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June 1967

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Abstract

New measurements of the nuclear magnetic resonance (NMR) of perchloric acid solutions furnish results of higher accuracy (about 0.002 ppm in the chemical shift) between 0 and 65°C. Discrepancies in the degrees of dissociation derived from older NMR data and Raman intensities are ascribed to shortcomings in the earlier interpretation.

Extension of the measurements to deuterium solutions furnishes information to be used in the discussion of the molecular state of the acid and of the hydrogen ion.

The two methods used for measuring the dissociation of strong electrolytes, Raman intensities and shifts of nuclear magnetic resonance (NMR), produced results which were in excellent agreement in the case of nitric acid. But for perchloric acid, discrepancies have been found which suggest an experimental re-examination leading to a more detailed and improved interpretation. With present instruments a proper development of the experimental technique results in considerably higher accuracy.

The extension of the measurements to the whole system $\text{HClO}_4\text{-DClO}_4\text{-H}_2\text{O-D}_2\text{O}$ was desirable as a means of broadening the experimental basis for estimating the dissociation and also as a source of information on the structure of the hydrogen ion.

1. Experimental Procedure

Several methods have been used for the preparation of perchloric acid.³⁻⁹ A procedure similar to that of Redlich, Holt and Bigeleisen⁹, starting from perchloric acid (70%) and sulfuric acid (96%), was used to prepare the anhydrous acid. The acid has been reported to be explosive, but preparations by earlier authors may be suspected to contain impurities such as chlorine heptoxide, which can explode violently upon shock or sudden heating.¹⁰ Organic impurities, of course, and temperatures above 65°C were carefully avoided. A second person was always present when anhydrous acid was prepared. No potentially dangerous incident occurred in the course of numerous preparations. Intensively yellow samples were discarded. Colorless samples can be kept in dry ice for months.

The deuterium sulfate required for the preparation of deuteroperchloric acid was obtained by distillation of Sulfan (stabilized sulfur

trioxide) into a receiver containing ice cold heavy water. The reaction of drops of sulfur trioxide with water was, of course, somewhat violent at the beginning, but ordinary precautionary measures were sufficient to prevent any accidents.

Distillation of DClO_4 from a slurry of D_2SO_4 (100% or slightly weaker) and NaClO_4 or KClO_4 has been used by Smith and Diehl¹¹ and by Giguère and Savoie.⁶ In this procedure the salt cake, which is formed from sodium perchlorate in direct contact with the concentrated acid, causes local overheating and subsequent decomposition of the acid. Efficient stirring might have prevented overheating but would have unduly complicated the equipment. First, the azeotropic mixture $\text{DClO}_4\text{-D}_2\text{O}$ was prepared from a slurry of 295 ml of D_2SO_4 (100%), 300g of NaClO_4 and 95 ml of D_2O (yield 150 g of DClO_4 73%). In this distillation the temperature was raised to 80°C, much higher than for the anhydrous acid. Anhydrous acid was obtained by the standard procedure used for the light acid, namely, from the azeotropic mixture and 100% D_2SO_4 .

Slight decoloration of an acid containing not more than 90% can be removed by bubbling dry nitrogen through the cold solution for several hours.

The acid concentrations of the stock solutions were determined by weight titration with a sodium hydroxide solution. The primary standard was a freshly distilled solution of hydrochloric acid analyzed by the gravimetric silver chloride method. A precision of about 0.01% was attained after repeated boiling of the slightly acidic solution in a stream of carbon dioxide-free air.

The small amounts of hydrogen present in deuterium solutions were determined by measuring the intensity of the proton magnetic resonance. The spectrum of each solution was calibrated by the addition of a small weighed amount of light acid of the same acid concentration. It was assumed that the integrated intensity of the proton magnetic resonance is proportional to the mole fraction in the range of 99 to 100% deuterium. In the determination of the mole fraction r of deuterium, the precision achieved was better than ± 0.001 .

Measurements of the chemical shift of acid solutions have been carried out by means of the standard sideband technique on a 60 MHz Varian spectrometer with a variable temperature probe. The external reference was positioned coaxially. The sideband technique has given results with a precision of ± 0.002 ppm.

A new temperature measurement technique¹² furnished results with a precision of $\pm 0.2^\circ\text{C}$. A parabolic calibration equation was used without further correction.

The volume magnetic susceptibilities of the acid solutions were measured by the method of Mulay and Haverbusch.¹³ The pyrex NMR tube was provided with a ground glass joint so that the acid concentration was not changed by absorption of atmospheric moisture.

2. Results

The variation of the shifts in the entire ternary system is represented in considerable detail by the data in Tables 1 and 2.

The immediate determinations were carried out with the methyl resonance of methanol as a reference. For a change of reference, shifts of $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures were determined in the same way. The results, referred to H_2O , are represented as a function of the temperature t and the mole fraction of deuterium r ($= \text{D}/(\text{D}+\text{H})$) by the "water function"

$$W = -0.021 r(1+0.0174 t). \quad (1)$$

All data in the tables are referred to pure water of the same deuterium content.

New bulk susceptibility measurements were smoothed together with those of Hood and Reilly.² The algebraic representation for the susceptibility correction g as a function of the mole fraction x of the acid

and the temperature t ($^{\circ}\text{C}$) is

$$g = (1.506 + 1.82 \cdot 10^{-4}t - 7.3 \cdot 10^{-6}t^2) \cdot \left\{ 1 - [1.0636 - 0.1786x - (3.100 \cdot 10^{-2}x^2 - 2.232 \cdot 10^{-2}x + 4.072 \cdot 10^{-3})^{1/2} \cdot [1.0 + (1.25 \cdot 10^{-2} - 5 \cdot 10^{-4}t)x^2]] \right\}. \quad (2)$$

The susceptibility correction g is added to the chemical shifts.

The chemical shifts were measured at two to five temperatures between 0 and 70°C . Results in ppm, obtained by parabolic interpolation for four fixed temperatures, are shown in Tables 1 and 2 and in Figure 1.

Table 1 contains the temperature t , the mole fraction x of HClO_4 , the susceptibility correction g of equation (2), and the corrected shift s referred to H_2O . Table 2 contains also the deuterium fraction r ; the shift is referred to the appropriate deuterated water mixture.

The limiting slopes $s_1 = \lim_{x \rightarrow 0} ds/dp$ of the shift with respect to Gutowsky's variable

$$p = 3x/(2-x) \quad (3)$$

were obtained from sets of four to eleven data points, which were represented by power series of third order in p . The slopes were taken from the sets that gave the best least squares representation. For dilute solutions the equation

$$s_1 = 8.666 + 2.070 \cdot 10^{-2}t + (2.412 - 1.24 \cdot 10^{-3}t)r + (3.392 - 8.41 \cdot 10^{-3}t)r^2 + (-0.530 - 2.20 \cdot 10^{-3}t)r^6 \quad (4)$$

represents the smoothed results from the limiting slopes s_1 as a function of r and t . The values of the limiting slopes s_3 for $p = 3$ have been represented by

$$s_3 = -0.175 + 2.03 \cdot 10^{-3}t - 2.5 \cdot 10^{-5}t^2(1-r) - 0.654 r^{1.3}. \quad (5)$$

Table 1. Chemical Shifts δ in ppm for HClO_4 .

