[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

A Note on the Density of Aqueous Solutions of Hydrochloric Acid

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An extensive table of the density of aqueous solutions of hydrochloric acid over large temperature and concentration ranges is given in Volume III of "International Critical Tables." A numerical study of these data seemed to indicate, however, that they contain serious errors (particularly at higher temperatures and acid concentrations) since least squaring according to a second order equation did not give a consistent series of constants. In connection with our study[1] of the thermodynamics of hydrochloric acid in concentrated solutions, a large number of density measurements were carried out and they seem to verify this conclusion. At corresponding temperatures and concentrations our density values differed from the "I. C. T." data in extreme cases by as much as 3 units in the third decimal place.

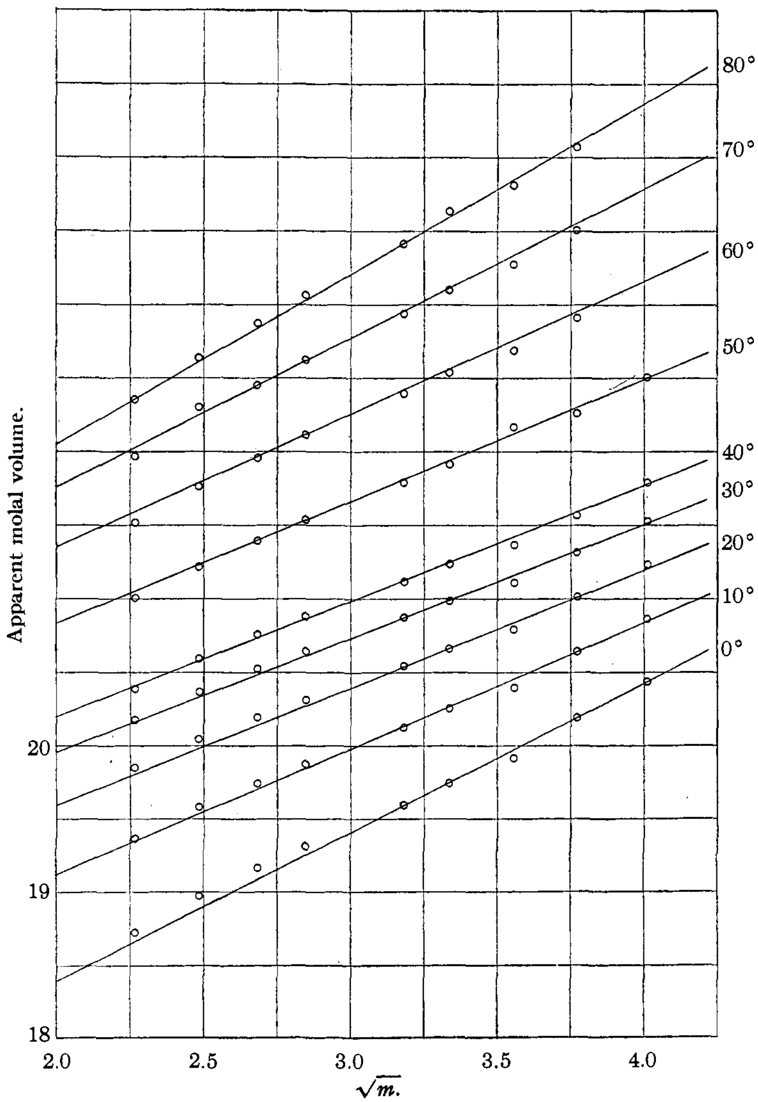

Fig. 1.—Calculated curves for the apparent partial molal volume of hydrochloric acid at various temperatures. The ordinates for the 50, 60, 70 and 80° curves have been shifted successively by 0.5.

To obtain the density data ordinary closed Pyrex glass pycnometers with an inner volume of about 130 cc. were used. They were made from standard 125-cc. flat-bottomed flasks by sealing on a 3″ (7.6 cm.) long capillary of about 1 mm. i. d. The capillary was provided with a ground cap and the flasks were carefully annealed. Before the pycnometers were adjusted for weighing, they were kept for about half an hour at the desired temperature in a fairly large water thermostat regulated with an accuracy of ±0.02°. The measuring temperature was determined with a mercury thermometer calibrated for total immersion against a platinum resistance thermometer certified by the Bureau of Standards. The change of the pycnometer volume with temperature was calculated from the known linear expansion coefficient of the glass. The standard acid solution employed in making up all of the more dilute solutions which were used for density measurements was analyzed gravimetrically as silver chloride. The calculation of the acid concentration was carried out using as values for the molecular weights of the acid and silver chloride 36.465 and 143.337, respectively. All vacuum corrections required were applied as usual.

