water or in a phosphate buffer with a P_H of 6.0. The blanks without charcoal did not change their strengths during the course of the experiments. A few results are given in Table VII.

In spite of the presence of the acid substance at the surface of the C400 the latter has less promoting effect upon the decomposition of thiosulfate than C900 has.

Summary

Charcoal activated at 900 to 1000° and heated thereafter in oxygen at 300 to 500° forms at its surface a definite chemical compound with acid character. The optimum temperature for preparing this "acid charcoal" is 400°. The acid on the surface is stable in a vacuum at temperatures as high as 500–550°. The "acid charcoal" is much more hygroscopic than the product activated at 950°.

The adsorbent and catalytic properties of the "acid charcoal" are quite different from those of carbon activated at 900–1000°

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THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN UNI-UNIVALENT CHLORIDE SOLUTIONS AT CONSTANT TOTAL MOLALITY

BY J. ERSKINE HAWKINS

In this investigation the electromotive force of cells of the following types was measured

(A) $H_2/HCl(m_1)/AgCl/Ag$ and

(B) $H_2/HCl(m_1), MCl(m_2)/AgCl/Ag$

M represents either lithium, sodium or potassium and the total molality $m_1 + m_2 = 4.0$, 5.0 and 6.0.

Harned[1] has measured cells of the same type, using calomel electrodes instead of the silver–silver chloride electrodes and where $m_1 + m_2 = 0.1$, 1.0 and 3.0. All calculations at these concentrations are based on his measurements. Recalculations were carried out, due to a slight error which Harned[2] pointed out.

A few investigators[3] have measured cells of the type (A) containing pure hydrochloric acid at a concentration above three molal. However, no previous determinations have been made with cells of type (B), wherein $m_1 + m_2$ is greater than three molal.

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¹ Harned, THIS JOURNAL, **48**, 326 (1926).

² Harned, Trans. Am. Electrochem. Soc., **51**, 571 (1927).

³ Ellis, THIS JOURNAL, **38**, 737 (1916); Linhart, ibid., **39**, 2601 (1917); Randall and Young, ibid., **50**, 989 (1928).

This investigation was carried out with the following purposes: (1) to test the linear variation of log γ of hydrochloric acid with concentration, at total electrolyte concentration above three molal; (2) to determine, over the wide range from 0.1 to 6.0 molal, how closely the measured values of the activity coefficients of hydrochloric acid in these solutions agree with those calculated by Hückel's theory.[4]

Experimental

The hydrogen electrodes were prepared by platinizing platinum foil in a solution of chloroplatinic acid containing 0.5 g. of platinum per 100 cc. of solution until a black deposit of platinum was obtained. Freshly prepared electrodes were used in every case.

The silver–silver chloride electrodes were prepared by baking two coatings of carefully prepared silver oxide paste on platinum spirals for three hours each, at a temperature of about 450°, followed by the electrolytic formation of the chloride in a three-fourths molal solution of hydrochloric acid. A current of two to three milliamperes was passed for two hours.

Reproducibility was obtained in almost every case within 0.2 millivolt and in many within 0.1 millivolt. The maximum variation was less than 0.5 millivolt, and this in only a few cases. Equilibrium was reached within from two to five hours.

The difficulty encountered in obtaining closer reproducibility was at first thought to be due to a solubility effect of the silver chloride electrodes. However, variations in the procedure failed to reveal this as the cause. For instance, the hydrogen electrode was permitted to come to equilibrium before the silver chloride electrode was inserted in the cell. The silver chloride electrode in question was thoroughly rinsed in a solution of the same composition as that in the cell just before it was introduced. Equilibrium was reached in a few minutes and no further change in the electromotive force of the cell was perceptible even after thoroughly shaking the cell. In other cases the solution to be used was made up and electrolytically deposited silver chloride was placed in the solution and allowed to stand for several days. During this period the mixture was shaken frequently, and then placed in the cell. These procedures gave entirely satisfactory check results on the same solution. Another point in favor of the absence of a large solubility effect is the fact that a comparison of the activity coefficients of hydrochloric acid at a concentration as high as 8.0 molal, determined by this method and by the vapor pressure method, shows a difference of only 0.25%, corresponding to a difference in electromotive force of less than 0.2 millivolt. This is an excellent agreement at such high concentration for two methods.