<u>t</u> Temp °C	<u>x</u> Mole fraction of the acid	<u>g</u> Susceptibility correction	<u>s</u> Shift ppm	<u>s₁</u> Limiting slope	<u>α</u> Degree of dissociation of the acid	<u>α_w</u> of water
0.0	.0160	.000	.207	8.666	—	—
	.0322	.000	.424		—	—
	.0469	.001	.628		—	—
	.0698	.001	.942		—	—
	.0992	.001	1.349		—	—
	.1356	.001	1.852		—	—
	.1658	.001	2.260		—	—
	.1890	.001	2.560		—	—
	.2372	.001	3.148		—	—
	.3056	.003	3.898		—	—
	.3611	.010	4.432		—	—
	.8234	.238	5.497		.213	.991
	.8353	.244	5.490		.196	.993
	.8761	.265	5.458		.140	.992
	.9097	.283	5.433		.099	.996
	.9526	.304	5.395		.050	.997
	.9764	.317	5.370		.024	.987
.9921	.325	5.356	.008	1.004		
25.0	.0160	.000	.219	9.183	(1.000)	—
	.0322	.000	.448		(1.000)	—
	.0469	.001	.662		(1.000)	—
	.0698	.001	.992		(1.000)	—
	.0992	.001	1.419		(.999)	—
	.1356	.001	1.944		(.999)	—
	.1658	.001	2.367		(.998)	—
	.1890	.002	2.680		(.997)	—
	.2372	.002	3.295		(.995)	—
	.3056	.005	4.085		(.988)	—
	.3611	.012	4.635		(.978)	—
	.7552	.213	5.684		.324	.999
	.8234	.249	5.630		.210	.982
	.8353	.255	5.626		.194	.984
	.8761	.277	5.604		.139	.986
	.9097	.295	5.586		.098	.992
	.9526	.318	5.558		.050	.999
.9764	.331	5.538	.024	.990		
.9921	.339	5.528	.008	1.022		
55.0	.0160	.000	.235	9.804	(1.000)	—
	.0322	.000	.477		(1.000)	—
	.0469	.001	.703		(1.000)	—
	.0698	.001	1.052		(1.000)	—
	.0992	.001	1.503		(.999)	—

Table 1 (cont.)

<u>t</u>	<u>x</u>	<u>g</u>	<u>s</u>	<u>s₁</u>	<u>α</u>	<u>α_w</u>
<u>Temp</u>	<u>Mole fraction</u>	<u>Susceptibility</u>	<u>Shift</u>	<u>Limiting</u>	<u>Degree of dissociation</u>	<u>of the acid</u>
<u>°C</u>	<u>of the acid</u>	<u>correction</u>	<u>ppm</u>	<u>slope</u>	<u>of the acid</u>	<u>of water</u>
55.0	.1356	.002	2.052	9.804	(.998)	—
	.1658	.002	2.496		(.997)	—
	.1890	.002	2.823		(.995)	—
	.2372	.004	3.467		(.991)	—
	.3056	.007	4.294		(.981)	—
	.3611	.015	4.854		(.966)	—
	.4132	.037	5.321		(.939)	—
	.5564	.113	5.709		.676	.848
	.5703	.120	5.716		.642	.853
	.6800	.180	5.796		.431	.916
	.7552	.222	5.817		.309	.952
	.8234	.260	5.777		.201	.936
	.8353	.266	5.773		.185	.936
	.8761	.289	5.762		.134	.944
	.9097	.308	5.759		.096	.970
	.9526	.331	5.736		.049	.981
	.9764	.345	5.721		.024	.990
	.9921	.353	5.709		.008	.987
65.0	.0160	.000	.241	10.011	(1.000)	—
	.0322	.000	.487		(1.000)	—
	.0469	.001	.716		(1.000)	—
	.0698	.001	1.073		(.999)	—
	.0992	.001	1.532		(.999)	—
	.1356	.002	2.088		(.997)	—
	.1658	.002	2.539		(.995)	—
	.1890	.003	2.870		(.994)	—
	.2372	.004	3.523		(.988)	—
	.3056	.007	4.360		(.975)	—
	.3611	.016	4.920		(.956)	—
	.4132	.038	5.364		(.923)	—
	.5564	.114	5.742		.655	.821
	.5703	.122	5.751		.623	.827
	.6800	.183	5.831		.418	.888
	.7552	.225	5.851		.298	.920
	.8234	.263	5.823		.196	.913
	.8353	.269	5.817		.179	.910
	.8761	.292	5.811		.130	.921
	.9097	.311	5.814		.095	.957
	.9526	.335	5.792		.048	.971
	.9764	.349	5.778		.024	.989
	.9921	.357	5.764		.008	.960

Table 2. Chemical Shifts δ in ppm for $\text{HClO}_4\text{-DClO}_4$.

<u>t</u> Temp °C	<u>r</u> Deuterium fraction	<u>x</u> Mole fraction of the acid	<u>g</u> Susceptibility correction	<u>s</u> Shift ppm	<u>s₁</u> Limiting slope
0.0	.3260	.0161	.000	.239	9.812
	.3282	.0362	.000	.538	9.822
	.3301	.0533	.001	.796	9.831
	.3330	.0788	.001	1.183	9.845
	.3349	.1049	.001	1.577	9.853
	.3393	.1324	.001	1.988	9.874
	.3413	.1608	.001	2.408	9.883
	.3492	.2099	.001	3.089	9.921
	.3358	.2940	.002	4.123	9.858
	.3334	.3617	.010	4.785	9.846
	.3117	.8074	.230	5.625	9.747
	.2313	.8977	.276	5.533	9.405
	.4155	.9912	.324	5.383	10.251
	.6891	.0132	.000	.229	11.882
	.6942	.0279	.000	.484	11.916
	.7009	.0472	.001	.816	11.960
	.7082	.0678	.001	1.178	12.009
	.7186	.0962	.001	1.667	12.078
	.7086	.1477	.001	2.500	12.011
	.6976	.2011	.001	3.309	11.938
	.6878	.2465	.001	3.947	11.874
	.6710	.3189	.004	4.841	11.763
	.6066	.9916	.324	5.394	11.351
	.9984	.0160	.000	.328	13.930
	.9983	.0344	.000	.700	13.930
	.9983	.0427	.000	.859	13.930
	.9981	.0683	.001	1.349	13.929
	.9980	.0906	.001	1.771	13.928
	.9978	.1152	.001	2.208	13.927
	.9976	.1497	.001	2.795	13.926
	.9974	.1749	.001	3.208	13.924
.9969	.2436	.001	4.268	13.921	
.9966	.2832	.002	4.858	13.919	
.9960	.3593	.010	5.674	13.916	
.9913	.8355	.245	5.968	13.887	
.9931	.9924	.325	5.410	13.898	
25.0	.3260	.0161	.000	.248	10.297
	.3282	.0362	.000	.564	10.307
	.3301	.0533	.001	.833	10.315
	.3330	.0788	.001	1.237	10.328
	.3349	.1049	.001	1.647	10.337
	.3393	.1324	.001	2.075	10.357
	.3413	.1608	.001	2.507	10.366
	.3492	.2099	.002	3.213	10.402
	.3358	.2940	.004	4.286	10.341

Table 2 (cont.)