From the density data obtained the apparent

(1) Åkerlöf and Teare, THIS JOURNAL, 59, 1855 (1937).

TABLE I

APPARENT PARTIAL MOLAL VOLUME OF HYDROCHLORIC ACID AT VARIOUS CONCENTRATIONS AND TEMPERATURES

		Values of φ								
HCl, *m*	$\sqrt{m}$	0°	10°	20°	30°	40°	50°	60°	70°	80°
5.1291	2.2647	18.726	19.368	19.850	20.175	20.386	20.507	20.518	20.469	20.355
6.1626	2.4824	18.978	19.584	20.045	20.370	20.592	20.716	20.761	20.731	20.635
7.1838	2.6802	19.164	19.747	20.193	20.523	20.753	20.895	20.958	20.951	20.878
8.0891	2.8441	19.311	19.875	20.317	20.645	20.881	21.035	21.113	21.123	21.069
10.1148	3.1804	19.592	20.122	20.545	20.873	21.118	21.289	21.393	21.439	21.415
11.1222	3.3350	19.746	20.252	20.661	20.985	21.234	21.416	21.537	21.600	21.637
12.2800	3.5043	19.912	20.395	20.790	21.109	21.361	21.670	21.688	21.773	21.810
14.2244	3.7716	20.197	20.643	21.014	21.318	21.565	21.759	21.906	22.009	22.071
16.0710	4.0088	20.437	20.868	21.233	21.530	21.797	22.009	....	....	....

TABLE II

DENSITY OF HYDROCHLORIC ACID SOLUTIONS

HCl, wt. %	HCl, *m*	0°	10°	20°	30°	40°	50°	60°	70°	80°
0	0.0000	0.99982	0.99948	0.99800	0.99553	0.99219	0.98809	0.98330	0.97789	0.97191
2	.5597	1.01055	1.00968	1.00780	1.00522	1.00175	.99761	.99287	.98758	.98182
4	1.1426	1.02116	1.01978	1.01771	1.01481	1.01122	1.00702	1.00230	.99712	.99152
6	1.7504	1.03176	1.02987	1.02751	1.02440	1.02066	1.01640	1.01169	1.00659	1.00114
8	2.3847	1.04237	1.03996	1.03731	1.03399	1.03011	1.02578	1.02107	1.01603	1.01070
10	3.0471	1.05299	1.05008	1.04714	1.04360	1.03958	1.03516	1.03043	1.02544	1.01994
12	3.7396	1.06365	1.06023	1.05701	1.05325	1.04907	1.04456	1.03980	1.03484	1.02970
14	4.4643	1.07434	1.07040	1.06690	1.06292	1.05858	1.05397	1.04917	1.04422	1.03915
16	5.2235	1.08507	1.08061	1.07683	1.07263	1.06812	1.06340	1.05854	1.05358	1.04856
18	6.0198	1.09581	1.09084	1.08678	1.08235	1.07768	1.07283	1.06790	1.06292	1.05792
20	6.8559	1.10658	1.10109	1.09675	1.09210	1.08725	1.08228	1.07726	1.07223	1.06723
22	7.7348	1.11736	1.11136	1.10675	1.10188	1.09684	1.09172	1.08660	1.08151	1.07648
24	8.6601	1.12815	1.12164	1.11677	1.11167	1.10643	1.10116	1.09592	1.09074	1.08565
26	9.6353	1.13893	1.13192	1.12678	1.12145	1.11602	1.11059	1.10520	1.09992	1.09474
28	10.6647	1.14970	1.14219	1.13680	1.13123	1.12560	1.11998	1.11445	1.10902	1.10374
30	11.7530	1.16044	1.15243	1.14679	1.14100	1.13516	1.13063	1.12490	1.11805	1.11261
32	12.9052	1.17113	1.16264	1.15677	1.15075	1.14469	1.13997	1.13276	1.12698	1.12135
34	14.1273	1.18175	1.17280	1.16669	1.16044	1.15416	1.14793	1.14178	1.13578	1.12993
36	15.4004	1.19280	1.18340	1.17706	1.17061	1.16409	1.15761	1.15122	1.14495	1.13885
38	16.8080	1.20272	1.19288	1.18634	1.17965	1.17290	1.16759	.....	.....	.....