Any effect on the silver chloride electrode due to diffusion of hydrogen through the solution was found to be negligible. Many of the measurements were made in cells having a stopcock between the two compartments and these were kept closed except when making the readings. Values by this method checked those obtained when the stopcocks were left open during the entire experiment. Had there been any diffusion of hydrogen into the silver electrode compartment, the electromotive force would have been altered due to the reaction $AgCl + \frac{1}{2}H_2 = Ag + H^+ + Cl^-$.

All measurements were made at $25 \pm 0.02°$.

Calculations and Discussion

1. After careful consideration of the data available the electromotive force of the cell H_2 (1 atm.) / HCl (0.1) / AgCl / Ag was taken to be

4 Hückel, *Z. physik. Chem.*, **26**, 93 (1925).

0.35265 volt at 25°. The activity coefficient γ of hydrochloric acid was calculated from the observed electromotive force by the equation

$$\log \gamma = \frac{0.35265 - E}{0.1183} + (8.8976 - 10) - 1/2 \log m_1(m_1 + m_2) \qquad (1)$$

E is the observed electromotive force corrected to a hydrogen pressure of one atmosphere. The activity coefficient of 0.1 molal hydrochloric acid was taken to be 0.79. The values of E and γ calculated by this equation are given in Table I, columns 2 and 3, respectively.

TABLE I

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ALKALI CHLORIDE MIXTURES AT CONSTANT TOTAL MOLALITY

Part 1. HCl–LiCl

(1) m_1	(2) E, volts	(3) γ obs.	(4) γ, Hückel	(5) γ
		$m_1 + m_2 = 0.1$		
0.01	...	0.786	0.781	0.790
.05	...	.788	.781	.789
		$m_1 + m_2 = 1.0$		
0.01	...	0.803	0.790	0.822
.10	...	.802	.789	.821
		$m_1 + m_2 = 3.0$		
0.01	...	1.302	1.310	1.409
.10	...	1.298	1.360	1.403
		$m_1 + m_2 = 4.0$		
0.10	0.2147	1.830	1.827	1.871
.50	.1735	1.824	1.824	1.874
1.00	.1578	1.823	1.821	1.863
2.00	.1390	1.827	1.810	1.860
3.00	.1289	1.777	1.802	1.846
		$m_1 + m_2 = 6.0$		
0.10	.1697	3.592	3.265	3.270
.50	.1285	3.582	3.258	3.270
1.00	.1113	3.536	3.255	3.265
2.00	.0945	3.469	3.230	3.244
3.00	.0856	3.365	3.210	3.228
4.00	.0793	3.325	3.197	3.210
5.00	.0742	3.259	3.182	3.190

Part 2. HCl–NaCl

		$m_1 + m_2 = 0.1$		
0.01	...	0.785	0.775	0.784
.05	...	.786	.777	.786
		$m_1 + m_2 = 1.0$		
0.01	...	0.765	0.725	0.757
.10	...	.766	.730	.762
.50	...	.782	.754	.786

TABLE I   (*Continued*)