<u>t</u> Temp °C	<u>r</u> Deuterium fraction	<u>x</u> Mole fraction of the acid	<u>g</u> Susceptibility correction	<u>s</u> Shift ppm	<u>s₁</u> Limiting slope
25.0	.3334	.3617	.013	4.971	10.330
	.3117	.8074	.240	5.773	10.234
	.2313	.8977	.289	5.686	9.904
	.4155	.9912	.339	5.557	10.719
	.6891	.0132	.000	.234	12.272
	.6942	.0279	.000	.498	12.304
	.7009	.0472	.001	.845	12.346
	.7082	.0678	.001	1.217	12.392
	.7186	.0962	.001	1.721	12.457
	.7086	.1477	.001	2.580	12.394
	.6976	.2011	.002	3.413	12.325
	.6878	.2465	.003	4.069	12.264
	.6710	.3189	.006	4.980	12.160
	.6239	.3894	.022	5.496	11.873
	.6066	.9916	.339	5.567	11.769
	.9984	.0160	.000	.332	14.153
	.9984	.0212	.000	.445	14.153
	.9983	.0344	.000	.712	14.152
	.9983	.0427	.001	.875	14.152
	.9981	.0683	.001	1.374	14.151
	.9980	.0906	.001	1.806	14.151
	.9978	.1152	.001	2.256	14.150
	.9976	.1497	.001	2.859	14.149
	.9974	.1749	.002	3.282	14.148
	.9969	.2436	.002	4.360	14.145
	.9966	.2832	.004	4.946	14.143
	.9960	.3593	.012	5.780	14.140
	.9913	.8355	.255	6.136	14.115
	.9931	.9924	.339	5.591	14.125
	55.0	.3260	.0161	.000	.263
.3282		.0362	.001	.595	10.888
.3301		.0533	.001	.877	10.897
.3330		.0788	.001	1.300	10.909
.3349		.1049	.001	1.730	10.917
.3393		.1324	.002	2.178	10.936
.3413		.1608	.002	2.629	10.945
.3492		.2099	.003	3.362	10.979
.3358		.2940	.006	4.472	10.921
.3334		.3617	.015	5.171	10.911
.3320		.4020	.031	5.506	10.905
.3624		.4943	.079	5.866	11.037
.3340		.6048	.139	5.986	10.913
.3085		.6912	.187	6.010	10.806
.3117		.8074	.251	5.921	10.819
.2313		.8977	.301	5.846	10.503

Table 2 (cont.)

<u>t</u>	<u>r</u>	<u>x</u>	<u>g</u>	<u>s</u>	<u>s₁</u>
Temp °C	Deuterium fraction	Mole fraction of the acid	Susceptibility correction	Shift ppm	Limiting slope
55.0	.4155	.9912	.353	5.744	11.281
	.6891	.0132	.000	.245	12.741
	.6942	.0279	.000	.520	12.770
	.7009	.0472	.001	.880	12.809
	.7082	.0678	.001	1.266	12.852
	.7186	.0962	.001	1.788	12.912
	.7086	.1477	.002	2.681	12.854
	.6976	.2011	.003	3.543	12.790
	.6878	.2465	.004	4.216	12.733
	.6710	.3189	.008	5.139	12.637
	.6555	.3804	.022	5.687	12.548
	.6239	.3894	.026	5.682	12.369
	.6156	.4564	.059	5.987	12.322
	.6086	.5084	.087	6.102	12.283
	.5981	.5802	.126	6.182	12.224
	.5743	.7198	.202	6.206	12.093
	.6066	.9916	.353	5.763	12.272
	.9984	.0160	.000	.343	14.420
	.9984	.0212	.000	.450	14.420
	.9983	.0344	.000	.731	14.419
	.9983	.0427	.001	.896	14.419
	.9981	.0683	.001	1.411	14.419
	.9980	.0906	.001	1.854	14.418
	.9978	.1152	.001	2.321	14.417
	.9976	.1497	.002	2.942	14.416
	.9974	.1749	.002	3.379	14.416
	.9969	.2436	.004	4.474	14.413
	.9966	.2832	.005	5.059	14.412
	.9960	.3593	.015	5.900	14.409
	.9958	.3912	.026	6.141	14.409
.9952	.4654	.064	6.413	14.406	
.9946	.5353	.101	6.496	14.403	
.9934	.6657	.173	6.530	14.398	
.9913	.8355	.266	6.287	14.389	
.9931	.9924	.354	5.779	14.397	
65.0	.3260	.0161	.000	.269	11.073
	.3282	.0362	.001	.605	11.082
	.3301	.0533	.001	.892	11.090
	.3330	.0788	.001	1.321	11.102
	.3349	.1049	.001	1.758	11.110
	.3393	.1324	.002	2.212	11.129
	.3413	.1608	.002	2.670	11.138
	.3492	.2099	.003	3.412	11.171
	.3358	.2940	.006	4.532	11.114
	.3334	.3617	.016	5.232	11.104

Table 2 (cont.)

<u>t</u>	<u>r</u>	<u>x</u>	<u>g</u>	<u>s</u>	<u>s₁</u>
Temp °C	Deuterium fraction	Mole fraction of the acid	Susceptibility correction	Shift ppm	Limiting slope
65.0	.3320	.4020	.032	5.569	11.098
	.3624	.4943	.080	5.911	11.229
	.3340	.6048	.141	6.020	11.107
	.3085	.6912	.189	6.046	11.001
	.3117	.8074	.254	5.963	11.014
	.2313	.8977	.304	5.893	10.703
	.4155	.9912	.357	5.801	11.468
	.6891	.0132	.000	.250	12.897
	.6942	.0279	.000	.528	12.926
	.7009	.0472	.001	.892	12.964
	.7082	.0678	.001	1.282	13.005
	.7186	.0962	.001	1.810	13.063
	.7086	.1477	.002	2.716	13.007
	.6976	.2011	.003	3.587	12.945
	.6878	.2465	.004	4.265	12.890
	.6710	.3189	.008	5.191	12.796
	.6555	.3804	.023	5.749	12.709
	.6239	.3894	.027	5.744	12.534
	.6156	.4564	.060	6.026	12.488
	.6086	.5084	.088	6.142	12.450
	.5981	.5802	.127	6.218	12.393
	.5743	.7198	.205	6.238	12.265
	.6066	.9916	.357	5.826	12.439
	.9984	.0160	.000	.347	14.509
	.9984	.0212	.000	.457	14.509
	.9983	.0344	.000	.739	14.508
	.9983	.0427	.001	.904	14.508
	.9981	.0683	.001	1.426	14.508
	.9980	.0906	.001	1.872	14.507
	.9978	.1152	.001	2.344	14.506
	.9976	.1497	.002	2.972	14.506
	.9974	.1749	.002	3.413	14.505
	.9969	.2436	.004	4.513	14.503
	.9966	.2832	.006	5.098	14.502
	.9960	.3593	.016	5.939	14.499
	.9958	.3912	.027	6.189	14.498
	.9952	.4654	.065	6.454	14.496
	.9946	.5353	.103	6.531	14.494
	.9934	.6657	.175	6.580	14.489
	.9913	.8355	.269	6.324	14.480
	.9931	.9924	.358	5.835	14.487

The shifts s_2 of the anhydrous acid

$$s_2 = 5.348 + 7.25 \cdot 10^{-3}t - 1.44 \cdot 10^{-5}t^2 \quad (6)$$

were calculated from the light acid shift data. The shifts s_2 have been found to be practically independent of r if referred to H_2O .

The parameter s_E (Table 3), which represents the observed shift for an equimolal solution, was obtained by interpolation of the observed data at $x = 0.5$.

The results for the shifts agree very well with the observations of Hood, Redlich and Reilly¹ ($s_1 = 9.17$) and Covington and co-workers¹⁴ (9.14). The values of s_1 are to be compared with $s_1 = 9.183$ at 25°C in Table 1. The slope s_1 agrees satisfactorily with Hindman's result¹⁵ 9.32. Larger differences exist between the present data and the early observations of Gutowsky and Saika¹⁶ (10.5) and Hood and Reilly² ($s_1 = 9.16$, recalculated following Covington's¹⁴ suggestion).

