

If there is any ozone present, iodine titration should indicate more oxidizing power than potassium permanganate titration. We therefore compared iodine titration with potassium permanganate titration. Several portions of radiated water were mixed and divided into two portions. One was titrated immediately with potassium permanganate and to the other potassium iodide was added. After standing for one hour, the iodine liberated was titrated with 0.002 *N* thiosulfate. The amounts of oxidizing power calculated from the two titration values were identical within the limit of experimental error (about 5%). If there is any ozone produced by radiation, the amount cannot be more than one part in 20 million. Such a small amount of ozone certainly cannot account for any of the oxidation observed.

Summary

Since it has been shown that oxygen is necessary

for ultrasonic oxidation, and that the amount of hydrogen peroxide, the only oxidizing agent formed during radiation, cannot account for all the reaction observed, we are forced to conclude that oxygen is directly activated under the influence of ultrasonic radiation. Cavitation being essential, it is clear that only the oxygen molecules on the surface of the bubbles are active *during radiation*. As soon as radiation ceases, the activity of the oxygen disappears. The active oxygen can liberate iodine from iodide or react with water to form hydrogen peroxide. When carbon tetrachloride or chloroform is present, it reacts with the active oxygen to give free chlorine.

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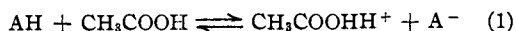
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Dissociation of Some Inorganic Acids, Bases and Salts in Glacial Acetic Acid as Solvent.¹ I

BY I. M. KOLTHOFF AND A. WILLMAN

The pioneer work of Conant and Hall² has opened the field of acidity and basicity in acetic acid as a solvent. These authors mainly concentrated on the measurement of the proton activity of various systems and were thus able to compare the acidity and basicity of different compounds. They were well aware of the fact that no quantitative conclusions could be drawn from their work with regard to the degree of dissociation of various electrolytes. In the present work this problem was approached by measuring the electrical conductivities of some acids, bases and salts and by studying the influence of small amounts of water upon the conductance of electrolyte solutions in glacial acetic acid.

Primarily the dissociation of an acid AH is determined by the tendency of the substance to split off protons and the affinity of acetic acid for protons

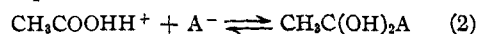


If the acid is weak, reaction (1) will be incomplete and much AH as such is left in the solution.

(1) From the experimental part of a thesis submitted by A. Willman to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1933.

(2) (a) N. F. Hall and J. B. Conant, *THIS JOURNAL*, **49**, 3047 (1927); (b) Conant and Hall, *ibid.*, **49**, 3062 (1927); (c) Hall and T. H. Werner, *ibid.*, **50**, 2367 (1928); (d) Conant and Werner, *ibid.*, **52**, 4436 (1930); (e) Hall, *ibid.*, **52**, 5115 (1930); for a complete review of the literature see (f) Hall, *Chem. Rev.*, **8**, 191 (1931).

If the acid is strong, the dissociation according to (1) has a tendency to go to completion. It should be realized, however, that acetic acid has a small dielectric constant and therefore it can be expected that part of the ions may combine to form ion pairs



Such ion pairs are comparable to the "acetacidium" compounds of Hantzsch and Voigt³ and Hantzsch and Langbein,⁴ and the hydronium perchlorate, H₃OCIO₄. It is quite possible that the weak acids can also associate with the solvent with the formation of addition compounds; the latter, however, will behave as non-electrolytes. This distinction between the character of the undissociated parts of strong and weak acids as "ion pairs" and un-ionized, respectively, is quite helpful in a qualitative interpretation of the effect of small amounts of water upon the electrical conductivity of solutions of acids in glacial acetic acid. Water is a much stronger base than acetic acid. Therefore it is to be expected that water will promote the dissociation of a weak acid AH. If on the other hand the acid is so strong that all of it is present in the form of ions and "ion-pairs," the effect of a trace of water will

(3) A. Hantzsch and W. Voigt, *Ber.*, **62**, 975 (1929).

(4) A. Hantzsch and V. Langbein, *Z. anorg. allgem. Chem.*, **204**, 193 (1932).

be very small and manifest itself by a change of the dielectric constant. This medium effect in the latter case should be comparable to that on the conductivity of neutral salts and may even be smaller if the hydronium ion has a smaller conductivity than the acetonium ion. The results in the experimental part show that the above conception is essentially correct.