(1) m_1	(2) E, volts	(3) γ, obs.	(4) γ, Hückel	(5) γ
		$m_1 + m_2 = 3.0$		
0.01	...	1.085	1.060	1.114
.10	...	1.084	1.068	1.123
.50	...	1.106	1.102	1.156
1.00	...	1.135	1.146	1.200
2.00	...	1.224	1.238	1.290
		$m_1 + m_2 = 4.0$		
0.10	0.2311	1.330	1.324	1.390
.50	.1884	1.367	1.363	1.424
1.00	.1686	1.416	1.418	1.480
2.00	.1472	1.521	1.532	1.588
3.00	.1337	1.624	1.652	1.704
		$m_1 + m_2 = 5.0$		
0.10	.2133	1.683	1.652	1.720
.50	.1708	1.724	1.705	1.769
1.00	.1513	1.778	1.769	1.830
2.00	.1299	1.908	1.904	1.903
3.00	.1159	2.046	2.052	2.105
4.00	.1048	2.199	2.213	2.254
		$m_1 + m_2 = 6.0$		
0.10	.1962	2.145	2.064	2.138
0.50	.1536	2.197	2.120	2.190
1.00	.1342	2.263	2.210	2.266
2.00	.1127	2.435	2.368	2.423
3.00	.0989	2.599	2.550	2.590
4.00	.0877	2.799	2.738	2.778
5.00	.0785	2.998	2.944	2.978
6.00	.0703	3.207	3.170	3.190

Part 3.   HCl–KCl

(1) m_1	(2) E, volts	(3) γ, obs.	(4) γ, Hückel	(5) γ
		$m_1 + m_2 = 0.1$		
0.01	...	0.778	0.769	0.777
.05	...	.782	.774	.781
.10	...	.790	.781	.788
		$m_1 + m_2 = 1.0$		
0.01	...	0.712	0.666	0.693
.10	...	.712	.676	.703
.50	...	.752	.723	.749
1.00	...	.806	.785	.816
		$m_1 + m_2 = 3.0$		
0.01	...	0.859	0.873	0.855
.10	...	.861	.835	.866
.50	...	.909	.888	.922
1.00	...	.963	.960	.994
2.00	...	1.123	1.123	1.180
3.00	...	1.311	1.340	1.382

TABLE I (*Concluded*)

(1) m_1	(2) E, volts	(3) γ, obs.	(4) γ, Hückel	(5) γ
		$m_1 + m_2 = 4.0$		
0.10	0.2474	0.969	0.978	1.005
.50	.2043	1.002	1.040	1.070
1.00	.1816	1.102	1.123	1.154
2.00	.1566	1.270	1.307	1.343
3.00	.1382	1.483	1.531	1.568
4.00	.1222	1.753	1.784	1.834
		$m_1 + m_2 = 5.0$		
1.00	.1709	1.213	1.293	1.318
2.00	.1450	1.422	1.504	1.530
3.00	.1266	1.660	1.750	1.778
4.00	.1096	2.005	2.038	2.070
5.00	.0955	2.358	2.378	2.420

In Fig. 1 the values of log γ are plotted against m_1. This definitely shows that the principle of the linear variation of log γ with concentration

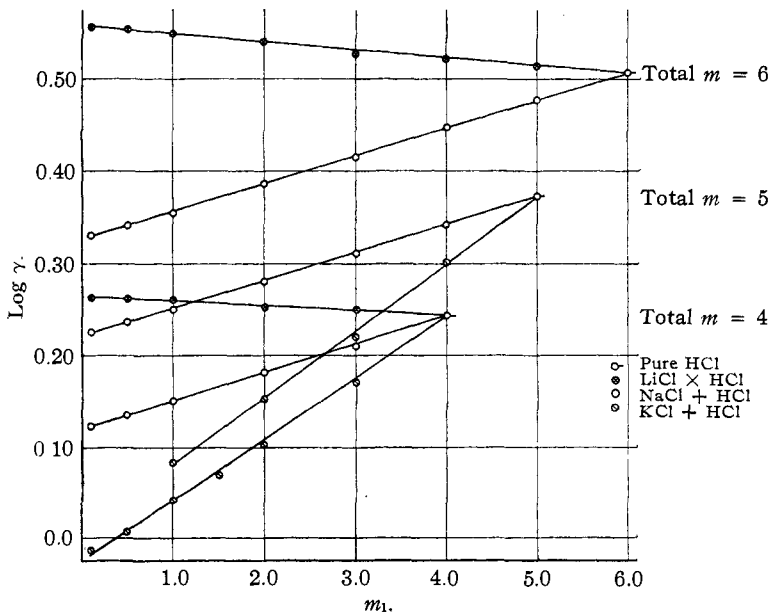Fig. 1.—The linear variation of the log γ of hydrochloric acid with the concentration of hydrochloric acid at very high constant total molality.