Table 3. Specific Shifts and Constants ($r=0$)

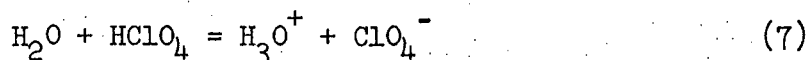
Temp t°C	H_3O^+ σ_1	$H_5O_2^+$ σ_2	$H_9O_4^+$ σ_4	$HClO_4$ s_2	s_E	α_E
0	5.698	4.487	2.889	5.348	--	--
25	5.800	4.698	3.061	5.520	(5.501)	(.845)
55	5.981	4.965	3.268	5.703	5.634	.806
65	6.056	5.058	3.337	5.759	5.668	.780

3. Specific Shifts

The data presented furnished more or less accurate information on the specific shifts of several molecular species.

According to the Raman spectra⁹ of 1943 and the subsequent NMR

data, the dissociation of water



is complete in nearly anhydrous perchloric acid. As long as there are only two molecular species with different specific shifts present, the observed shift s is always a linear function of p . In other words, the straight line of the limiting slope shown in Figure 1 between $p = 1$ and $p = 3$ represents complete dissociation of water to H_3O^+ and ClO_4^- . At $p = 1$ no excess of HClO_4 is left; the linearly extrapolated value of s at $p = 1$ in Figure 1 furnishes the specific shift $\sigma_1 = 6.056$ (65°C) of H_3O^+ (referred to H_2O). This value of σ_1 may be compared to Grahn's two theoretical values¹⁷, 8.3 and 9.9. Deviations of the observed shift from the straight line are to be interpreted as indicating incomplete dissociation and the formation of higher hydrates of the hydrogen ion.

The limiting slope s_1 for dilute solutions furnished the specific shift of the hydrated hydrogen ion species existing at infinite dilution. Following numerous authors^{18,19,20,21,22}, we assume that this is the tetrahydrate H_9O_4^+ . Replacing the tetrahydrate by the pentahydrate²³ would not lead to any essential change in the calculation of the degrees of dissociation. But the earlier assumption that the specific shift has the same value s_1 for all hydrogen ions cannot be maintained. Hood and Reilly² had already pointed out that this assumption was questionable... a comment repeated later by Covington, Tait, and Wynne-Jones²⁴.

Since s_1 is defined as a slope with respect to p (i.e., as a slope for H_3O^+), the specific shift σ_4 of a single proton in H_9O_4^+ is given by

$$\sigma_4 = s_1/3 \quad (8)$$

Table 3 shows that large differences exist between σ_1 and σ_4 . Similar data are given in Table 4 for the corresponding specific shifts $\bar{\sigma}_1$ and $\bar{\sigma}_4$ in heavy acid solutions.

Table 4. Specific Proton Magnetic Shifts for r=1.

<u>t°C</u>	<u>$\bar{\sigma}_1$</u>	<u>$\bar{\sigma}_4$</u>	<u>\bar{s}_E</u>
0	7.003	4.647	--
25	7.074	4.720	--
55	7.136	4.809	6.48
65	7.150	4.838	6.53

We have no direct experimental information on specific shifts of the dihydrate and trihydrate. An interpolation of specific shifts can be plausibly based on the assumption that σ is a smooth function of the average charge residing on one hydrogen, that is, $1/3$ for the monohydrate, $1/9$ for the tetrahydrate, and zero for water. On this basis, the values σ_2 in Table 3 have been obtained by parabolic interpolation for a charge $1/5$.

4. Dissociation in the Upper Range

The primary problem in the investigation of the molecular structure of perchloric acid solutions arises in the middle range around $x = 0.5$. The complete dissociation of the acid in dilute solutions and of water in nearly anhydrous solutions are well established. The absence of a cusp in the freezing diagram and abrupt changes in properties of the solutions near $x = 0.5$ indicate sufficiently that the dissociation is incomplete in the middle region.

The concentration of free water is very low around $x = 0.5$. Mascherpa's vapor pressure measurements⁷ show that the activity of water (referred to pure water) at 25°C and at the azeotropic composition ($x = 0.32$) is about 0.01; for $x = 0.5$ we estimate²⁵ its value at 0.0013. This is, of course, no basis for a quantitative estimate of the concentration of free water but it may be safely assumed that the water concentration is small.

However, an incompletely dissociated equimolar solution must contain at least one other species in addition to H_3O^+ , ClO_4^- and $HClO_4$. The most likely species is the dihydrate $H_5O_2^+$, provided that different definite hydrates exist at all. If there are none, a representation by definite species may still be used as an approximate model.

For the upper range, namely, for $x \geq 0.5$, the assumption that the species H_3O^+ , $H_5O_2^+$, ClO_4^- and $HClO_4$ exist is both necessary and sufficient. Higher hydrates cannot be present in appreciable amounts. The degree of dissociation of the acid will be denoted by α , so that the "true" mole fractions are

$$\begin{array}{ll} (1-\alpha)x & \text{for } HClO_4 \text{ (specific shift } s_2) \\ 2\alpha x - 1 + x & \text{for } H_3O^+ \text{ (specific shift } \sigma_1) \\ 1 - x - \alpha x & \text{for } H_5O_2^+ \text{ (specific shift } \sigma_2) \\ \alpha x & \text{for } ClO_4^- . \end{array}$$

The mole fractions of the monohydrate and dihydrate result from the condition of electroneutrality and the stoichiometric mole fraction $(1 - x)$ of water.

The shift in the upper range is to be interpreted, therefore, as

$$\begin{aligned}
 s &= [3\sigma_1(2\alpha x - 1 + x) + 5\sigma_2(1 - x - \alpha x) + s_2(1 - \alpha)x]/(2 - x) \\
 &= [-1.5 + (0.5 + 2\alpha)p]\sigma_1 + [3 - (1 + 2\alpha)p] \cdot 5\sigma_2/6 + (1 - \alpha)ps_2/3. \quad (9)
 \end{aligned}$$

The values of α computed from this equation are shown in Table 1 and Figure 3. They approach zero at $x = 1$ with a finite slope. The limiting slope (indicated in Figure 3), is represented by

$$\alpha = 1 - x, \quad (10)$$

i.e., in the limit an ion is formed for each water molecule added to the anhydrous acid. The result establishes with a much higher accuracy a conclusion drawn before from Raman intensities.⁹

We may also express the data as degrees of dissociation of the water α_W , namely, as the number of ClO_4^- ions divided by the stoichiometric number of water molecules, or

$$\alpha_W = \alpha x / (1 - x) \quad (11)$$

with the limit

$$\alpha_W = x. \quad (12)$$

The observed values of α_W are also given in Table 1 and Figure 3. The deviations of α_W from the smooth curve between $x = 0.8$ and $x = 0.9$ appear to be experimentally well established.

5. Dissociation in the Lower Range

The interpretation of the upper range was based on the reasonable assumption that only three hydrogen-containing species are present. On dilution below $x = 0.5$ higher hydrates appear and a straightforward computation of α becomes impossible.

The following information is available. From the upper range we have the value of α_E at $x = 0.5$ and the slope $(d\alpha/dx)_E$ at the same point (Table 3). Moreover, from the data of Figure 2 we can conclude

that $d\alpha/dx$ is zero in the limit for $x = 0$. In a power series of s/p , any deviation of α from unity at low concentrations would result in a deviation of first order in p . Since the linear coefficient in this series is zero, there cannot be a linear deviation of α from unity.

The horizontal limiting slope of s/p (Figure 2) indicates, moreover, a finite limit for the hydration number of the hydrogen ion. If the hydration number were not limited, the specific shift of the hydrogen ion would indefinitely increase on dilution (even if $\alpha = 1$) and s/p would vary linearly even at low concentrations.