Materials Used

Glacial Acetic Acid.—Since traces of water may exert a great influence upon the conductivity of acids in acetic acid, great care was taken to prepare a pure solvent. C. p. products were first distilled over chromium trioxide and then fractionated by repeated freezing until a constant melting point was obtained. By proceeding in the manner described a product having a melting point of $16.62 \pm 0.005^\circ$ was obtained (thermometer calibrated by the Bureau of Standards in 1932). The specific conductance of the best acid obtained varied from 0.5×10^{-8} to 0.8×10^{-8} (25°), while the melting points of the various products were quite constant. The specific gravity of our purified acid was 1.05605 ($15/15^\circ$).

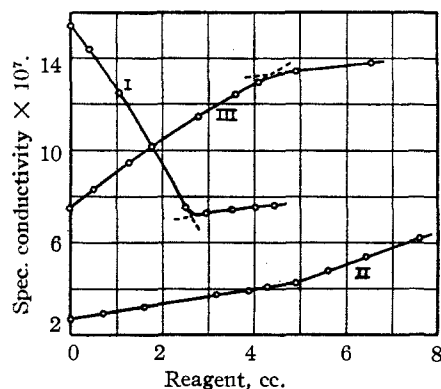


Fig. 1.—I, Conductometric titration of perchloric acid with sodium acetate; II, of sodium acetate with hydrobromic acid; III, of silver perchlorate with hydrobromic acid.

Solutions of Perchloric Acid in Acetic Acid.—Dry silver perchlorate was introduced into a bottle containing a known volume of acetic acid. Dry hydrochloric acid was bubbled in until precipitation was complete. The solution was then allowed to stand for a day in a warm place (approximately 75°), the clear solution siphoned off and purified dried air then passed through until no test for chloride was obtained. The concentration of the acid was determined by titration with a standard sodium acetate solution in acetic acid, using thymolbenzein as indicator (tropaeolin 00 gave practically the same results). Subsequent conductimetric titrations gave identical results. The shape of the curve in the titration of dilute perchloric acid with $0.06 N$ sodium acetate is given in Fig. 1.

Hydrochloric Acid in Acetic Acid.—Dry hydrogen chloride was passed into the solvent and the solution standardized gravimetrically by precipitating as silver chloride.

Hydrobromic Acid Solution.—Dry hydrogen bromide was passed into the pure solvent and the solution standardized gravimetrically by precipitation as silver bromide and volumetrically with standard sodium acetate, using thymolbenzein as indicator. It was also found that this acid as well as hydrochloric acid can be titrated with a silver perchlorate solution in acetic acid, using eosine as adsorption indicator provided that enough sodium or potassium acetate is added to neutralize the strong acid. A few conductimetric titrations were carried out. The curve obtained in the titration of approximately $0.001 N$ sodium acetate with $0.036 N$ hydrobromic acid is given in Fig. 1.

In order to determine the specific conductance of perchloric acid in an independent way, a solution of $0.0008 N$ silver perchlorate was titrated conductimetrically with the hydrobromic acid solution. The shape of the curve is given in Fig. 1. Both hydrogen chloride and hydrogen bromide are quite volatile in acetic acid, necessitating frequent standardizations.

Sulfuric Acid Solutions.—By mixing c. p. sulfuric acid and a 115% acid, 100% sulfuric acid was obtained. Weighed amounts of this acid were dissolved in acetic acid; the calculated strengths agreed within the experimental error with those found by gravimetric analysis.

Nitric Acid.—Various samples of this acid were prepared by distillation under reduced pressure from mixtures of concentrated nitric and sulfuric acids and from potassium nitrate and sulfuric acid. Weighed samples were titrated with standard base, showing a nitric acid content of 99.6 to 100%. Conductivities determined in acetic acid with various samples yielded identical results.

Sodium Acetate and Potassium Acetate.—C. p. products were twice recrystallized from pure acetic acid. The sodium acetate was dried for twenty-four hours at 140° and the potassium acetate for a short time at about 250° . Analysis of the aqueous solutions of these salts showed their purity.

Pyridine.—A commercial product was distilled over potassium hydroxide and redistilled. The fraction boiling at 113.4 to 114° at 740 mm. pressure was collected.

Lithium Chloride.—A c. p. product was recrystallized from water and dried at 150° to constant weight.

Experimental Method

Conductivity Determinations.—All measurements were made at a temperature of $25 \pm 0.05^\circ$. A cell was made of the form indicated in Fig. 2.