of the hydrochloric acid, in mixtures with uni-univalent chlorides at constant total molality, holds at very high concentration as predicted by Harned. In addition, this plot distinctly shows that, above a total concentration of three molal, the activity coefficient of hydrochloric acid in

lithium chloride is greater than that of the pure acid at the same concentration. Although Hückel[4] discusses this case on page 141 of his article, no satisfactory explanation for this behavior is available. It is believed that a correct application of Scatchard's[5] treatment of the Debye theory will not predict this result. The author is convinced that it is illogical to assume that the activity of the lithium ion becomes greater with increase in salt concentration and decrease in acid concentration than it is in a pure salt solution. This would necessitate a greater activity for lithium chloride than for hydrochloric acid at the same concentration and such has not been shown to be the case.

2. Hückel's theoretical treatment[4] of concentrated solutions was tested. This procedure is briefly as follows. The activity coefficient of the acid was calculated by the equation

$$\log \gamma = \frac{-0.354 \sqrt{2C_T}}{1 + A \sqrt{2C_T}} + B(2C_1) + B'(2C_T - 2C_1) - \log(1 + 0.002 \, wm_T) \quad (2)$$

in which A, B and B' are constants. The points of measurements chosen for the determination of A corresponded to 0.1, 1.0 and 6.0 molal hydrochloric acid. The following are the values obtained for these constants: $A = 0.607$, $B = 0.091$, $B' = 0.055$, 0.073 and 0.091 for potassium, sodium and lithium chlorides, respectively. These values are somewhat different from those obtained by Harned[1] and by Scatchard.[6] This is of course due mainly to the fact that their values were derived from data covering a narrower range of concentration, and from an equation which is an approximation and cannot be expected to be exactly valid from 0.0 to 6.0 molal. C_T is the total molar concentration of the solution and C_1 is the molar concentration of the acid present. The values of C_T for the total concentrations from 0.1 to 3.0 molal were taken as published by Harned and Åkerlöf,[7] those for C_T of pure acid above 3.0 molal were calculated from the density data published in the "International Critical Tables,"[8] and for mixtures above 3.0 molal the densities were determined by use of a Mohr-Westphal balance at 25 ± 0.2° and C_T then calculated; w is the formula weight of water and m_T is the total molal concentration.

The values of γ determined by equation (2) are given in column 4 of Table I. A comparison with the experimental values (column 3) shows that about 75% of the observed values and those calculated by the Hückel equation agree within 3%. The greatest deviation (less than 10%) occurs in the lithium chloride–acid mixtures at a total concentration of 6.0 molal.

3. Another method was used to determine the constants of the Hückel equation, (2). The resulting values of γ are given in column 5 of Table I.

[5] Private communication 1925: *Physik. Z.*, **33**, 22 (1932).

[6] Scatchard, THIS JOURNAL, **47**, 2098 (1925).

[7] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[8] Vol. III, 1928, p. 54.

These values agree with the observed values almost as well as those calcuated by the Hückel method, which are given in column 4.