Since incomplete dissociation would also entail an increase of s/p on dilution, the two effects cannot compensate each other. It may be concluded that both are absent.

The total available information consists, therefore, of the values of α and $d\alpha/dx$ at the end points $x = 0$ and $x = 0.5$. A similar interpolation problem has been solved before by a hyperbola.²⁶ The interpolated hyperbola is shown in Figures 3 and 4. The interpolated values of α are shown in parentheses in Table 1.

A glance at Figure 3 shows that the hyperbolic interpolation is reasonable and that no interpolation satisfying the two end points and the two limiting slopes could be much different. Nevertheless, the accuracy and reliability of such an interpolation are obviously limited.

As early as 1959 Professor T. F. Young pointed out in a personal communication²⁷ that the degrees of dissociation obtained from Raman intensities are considerably higher than those derived before from proton magnetic resonance.^{1,2} This information was substantiated by Gasner²⁸, who estimated complete dissociation within one percent up to $x = 0.194$

and $\alpha = 0.96 \pm 0.03$ for $x = 0.309$ at 30°C .

Heinzinger and Weston²⁹ found even lower values by the same method. Covington, Tait and Wynne-Jones²⁴ also repeated the Raman measurements.

All these results, as seen in Figure 4, are scattered considerably above or below the lines obtained by interpolation. They lead to the conclusion that no set of experimental data restricted to concentrations below the azeotrope ($x = 0.32$ or $c = 12$ moles/liter) can give significant information on the dissociation of perchloric acid.

The agreement with previous NMR determinations has been discussed before. But the limiting slope s_1 (equal to 9.183 at 25°C) cannot be interpreted any more as the specific shift of H_3O^+ . Figure 1 shows that the specific shift σ_1 of H_3O^+ , obtained by back extrapolation from $p = 3$ to $p = 1$, is 6.056 at 65°C , much lower than s_1 . This limiting slope, therefore, must be interpreted as $3\sigma_1$ (equation (8)). Since the experimental data cannot be resolved into separate contributions of the various hydrates from tetrahydrate to monohydrate, the hyperbolic interpolation between $x = 0$ and $x = 0.5$ appears to be the only practical method. The experimental results in this range, though not directly appearing in the computation of α , actually determine, together with the data of the upper range, the parameters of the hyperbola.

6. Dissociation Constants

The derivation of the dissociation constant

$$K_c = a_2' / [(1-\alpha)\beta'c] \quad (13)$$

by means of the activity a_2' of the solute, the activity coefficient β' of the undissociated molecule, and the concentration c (moles of solute per liter) has been discussed in the first paper³⁰ of this series. In

the present work, the definition

$$K_2 = a_2 / [(1-\alpha)\beta_2 x a_1] \quad (14)$$

has been preferred because of the high concentrations involved and because the use of the volume concentration c is inconvenient for precise measurement in a larger temperature range. In equation (14) the standard state of the solute is defined by

$$\lim_{x=0} (a_2/x^2) = 1. \quad (15)$$

Similarly, the activity of the undissociated acid is represented by

$(1-\alpha)\beta_2 x$ with

$$\lim_{x=0} \beta_2 = 1. \quad (16)$$

The activity a_1 of water ($\lim_{x=0} a_1 = 1$ at $x = 0$) is introduced in K_2 so that the reaction given in equation (7) is more closely represented by equation (14); actually the introduction of a_1 or, in addition, the insertion of the tetrahydrate in equation (7) has no noticeable influence on the value of K_2 obtained by extrapolation to $x = 0$.

But the definitions of K_c and K_2 are different. Since

$$\lim_{x=0} (c/x) = 55.51; \quad \lim_{x=0} (a_2'/a_2) = 55.51^2, \quad (17)$$

one concludes that

$$K_c = 55.51 K_2. \quad (18)$$

The activities²⁵ a_1 and a_2 have been derived over the whole range by Mr. W. Gargrave from isopiestic determinations^{31,32} and vapor pressures.⁷ The results for $\log (K_2 \beta_2)$ at 65°C are shown in Figure 5. The influence of the temperature is too small to be represented in the diagram.

The most likely extrapolation leads to $K_2 = 10$, the lowest reasonable

value would be $K_2 = 1$; a value as high as $K_2 = 100$ would still not be in contradiction with the results. The most likely corresponding value of K_c is

$$K_c = 550 \tag{19}$$

with the limits 55 and 5500. The range of uncertainty is still quite large. The previous estimate^{1,2} 38 was an approximation based on an insufficient model; the second estimate²⁴ 1000 was based on insufficient experimental information.

Since the degrees of dissociation are better known for the upper range, a determination of the constant K_1 for the dissociation of water in perchloric acid is considerably more certain than that of K_2 . One defines K_1 as a function of the activities b_1 of water, considered to be a strong electrolyte, and b_2 of perchloric acid, taken as a non-electrolyte, and of the degree of dissociation α_w of water as

$$K_1 = b_1 / [(1-\alpha_w)(1-x)\beta_1 b_2] \tag{20}$$

The true activity coefficient of undissociated water is called β_1 .

The activities b_1 and b_2 are defined by

$$\lim_{x=1} b_1 = (1-x)^2; \quad \lim_{x=1} b_2 = 1 \tag{21}$$

A diagram of $\log (K_1 \beta_1)$ (Figure 6) furnishes the values of K_1 by extrapolation to $x = 1$. They can be represented by

$$\log K_1 = \frac{12600}{T} - 115.0 \log T + 329.1 \tag{22}$$

The factor of $\log T$ is in sufficient accord with Pitzer's findings³⁴, that ΔC_p for the ionization of weak acids is usually between -34 and -50 cal/deg mole.

7. Deuterium Substitution

The nuclear magnetic resonance of both the proton and the deuteron may be observed, but preliminary measurements indicated that only the proton magnetic resonance measurements would give significant results at a field strength of 14,200 gauss. In anhydrous DClO_4 containing 0.2% H, the signal is strong enough for a good measurement of the proton chemical shift; this shift is practically equal to that obtained for the anhydrous acid with any given deuterium content.

The limiting slopes s_1 for light and heavy solutions of nitric and perchloric acids at four different temperatures are given in Table 5. The differences between the limiting slopes for DNO_3 and DClO_4 are significantly lower than for HNO_3 and HClO_4 ; they are believed to be due to the influence of different anions in the environment of the proton (which may be efficiently screened against anions in the deuterium solutions).

The influence of deuterium substitution on the shift in acid solutions is unexpectedly large. Moreover, the relation (Figure 2)

$$\lim_{p=0} d(s/p)/dp = 0 \quad (23)$$

does not hold at all for deuterium solutions. In accord with Allred and Kresge³³, these observations indicate a strong preference of the proton for the ions rather than for water. A more detailed discussion will be presented in a future paper of this series.

Table 5. Specific Shifts of the Hydrogen Ion.

<u>T°C</u>	<u>HNO₃</u>	<u>HClO₄</u>	<u>diff</u>	<u>DNO₃</u>	<u>DClO₄</u>	<u>diff</u>
0	10.170	8.666	1.504	14.220	13.940	.280
25	10.925	9.184	1.742	14.165	14.161	.004
65	12.133	10.012	2.123	14.077	14.515	-0.438

8. Conclusions

The present results are in sufficient agreement with the chemical shifts directly observed in prior work of lower accuracy. For solutions more concentrated than equimolar ($x = 0.5$), the existence of the molecular species H_5O_2^+ , H_3O^+ , ClO_4^- and HClO_4 appears to be well established and their concentrations are estimated. The dissociation constant of water in perchloric acid has been obtained in the range of 0 to 65°C.

