3$	Φ_3	$\bar{V}_3$
		Hydrochloric Acid			
0	0	0	(18.44_5)	18.07_2	18.07_2
0.04023	0.2006	0.735	18.27	18.26	18.36
.04007	.2002	0.731	18.23		
$.1565_1$	.3956	2.830	18.08	18.45	18.63
$.1551_6$	.3939	2.806	18.09		
$.3487_0$	.5905	6.238	17.89		
$.3589_8$	.5992	6.421	17.89	18.63	18.90
$.6330_7$	.7957	11.207	17.70_3	18.81	19.17
$.6299_3$	.7937	11.154	17.70_7		
$.9875_7$	.9938	17.311	17.52_9	18.99	19.42
1.033_1	1.0164	18.083	17.50_5		
2.257_8	1.5026	38.606	17.09_9		
2.244_9	1.4983	38.393	17.10_2	19.43	20.04
3.897_5	1.9742	65.061	16.69_3		
4.001_9	2.0005	66.715	16.67_1	19.85	20.61

TABLE II

APPARENT AND PARTIAL MOLAL VOLUMES OF SODIUM CHLORIDE IN HYDROCHLORIC ACID SOLUTION (25°)

C_1	C_3	$\mu_v^{1/2}$	$(d_3 - d_2)1000$	$-F_3$	Φ_3	$\bar{V}_3$
		$C_2^\circ = 0.04154_3$, $d_2 = 0.997832$				
0.04154	0	0.2038_2	0	(41.34)	17.15	17.15
.04151	0.04996	$.3024_4$	2.058	41.20	17.29	17.41
.04151	.04967	$.3019_6$	2.047	41.21		
.04146	$.1153_9$	$.3960_4$	4.738	41.06	17.43	17.65
.04146	$.1148_4$	$.3953_5$	4.717	41.07		
.04131	$.3139_7$	$.5960_6$	12.789	40.73_3	17.75	18.20
.04107	$.6309_8$	$.8197_9$	25.448	40.33_1	18.16	18.89
		$C_2^\circ = 0.1558_2$, $d_2 = 0.999885$				
0.1558_2		0.3947_4	0	(40.93)	17.53	17.53
$.1555_7$	0.08916	$.4947_0$	3.635	40.77	17.69	17.83
$.1555_8$	.08872	$.4942_7$	3.617	40.77		
$.1552_7$	$.1972_0$	$.5936_9$	8.006	40.60	17.85	18.13
1552_7	$.1992_9$	$.5954_5$	8.093	40.61		
$.1544_8$	$.4705_7$	$.7906_0$	18.949	40.26_8	18.19	18.71
$.1534_3$	$.8268_8$	$.9901_1$	32.995	39.90_2	18.55	19.33
		$C_2^\circ = 0.3596_4$, $d_2 = 1.003507$				
0.3596_4		0.5997_0	0	(40.45)	17.94	17.94
$.3588_0$	0.1294_5	$.6987_5$	5.214	40.28	18.10	18.26
$.3588_0$	$.1287_2$	$.6982_2$	5.187	40.29		

TABLE II (*Concluded*)