partial molal volume φ of the acid was first calculated using the values of Smith and Keyes[2] for the specific volume of the solvent. The values of φ summarized in Table I were then least squared according to the equation

$$\varphi = \varphi^0 + k\sqrt{m} \qquad (1)$$

where φ^0 is the partial molal volume of hydrochloric acid at infinite dilution, k an empirical constant and m the acid concentration in molality. It has been shown previously by Masson, Redlich and Rosenfeld, Gucker, Geffcken and others[3] that equation (1) appears to be valid with great precision over large concentration ranges in the case of a number of strong electrolytes. That this is true also in the case of hydrochloric acid is shown in Fig. 1. After least squaring the values of φ^0 with respect to temperature, using a second order equation, the new values were introduced in the normal equations and a second series of values was obtained for k, which were then also least squared in the same manner as φ^0 with respect to the temperature. Thus the following two equations were obtained for φ^0 and k

$$\varphi^0 = 16.401 + 0.08571t - 0.0009016t^2 \qquad (2a)$$

$$k = 0.9461 - 0.01066t + 0.0001666t^2 \qquad (2b)$$

where t indicates the temperature in centigrade degrees. These two equations were employed for the calculation of the position of the curves shown in Fig. 1. The magnitude of the circles representing the experimental points is 0.04 cc. There are only a few points for the 0° isotherm that show any larger deviations from the calculated curves.

We have now available all data needed for making a density table similar to the one in the "I. C. T." The density d of the acid solution is given by the equation

(2) Smith and Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 285 (1934).

(3) Masson, *Phil. Mag.*, [7] **8**, 218 (1929); Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931); Redlich and Rosenfeld, *ibid.*, **155**, 65 (1931); Gucker, THIS JOURNAL, **55**, 2709 (1933).

$$d = \frac{1000}{\varphi m w/1000 + V} \quad (3)$$

where w is the weight and V the apparent volume of water per 1000 grams of solution. Changing from concentration per 1000 g. of solvent m to concentration per 1000 cc. of solution c may be carried out according to the equation

$$c = \frac{1000m}{\varphi m + 1000\, v_s} \quad (4)$$

where v_s is the specific volume of the pure solvent. Equation (4) eliminates tedious graphical interpolation in going from one concentration scale to the other. Table II shows a summary of the density values calculated using equation (3). At lower temperatures and concentrations the values obtained agree within 2–3 units in the fourth decimal place but, as indicated above, at higher values large differences with the "I. C. T." data begin to appear.

The values obtained for k have a considerable interest since they are very much smaller than those computed for a number of other uni-univalent strong electrolytes as shown in Table III for a few typical examples. According to the present preliminary theory, at a given temperature, as a limiting law k is a universal constant dependent only on the valence type of the electrolyte considered. Therefore the question appears whether we are justified in extrapolating our density measurements at high concentrations to dilute solutions. The only accurate density data available for dilute solutions of hydrochloric acid are those of Kohlrausch and Hallwachs[4] at a temperature of 17.15°. The values derived from their data for φ follow when plotted against $\sqrt{m}$ very closely a straight line and extrapolation to infinite dilution gives $\varphi^0 = 17.540$ while equation (2a) gives $\varphi^0 = 17.606$. The difference is well within the uncertainty caused by the experimental errors which tend to increase very rapidly with decreasing acid concentration. Thus it would seem to be probable that extrapolation of our data to dilute solutions does not involve any serious error and also that the value of k does not change materially with the acid concentration.

(4) Kohlrausch and Hallwachs, *Ann. Physik*, **50**, 118 (1893); **53**, 14 (1894).

TABLE III

THE k VALUE FOR EQUATION (1) FROM 0 TO 100° IN THE CASE OF AQUEOUS SOLUTIONS OF HCl, NaCl, KCl, $NaNO_3$ AND KNO_3. DATA FROM "I. C. T." USED

Temp., °C.	k HCl	k NaCl	k KCl	k $NaNO_3$	k KNO_3
0	0.946	2.98	3.14	5.06	3.98
10	.856	2.52	2.56	4.22	2.96
20	.800	2.11	2.27	3.30	2.53
30	.776	1.85	2.11	2.73	2.11
40	.786	1.71	1.97	2.20	1.83
50	.830	1.70	1.84	1.94	1.58
60	.906	1.67	1.87	1.62	1.46
70	1.016	..	..	..	..
80	1.160	1.75	1.97	1.33	1.38
100	(1.546)	1.97	2.23	..	..

Summary

The density of hydrochloric acid solutions has been determined at a number of concentrations from 0 to 80°. From the experimental data equations have been derived for a calculation of the density at arbitrary concentrations and temperatures. The equations were used to compute a table of densities for solutions containing 0 to 38 wt.% hydrochloric acid in the temperature range 0 to 80°.

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