In the lower range ($x < 0.5$) NMR data are not sufficient for the direct calculation of the dissociation constant of perchloric acid. In combination with the results for higher concentrations, one can estimate that the logarithm of the dissociation constant $\log K_c = 2.7 \pm 1.0$.

The shift of HClO_4 is independent of the deuterium content. In all mixtures with water the influence of deuterium is surprisingly large.

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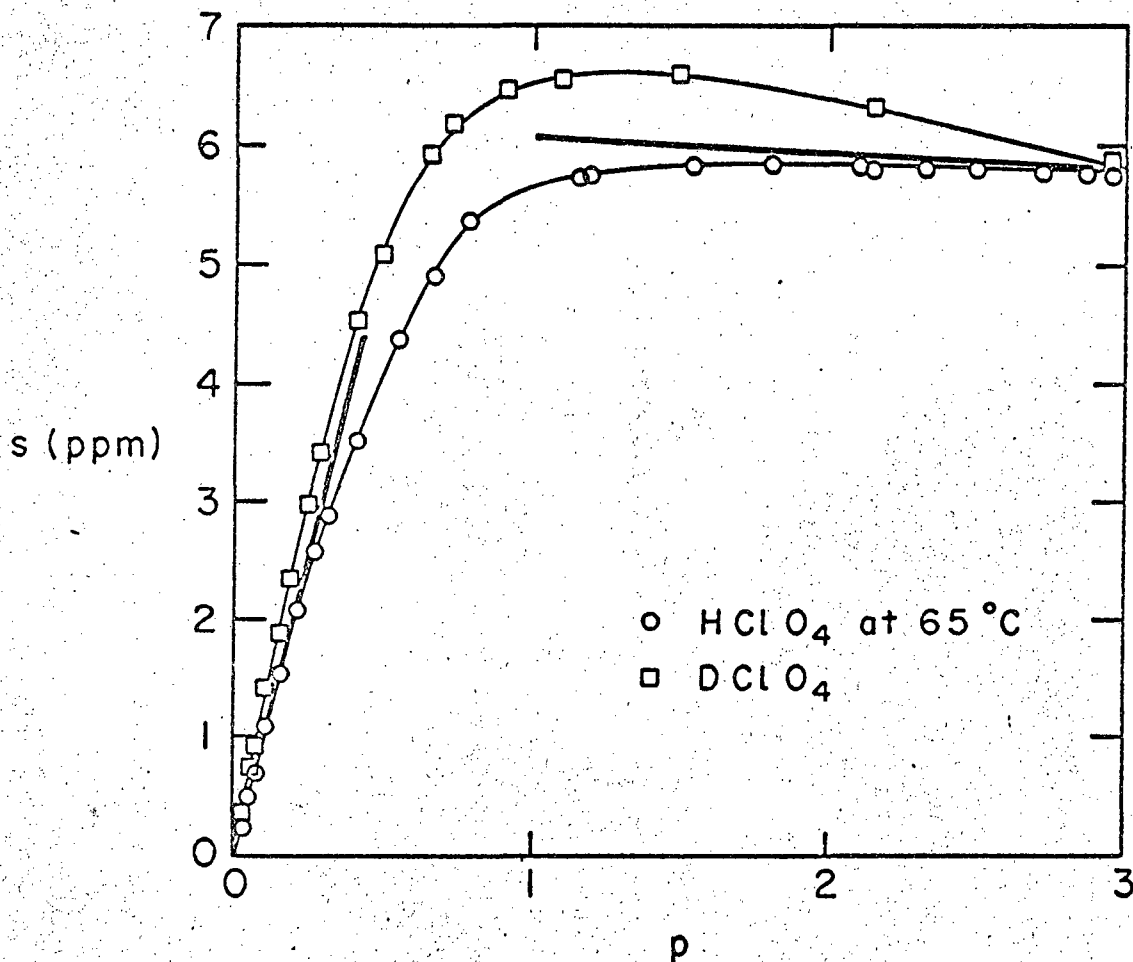
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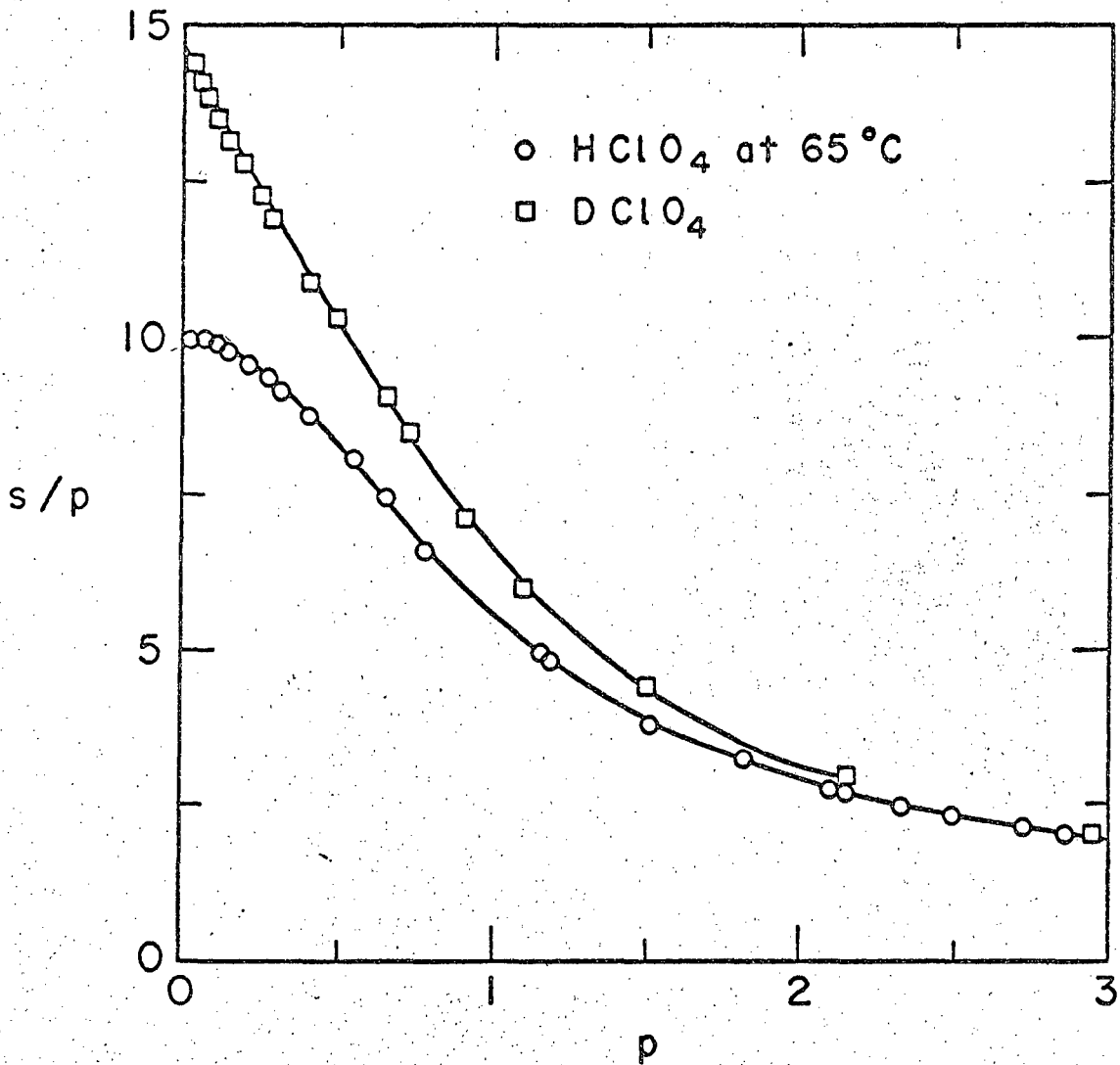
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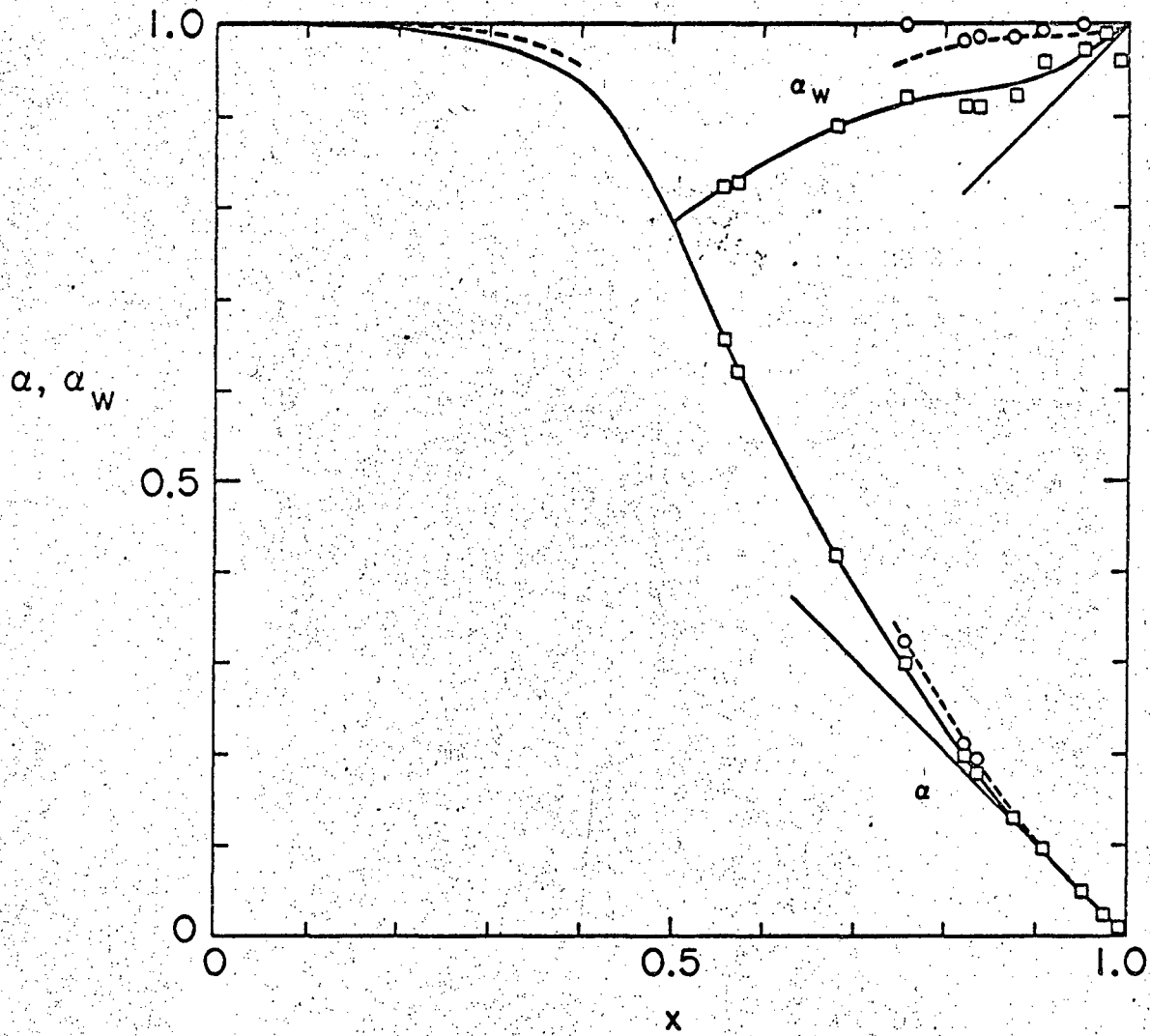
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Figure 1. Proton shift s (in ppm) of perchloric acid vs. Gutowsky's variable p at 65°C .