C_2	C_3	$\mu_V^{1/2}$	$(d_3 - d_2)1000$	$-F_3$	Φ_3	$\bar{V}_3$
0.3578$_2$	0.2771$_4$	0.7968$_4$	11.118	40.12	18.27	18.57
.3578$_3$	.2762$_6$	.7963$_0$	11.084	40.12		
.3554$_4$	.6265$_0$	.9909$_3$	24.908	39.75$_7$	18.63	19.22
.3524$_8$	1.0476	1.1832	41.249	39.37$_6$	19.01	19.90
$C_2^0 = 0.9891_0$, $d_2 = 1.014416$						
0.9891$_0$	0	0.99454	0	(39.39)	18.80	18.80
.9852$_2$	0.2068$_5$	1.0918	8.111	39.21	18.97	19.13
.9852$_0$	.2079$_0$	1.0923	8.153	39.22		
.9810$_2$	.4268$_6$	1.1865	16.661	39.03	19.14	19.48
.9809$_6$	.4295$_1$	1.1876	16.767	39.04		
.9712$_5$	.9239$_8$	1.3766	35.706	38.64$_3$	19.53	20.23
$C_2^0 = 2.1789$, $d_2 = 1.034366$						
2.1789		1.4762	0	(37.92)	19.85	19.85
2.1659	.2972$_5$	1.5694	11.214	37.73	20.04	20.23
2.1659	.2979$_0$	1.5696	11.239	37.73		
2.1510	.6331$_8$	1.6686	23.751	37.51$_1$	20.25	20.62
2.1509	.6352$_1$	1.6692	23.826	37.50$_9$		
2.1190	1.330$_8$	1.8574	49.366	37.09$_3$	20.65	21.38
$C_2^0 = 4.2338$, $d_2 = 1.067394$						
4.2338	0	2.0576	0	(36.02)	21.02	21.02
4.1980	0.3981$_9$	2.1439	14.261	35.82	21.20	21.37
4.1981	.3977$_1$	2.1438	14.252	35.84		
4.1590	.8267$_6$	2.2329	29.454	35.62$_6$	21.38	21.73
4.1588	.8291$_1$	2.2334	29.542	35.63$_2$		

TABLE III

APPARENT AND PARTIAL MOLAL VOLUMES OF HYDROCHLORIC ACID IN SODIUM CHLORIDE SOLUTION (25°)

C_2	C_3	$\mu_V^{1/2}$	$(d_3 - d_2)1000$	$-F_3$	Φ_3	$\bar{V}_3$
$C_2^0 = 0.03986_1$, $d_2 = 0.998728$						
0.03986	0	0.1996$_5$	0	(18.04)	18.45	18.45
.03982	0.05052	.3005$_6$	0.908	17.97	18.50	18.55
.03982	.04999	.2996$_9$	0.900	18.01		
.03977	.1217$_5$	.4019$_0$	2.185	17.94	18.56	18.66
.03977	.1179$_1$	.3971$_0$	2.113	17.92		
.03964	.2983$_6$	.5813$_8$	5.306	17.79	18.70	18.91
.03964	.2992$_1$	.5821$_1$	5.321	17.78		
.03941	.5964$_3$	.7974$_0$	10.500	17.60$_5$	18.90	19.29
$C_2^0 = 0.1591_1$, $d_2 = 1.003621$						
0.1591$_1$		0.3988$_9$	0	(17.61)	18.79	18.79
.1588$_4$	0.0878$_1$	.4966$_4$	1.542	17.56	18.84	18.89
.1588$_3$	.0929$_3$	.5017$_6$	1.632	17.56		
.1584$_9$	.1960$_3$	.5954$_1$	3.429	17.49	18.90	19.00
.1584$_9$	.1993$_2$	.5981$_7$	3.488	17.50		
.1576$_3$	.4826$_3$	.8001$_6$	8.377	17.36	19.04	19.28
.1576$_3$	.4723$_5$	.7937$_1$	8.198	17.36		
.1565$_3$	.8433$_0$	.9999$_1$	14.492	17.18$_4$	19.21	19.60
$C_2^0 = 0.3567_3$, $d_2 = 1.011626$						
0.3567$_3$		0.5972$_7$	0	(17.07)	19.18	19.18
.3558$_7$	0.1258$_0$	.6940$_2$	2.142	17.03	19.22	19.25
.3558$_1$	.1345$_4$	.7002$_5$	2.290	17.02		
.3540$_6$	.2785$_5$	.7953$_7$	4.732	16.99	19.26	19.35
.3547$_7$	.2853$_9$	.8001$_0$	4.844	16.97		
.3523$_9$	.6281$_9$	.9902$_4$	10.599	16.87$_2$	19.37	19.56
.3524$_3$	.6226$_5$	.9874$_6$	10.503	16.86$_8$		
.3494$_1$	1.0539	1.1846	17.645	16.74$_2$	19.50	19.81

TABLE III (*Concluded*)