It was assumed (1) that the actual volume occupied by a mole of water remained constant at each concentration of solution, (2) that the diameter of all ions was the same, (3) that there exists a physically homogeneous distribution of all ions, (4) that the shape of the ions is spherical, or that the effect of variation in shape is eliminated by assuming a solution in which the ions are spherical and have properties equivalent to those in the solution under consideration. The constants obtained from consideration of pure hydrochloric acid solutions were applied to the solutions containing the alkali chlorides.
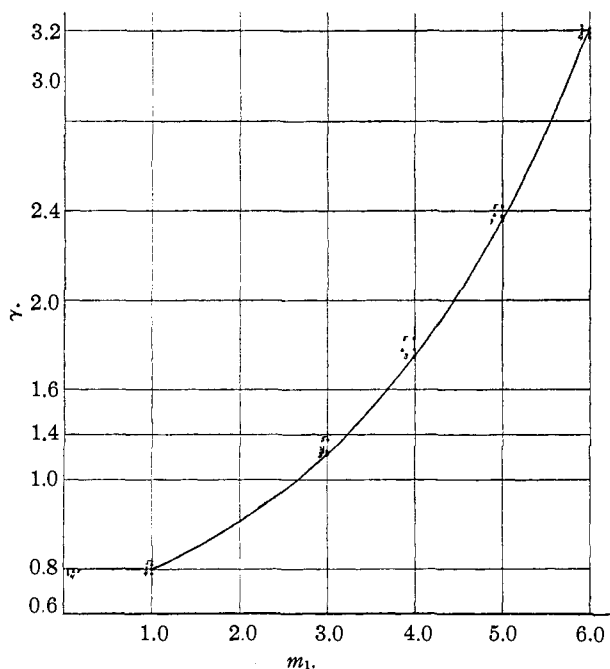

Fig. 2.—The activity coefficients of pure hydrochloric acid determined by various methods. The numbers correspond to the columns of Table I from which the data are taken.

The term "nearest distance of approach" of the ions is taken to mean the shortest distance between the centers of the nuclei of two ions of unlike charge. From consideration of the densities of solutions of hydrochloric acid it was found that the volume increase per mole of acid becomes constant with increase in concentration. This constant is 21.0 cc. per mole of hydrochloric acid. Dividing by $2 \times 6.06 \times 10^{23}$ gives 17.4×10^{-24} (approx.). From this the nearest distance of approach or apparent ionic

diameter, a, is found to be 3.22×10^{-8}, and the constant $A = a \sqrt{4\pi\epsilon^2 4N/D_0 kT}$ 1000, is 0.747 at 25°. The other constants of equation (2) were evaluated by the same procedure as in part 2. The values thus obtained are: $B = 0.0864$ and $B' = 0.0503$, 0.0698 and 0.0875 for potassium, sodium and lithium chlorides, respectively.

In Fig. 2 the activity coefficients of pure acid, determined by the various methods, are plotted against molality.

Summary

1. The electromotive force of hydrochloric acid–alkali chloride cells at constant total molality has been measured.

2. Various methods of calculating the activity coefficients of hydrochloric acid in alkali chloride mixtures have been used and a comparison of the results has been given.

3. It has been shown that the linear variation of log γ with concentration is valid at the high concentrations used.

4. An approximate simplified method for the determination of the constants of the Hückel equation has been used with satisfactory results.

PHILADELPHIA, PENNSYLVANIA

THE ACCURATE DETERMINATION OF CYANIDE BY DISTILLATION FROM SULFURIC ACID SOLUTION

BY H. ARMIN PAGEL AND WARNER CARLSON

In a certain investigation in this Laboratory it became necessary to determine accurately alkali cyanide in the presence of relatively large amounts of chloride, bromide, nitrate or sulfate by distillation from moderately strong sulfuric acid solution. A large number of methods in use for industrial, agricultural and biological analysis involve the isolation of cyanide by distillation from sulfuric acid solution. In such cases, however, the highest degree of accuracy is rarely demanded. Roe[1] discourages the practice of distilling from strong acid solution, stating that (1) at higher temperatures there is a loss of hydrocyanic acid due to hydrolysis to ammonium formate; (2) the hydrocyanic acid is evolved too rapidly to be quantitatively absorbed in the alkaline absorbing solution.

No contradiction to Roe's statement, or data on either the maximum obtainable accuracy or the possible interference of large amounts of salts could be found, hence this investigation was carried out.

Materials and Apparatus.—All salts used in this work were reagent grade. Arbitrary strength (approx. 0.19 N) solutions of potassium cyanide

[1] J. H. Roe, THIS JOURNAL, **45**, 1878–1883 (1923).