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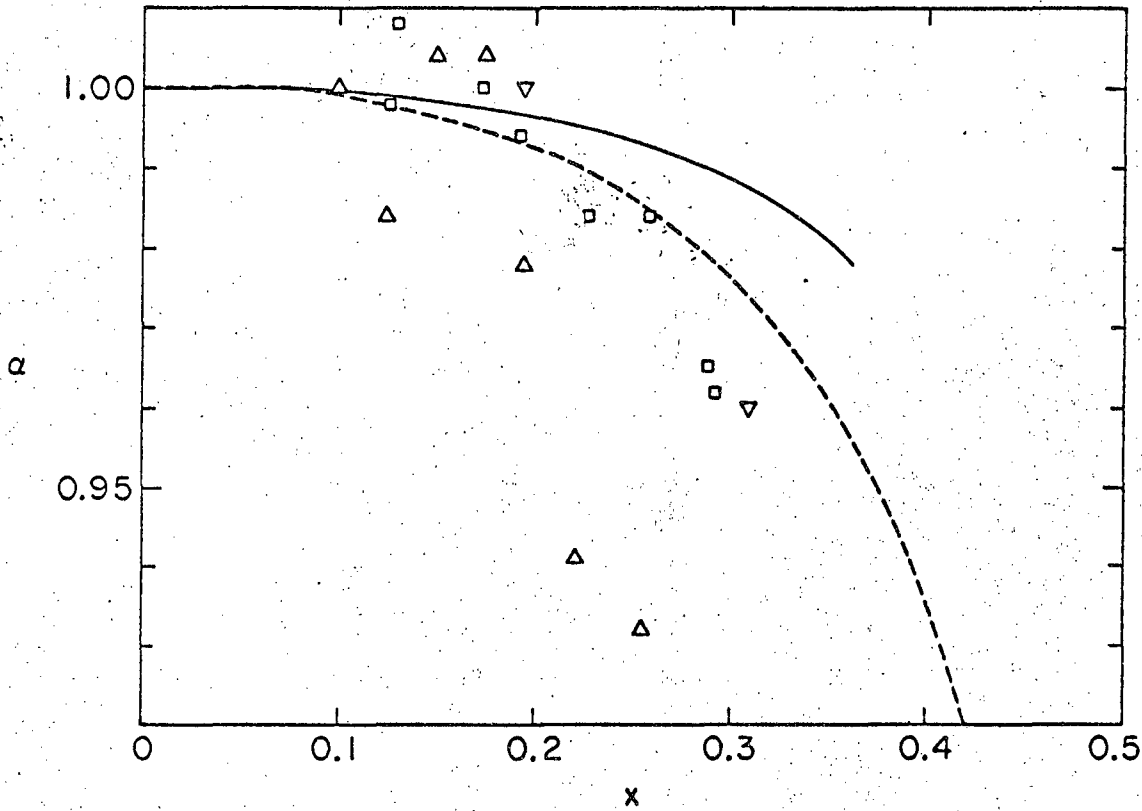
Figure 2. Diagram of s/p against p at 65°C.



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Figure 3. Degrees of dissociation α of the acid and α_w of water.