C_2	C_3	$\mu_V^{1/2}$	$(d_3 - d_2)1000$	$-F_3$	Φ_3	$\overline{V}_3$
			$C_2^0 = 0.97918,\ d_2 = 1.036277$			
0.97918	0	0.98953	0	(15.85)	19.90	19.90
.97546	0.19075	1.0799	3.016	15.81	19.93	19.95
.97484	.22262	1.0943	3.522	15.82		
.97088	.42460	1.1813	6.696	15.77	19.96	20.04
.97081	.42911	1.1832	6.773	15.78		
.96104	.92486	1.3733	14.505	15.683	20.06	20.24
			$C_2^0 = 2.2512,\ d_2 = 1.08473$			
2.2512		1.5004	0	(13.91)	20.79	20.79
2.2375	0.29181	1.5904	4.040	13.84	20.82	20.84
2.2231	.59933	1.6800	8.305	13.86	20.84	20.88
2.1907	1.2864	1.8647	17.760	13.81	20.89	20.97
2.1592	1.9514	2.0275	26.853	13.76	20.93	21.05

TABLE IV

CONSTANTS IN THE EQUATION:

$$-F = a + b(\mu_V^{1/2} - C_2^{0^{1/2}}) + c(\mu_V^{1/2} - C_2^{0^{1/2}})^2$$

$C_2^{0^{1/2}}$	a	b	c	Average Deviation	d_2	$\partial C_3/\partial C_2$
		NaCl (58.454) in H_2O and in HCl Solution				
0 (0–2.25 *N*)	41.833	−1.609	−0.213	0.003	0.997074	
(1 *N*-Sat.)	42.067	−2.004	− .052	.002	.997074	
.2038	41.343	−1.345	− .477	.005	.997832	−0.000754
.3974	40.926	−1.552	− .281	.003	.999885	− .00306
.5997	40.451	−1.610	− .401	.003	1.003507	− .00684
.9945	39.388	−1.728	− .590	.002	1.014416	− .0193
1.4762	37.924	−2.097	− .216	.001	1.034366	− .0450
2.0576	36.017	−2.213	.....	.007	1.067394	− .0905
		HCl (36.465) in H_2O and in NaCl Solution				
0	18.445	−0.952	0.033	0.008	0.997074	
.1997	18.042	− .466	− .484	.014	.998728	−0.000754
.3989	17.611	− .499	− .359	.002	1.003621	− .00306
.5973	17.065	− .373	− .305	.004	1.011626	− .00694
.9895	15.845	− .277	− .383	.005	1.036277	− .0196
1.5004	13.910	− .285	.....	.011	1.08473	− .0471

the extrapolation to infinite dilution and does not represent a great variation in reported densities. Densities calculated from the equation in Table IV agree with those reported by Jones and Christian[8] with an average deviation of 0.0008% which is within the experimental error of their results. $\overline{V}_3^0$ calculated from the equation given by Jones and Christian is 16.62_1.

For comparison values of the apparent molal volumes at 18.55° as determined by Kohlrausch and Hallwachs[9] are also given in Fig. 1. The results of Prang[10] for concentrations below 0.015 *N* are in essential agreement and indicate that the value found by Kohlrausch and Hallwachs in the most dilute solution is probably in error.

The apparent molal volumes of hydrochloric acid in aqueous solutions are compared with the values determined by Hedestrand as reported by Geffcken[11] in Fig. 1. These are apparently the only values in the literature for the concentrations and temperature studied here. Hedestrand's value for $\overline{V}_3^0$ is 18.20 as compared with 18.07. The equation of Åkerlöf and Teare[12] derived from data at much higher concentrations and at other temperatures yields a value of 17.98_0 for $\overline{V}_3^0$ at 25°. Values of the apparent molal volumes at 17.15° as reported by Kohlrausch and Hallwachs[9] are also plotted in Fig. 1.

The partial molal volumes of sodium chloride are much less in the acid solutions than in solutions of the same volume ionic strength containing sodium chloride alone (Fig. 2). In the five cases ($\mu_V^{1/2}$ = 0.4, 0.6, 0.8, 1.0 and 1.2) where it is pos-

---

[8] G. Jones and S. M. Christian, THIS JOURNAL, **59**, 484 (1937).

[9] F. Kohlrausch and W. Hallwachs, *Wild, Ann. Physik*, **53**, 14 (1894).

[10] W. Prang, *ibid.*, **31**, 681 (1938).

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

[12] G. Åkerlöf and J. W. Teare, THIS JOURNAL, **60**, 1226 (1938).

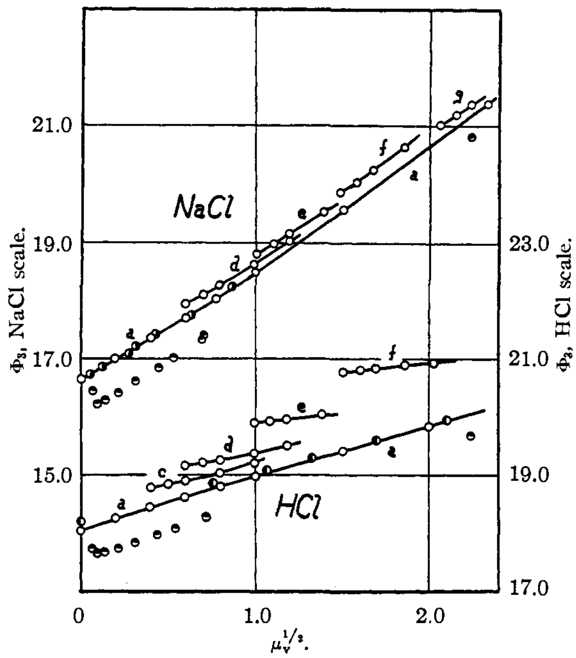

Fig. 1.—Apparent molal volumes of sodium chloride in water (a), and in 0.36 *N* (d), 0.99 *N* (e), 2.18 *N* (f) and 4.23 *N* (g) hydrochloric acid solutions (upper curves). Apparent molal volumes of hydrochloric acid in water (a), and in 0.16 *N* (c), 0.36 *N* (d), 0.98 *N* (e) and 2.25 *N* (f) sodium chloride solutions (lower curves). ◑, Kruis (25°); ⊖, Kohlrausch and Hallwachs (18°); ◐, Hedestrand (25°); ○, Wirth (25°).

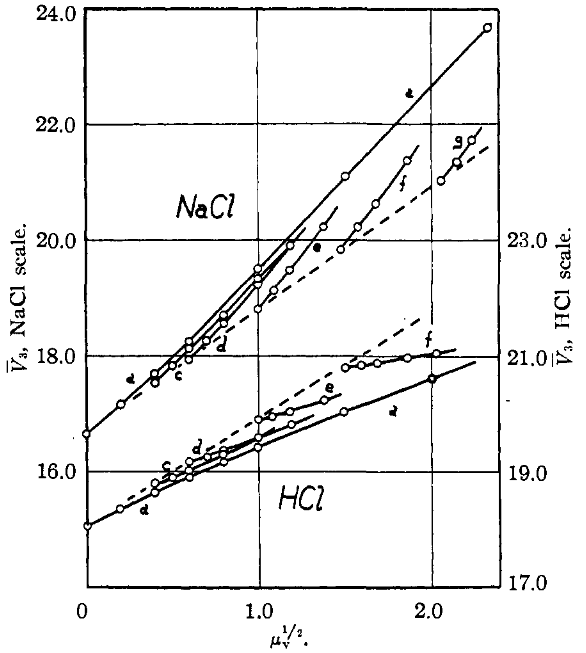

Fig. 2.—Partial molal volumes of sodium chloride in water (a), and in 0.16 *N* (c), 0.36 *N* (d), 0.99 *N* (e), 2.18 *N* (f) and 4.23 *N* (g) hydrochloric acid solutions (upper curves). Partial molal volumes of hydrochloric acid in water (a), and in 0.16 *N* (c), 0.36 *N* (d), 0.98 *N* (e) and 2.25 *N* (f) sodium chloride solutions (lower curves) (25°).

sible to make a comparison it was found that at constant total volume ionic strength the decrease in the partial molal volume is very accurately a linear function of the concentration of the acid (Fig. 3).

The partial molal volumes of hydrochloric acid are greater in solutions containing sodium chloride than in solutions of the same volume ionic strength containing acid alone (Fig. 2). Although there are two exceptions (the highest concentrations studied in 0.04 and 0.16 *N* sodium chloride solutions) it appears that at constant total volume ionic strength the increase in the partial molal volumes of hydrochloric acid is a linear function of the concentration of sodium chloride (Fig. 3).