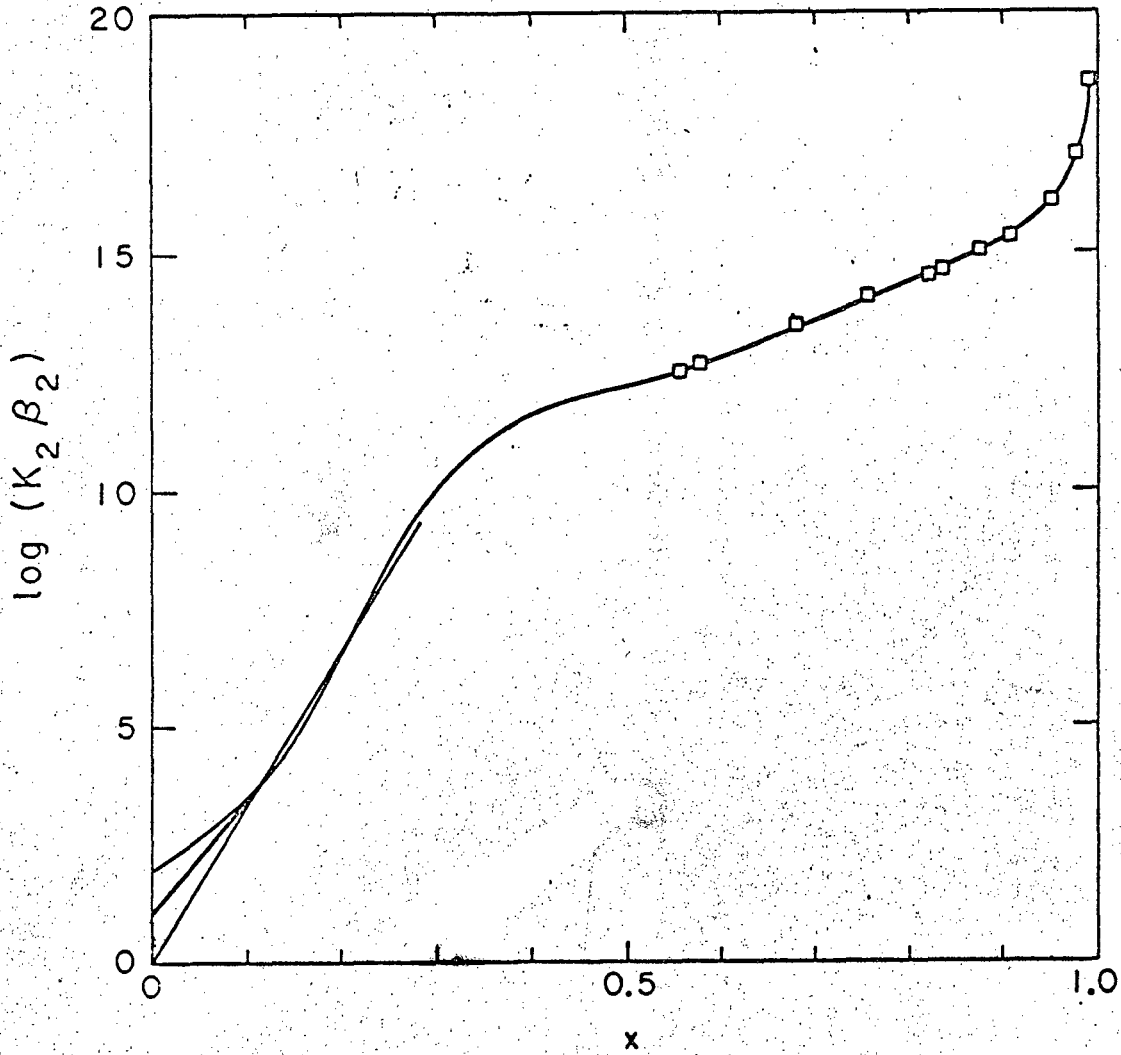
- 25°C.
- △ 55°C.
- 65°C.



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Figure 4. Degree of dissociation α against the mole fraction x .

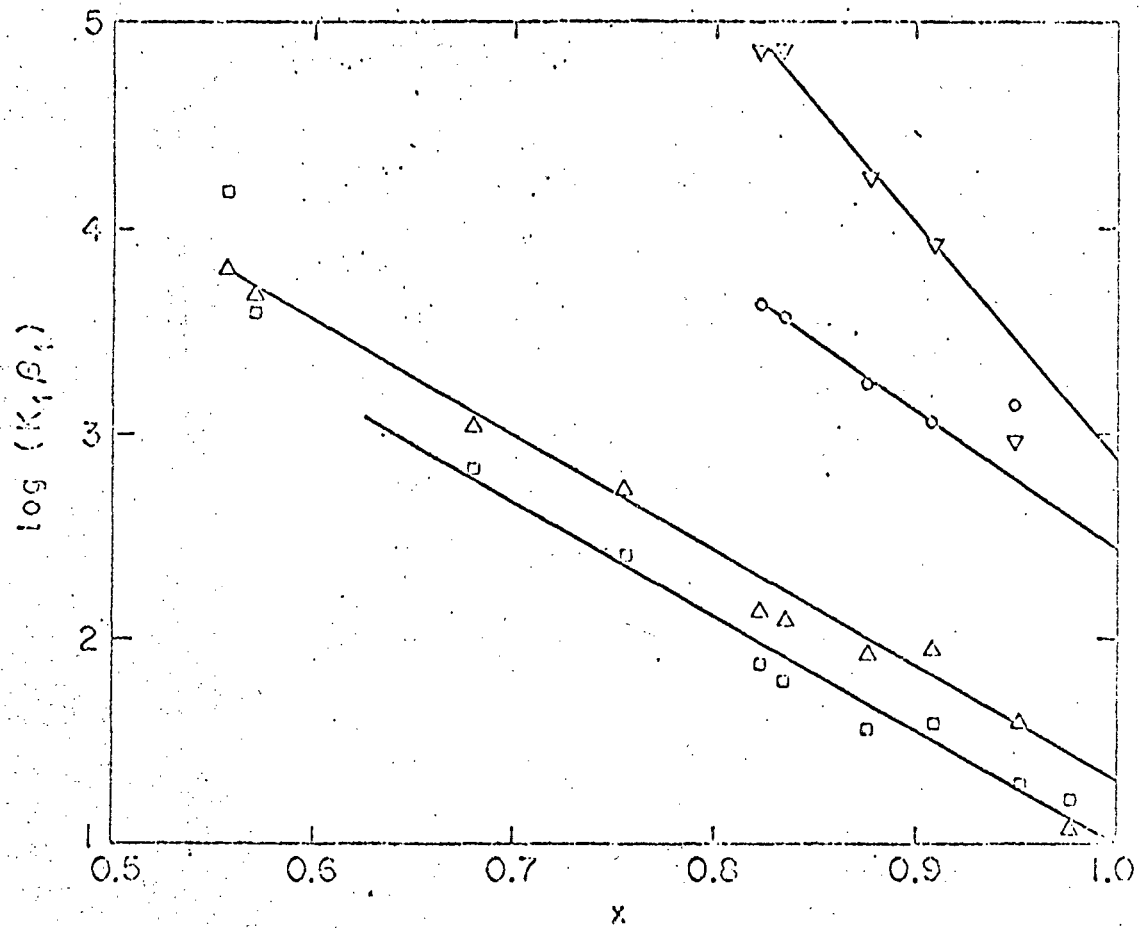
- \triangle Heininger and Weston (33°C)
- ∇ Gasner (30°C)
- \square Covington, Tait, Wynne-Jones (25°C)
- Present results (65°C) -----
- Present results (25°C) —————



XBL676-3222

Figure 5. Estimation of the dissociation constant of perchloric acid at 65°C.

$\square \log [a_2 / ([1-\alpha] \beta_2 x a_1)]$



XSL676-3223

Figure 6. Estimation of the dissociation constant of water in perchloric acid.

- ▽ 0°C
- 25°C
- △ 55°C
- 65°C

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