In both cases presented in Fig. 2 it is possible to draw straight lines through the limiting values of the partial molal volumes ($\bar{V}_3^0$). All possible values of $\bar{V}_3$ are included between this line and the curve for $\bar{V}_3$ in aqueous solution. The slopes of the limiting lines are 1.81 for hydrochloric acid and 2.06 for sodium chloride. These values may be compared with a slope of 1.28 for hydrochloric acid and a slope of 3.12 for sodium chloride in water solutions at a concentration of 1 *N*.

The independent determination of the partial molal volumes of the two solutes in the mixed solutions makes possible the calculation of the partial molal volumes of water in most of the solutions studied.

In solutions containing only one solute, $\bar{V}_1$ can be calculated from the relation

$$\bar{V}_1 = \frac{(1000 - C_3\bar{V}_3)\,M_1}{1000d_3 - C_3M_3} \qquad (2)$$

For two solutes, $\bar{V}_1 = (1000 - C_2\bar{V}_2 - C_3\bar{V}_3)/n_1$. But since $n_1 = C_2K$ for all solutions of a given series and $K = (1000\,d_2 - C_2^0M_2)/C_2^0M_1$, the equation used in calculation becomes

$$\bar{V}_1 = \frac{(1000 - C_2\bar{V}_2 - C_3\bar{V}_3)\,M_1C_2^0}{C_2(1000d_2 - C_2^0M_2)} \qquad (3)$$

Values of $\bar{V}_3$ for even volume ionic strengths were taken directly from Table V[1] or VI,[1] while values of $\bar{V}_2$ were interpolated from Table VI[1] or V,[1] respectively. The calculated values of $\bar{V}_1$ are given in Tables VII[1] and VIII[1] and in Fig. 4.

In aqueous solutions $\bar{V}_1$ is decreased less by hydrochloric acid than by sodium chloride, and in mixed solutions the values are intermediate between those for the single solutes.

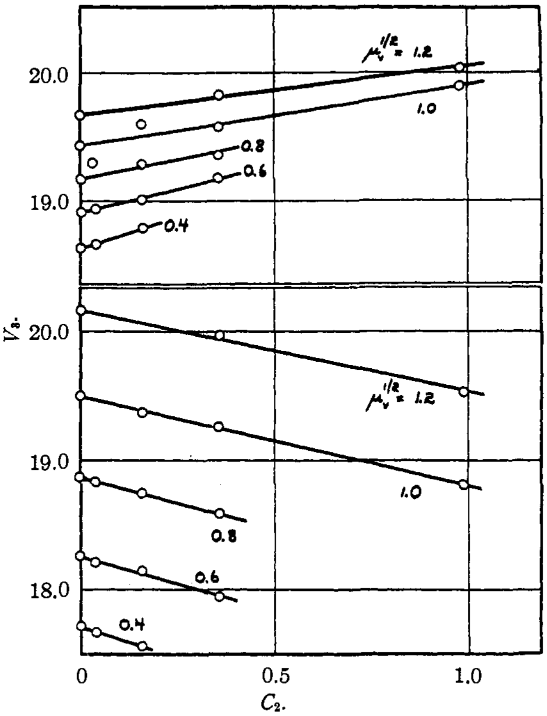

Fig. 3.—Partial molal volumes of hydrochloric acid *vs.* concentration of sodium chloride at constant total volume ionic strengths (upper graph), and partial molal volumes of sodium chloride *vs.* concentration of hydrochloric acid at constant total volume ionic strengths (lower graph) (25°).

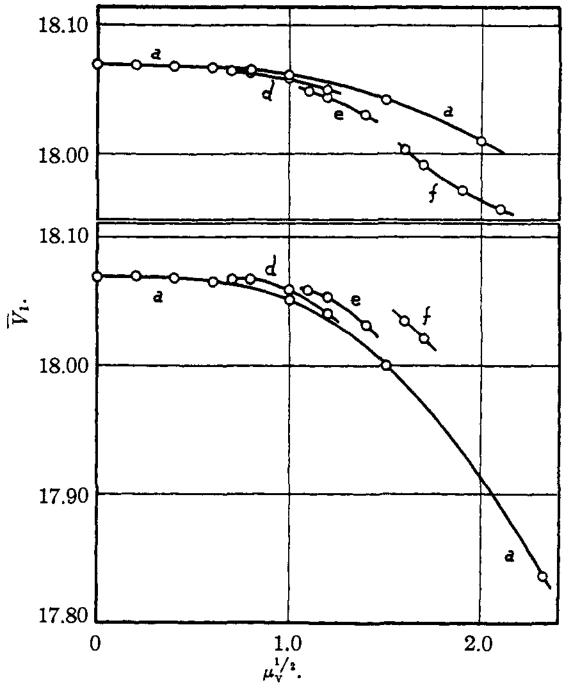

Fig. 4.—Partial molal volumes of water in hydrochloric acid solutions (a), and in hydrochloric acid solutions 0.36 *N* (d), 0.98 *N* (e) and 2.25 *N* (f) in sodium chloride (upper graph). Partial molal volumes of water in sodium chloride solutions (a), and in sodium chloride solutions 0.36 *N* (d), 0.99 *N* (e) and 2.18 *N* (f) in hydrochloric acid (lower graph) (25°).

Discussion

The slope of the apparent molal volume–square root of concentration curve for hydrochloric acid in water is less than for any highly ionized, uni-univalent electrolyte with the possible exception of nitric acid.[12,13,14] While the results obtained here do not exclude the possibility of $\partial\Phi/\partial C^{1/2}$ attaining the theoretical limiting value, this would require an abrupt change at concentrations below 0.04 *N*.

Since $\partial\Phi/\partial C^{1/2}$ is apparently least for substances containing hydrogen or lithium ions, the effect may be related to ion size. The second approximation derived by Redlich and Rosenfeld[4] from the Debye–Hückel expression involving ionic radii predicts however that $\partial\Phi/\partial C^{1/2}$ will be increased as the ionic size is decreased. The breakdown of the Debye–Hückel theory in other cases where small ions are involved has been attributed to ion association.[15]

The relationship between $\partial\Phi/\partial C^{1/2}$ and the partial molal volume of the solvent is of significance. For a single solute, the relations $(1000 - n_1\overline{V}_1^0)/C_3 = \Phi_3 = \overline{V}_3^0 + k_1C_3^{1/2}$, $\overline{V}_3 = \overline{V}_3^0 + kC_3^{1/2}$, and $k_1 = {}^2/_3k$(Geffcken[11]) can be combined with the equation $V = 1000 = n_1\overline{V}_1 + C_3\overline{V}_3$ to give the expression

$$\overline{V}_1 = \frac{\overline{V}_1^0(1000 - C_3\overline{V}_3^0 - kC_3^{3/2})}{1000 - C_3\overline{V}_3 - {}^2/_3kC_3^{3/2}} \tag{4}$$

This equation holds with considerable accuracy at least up to concentrations of 1 *N* and shows that the partial molal volume of the solvent at a given concentration is determined by $\partial\Phi/\partial C^{1/2}$ $(= k)$, or *vice versa*.

Since $\partial\Phi/\partial C^{1/2}$ for moderately concentrated solutions cannot now be predicted accurately from theory, it may be convenient to take the view of Stewart[16] and others that the change in structure of water through decrease in coördination number in the presence of ions is the controlling factor.[17]

---

(13) D. O. Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(14) G. Åkerlöf and G. Kegeles, THIS JOURNAL, **61**, 1027 (1939).

(15) H. Falkenhagen, "Electrolytes," translated by R. P. Bell, Oxford University Press, New York, N. Y., 1934, p. 257.

(16) G. W. Stewart, *J. Chem. Phys.*, **7**, 869 (1939).

(17) This should be done without discarding the Debye–Hückel theory, since this theory correctly predicts the choice of variable ($C^{1/2}$ or $\mu_v^{1/2}$), the order of magnitude of $\partial\Phi/\partial C^{1/2}$, and the effect of valence on $\partial\Phi/\partial C^{1/2}$,

From this standpoint, the low value for $\partial\Phi/\partial C^{1/2}$ for hydrochloric acid is due to the ease with which the hydrogen ion fits into the existing structure of water, and only the chloride ion is effective in changing that structure.

The observed increase in the partial molal volume of hydrochloric acid at constant total volume ionic strength when the hydrogen ion is replaced by sodium ion must be due to the greater effect of the sodium ion on the water structure. The fact that the increase is a linear function of the amount of sodium ion added is in harmony with this view. The decrease in the partial molal volume of sodium chloride on replacing the sodium ion with hydrogen ion is explained in the same manner.

Summary

The apparent and partial molal volumes of sodium chloride and hydrochloric acid have been determined in water and in mixed solutions.

The partial molal volumes of sodium chloride are decreased at constant total volume ionic strength by the addition of hydrochloric acid. The decrease is a linear function of the acid concentration.

The partial molal volumes of hydrochloric acid are increased at constant total concentration by the addition of sodium chloride. The increase is a linear function of the sodium chloride concentration.

The partial molal volumes of water have been determined in the mixed solutions. At a given concentration they are largest in solutions of pure hydrochloric acid and least in pure sodium chloride solutions.

The observed behavior may be interpreted in terms of changes in the structure of water caused by ions in solution.

RECEIVED DECEMBER 11, 1939

[CONTRIBUTION FROM THE CHEMICAL AND METALLURGICAL ENGINEERING DEPARTMENT, UNIVERSITY OF MICHIGAN]

An X-Ray Investigation of the System Cr_2O_3–NiO[1]

BY L. THOMASSEN

The present work has for its purpose to investigate the phases that are present in the above system. This equilibrium diagram is of considerable practical interest since the scale formed on the common electric resistance wires of nominal composition 80% Ni 20% Cr mainly consists of these oxides.

An earlier investigation[1a] has shown that the compound $NiO \cdot Cr_2O_3$ is formed when mixtures of this composition are heated with a mineralizer such as potassium chloride. This compound crystallizes in the widely distributed spinel type of structure.[2] Regarding the rest of the system, no information seems to be available. Similar systems with ferric oxide as the trivalent metal oxide have been investigated.[3]

Experimental Procedure

Most of the samples were made by mixing the oxides in the proper proportions, grinding them intimately and heating them with potassium chloride in platinum crucibles at 1000° for one to two hours. An electric furnace with automatic temperature control was used for the heating. After fusion, the crucibles were taken out and allowed to cool rapidly in the air. Unless changes take place very rapidly, the material as investigated would represent equilibrium conditions at 1000°.

The chromic oxide used was obtained by heating C. P. ammonium chromate to 900°. Upon heating a sample to 1000° for ten hours, a loss of 0.2% was obtained. According to Wretblad[4] there is no danger of forming CrO_2 when heating Cr_2O_3 to 1000° in oxygen and there should be still less chance of forming such a compound in air.

The nickel oxide was obtained by heating C. P. nickel nitrate, cobalt free, to 400°. The oxide obtained analyzed 77.3% Ni instead of 78.5% theoretically. Both the weight loss of the chromic oxide and this deviation from the theoretical composition were taken into account when making up mixtures to be fused.

After fusion the samples were washed carefully to remove all the potassium chloride present. Invariably, the first wash water was yellow, showing that some chromic oxide was oxidized to chromate.

Boric oxide was also tried as a mineralizer but with the straight $NiO \cdot Cr_2O_3$ composition, a number of extra lines appeared on the X-ray diagram. This observation confirmed the doubts expressed by Holgersson[1a] regarding the advisability in using boric oxide in this synthesis.

---

[1] Original manuscript received July 31, 1939.

[1a] S. Holgersson, *Z. anorg. allgem. Chem.*, **204**, 382 (1932).

[2] See for instance S. Holgersson, "Lunds Universitetets Arsskrift," N. F. Avd. 2. Vol. 23, Nr. 9; G. L. Clark, *Am. J. Sci.*, **22**, 539 (1931).

[3] A. E. van Arkel, E. J. W. Verwey and M. G. van Bruggen, *Rec. trav. chim.*, **55**, 331, 340 (1936).

[4] Wretblad, *Z. anorg. allgem. Chem.*, **189**, 329 (1930).