The electrodes consisted of sand-blasted platinum and were braced by four glass beads. Experiments showed that the resistance of a solution in this cell became constant when the plates were at least 1.75 cm. under the liquid. The cell constant was determined with dilute solutions of potassium

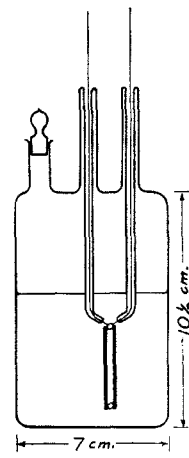


Fig. 2.—Conductance cell.

chloride in the purest conductivity water and was found to be 0.0300. The frequency of the current obtained from the oscillator was 1000. The sound of the telephone in the Wheatstone bridge was amplified by a vacuum tube circuit. In this way a sensitivity of 0.2% was obtained for resistances from 300 to 200,000 ohms, the range over which most measurements were made.

In the determinations the dry cell was weighed, then partly filled with pure acetic acid and reweighed. From the known specific gravity the volume of the acid was calculated. A standard solution of the substance, the conductivity of which was to be measured, was added from a weight buret and the concentration of the resulting solution calculated. After each measurement another amount of standard solution was added and the new concentration calculated. Each set of experiments was run in duplicate or triplicate and agreed within 1%.

No correction was applied for the conductivity of the solvent (0.5 to 0.8×10^{-8}) except in the case of lithium chloride. In the presence of acids or of acetates, it was assumed that the dissociation of the acetic acid could be neglected as a result of the common ion effect. This assumption involves an uncertainty in the values found in the very dilute solutions, especially of the weak acids—hydrochloric and nitric.

Conductivity Measurements in Pure Acetic Acid.—The experimental results are given in the following tables. The concentrations are expressed in moles per liter.

Discussion of the Results

1. The conductivities of sulfuric acid in acetic acid as reported by Hantzsch and Langbein⁴ are much greater than our values. A satisfactory agreement was found between the data reported

by Hall and Voge⁵ and our own data as is indicated in Fig. 3, and also with those of W. C. Eichelberger and V. K. La Mer.⁶ The solvent used by H. and L. probably contained some water. This, however, does not explain why the data given by H. and L. for perchloric acid are smaller than those found by us. The latter have

TABLE II
SULFURIC ACID (FIG. 3)

Molarity $\times 10^4$	$10^2 \sqrt{\kappa}$	Spec. cond. $\times 10^6$	Δc
2.97	1.725	0.0974	(0.327)
7.15	2.67	.136	.191
30.9	5.55	.278	.0898
71.8	8.47	.445	.0619
122.5	11.07	.618	.0505
160.6	12.68	.737	.0459
247	15.7	1.014	.0410
310	17.6	1.246	.0401
493	22.2	1.987	.0403
704	26.5	3.12	.0443
888	29.8	4.40	.0496
1047	32.3	5.79	.0554

TABLE III
HYDROCHLORIC ACID (FIG. 4)

Molarity $\times 10^4$	$10^2 \sqrt{\kappa}$	Spec. cond. $\times 10^6$	Δc
0.358	0.598	0.0611	(0.171)
1.317	1.147	.123	.0925
2.752	1.79	.177	.0644
5.22	2.28	.256	.0491
10.73	3.28	.385	.0360
37.7	6.14	.905	.0250
56.7	7.53	1.14	.0200
106.4	10.32	1.63	.0153

TABLE IV
HYDROBROMIC ACID (FIG. 4)

Molarity $\times 10^4$	$10^2 \sqrt{\kappa}$	Spec. cond. $\times 10^6$	Δc
0.50	0.707	0.134	(2.69)
2.87	1.69	.362	1.26
9.82	3.13	.767	0.781
18.8	4.34	1.167	.615
38.8	6.23	1.676	.432
55.9	7.48	2.11	.377

TABLE I
PERCHLORIC ACID (FIG. 4)

Molarity $\times 10^4$	$10^2 \sqrt{\kappa}$	Spec. cond. $\times 10^6$	Δc
0.1964	0.443	0.177	(8.98)
.756	.870	.383	5.03
1.396	1.18	.535	3.805
2.63	1.62	.767	2.90
4.56	2.14	1.05	2.29
8.04	2.84	1.45	1.83
13.46	3.67	1.97	1.45
25.23	5.02	2.94	1.16
33.11	5.75	3.52	1.06
49.16	7.01	4.75	0.959

TABLE V
NITRIC ACID (FIG. 4)

Molarity $\times 10^4$	$\sqrt{\kappa} \times 10^2$	Spec. cond. $\times 10^6$	$\Delta c \times 10^4$
4.06	2.0	0.87	(23.0)
52.8	7.27	1.19	2.3
173	13.1	1.64	0.96
538	23.2	2.64	.50
653	25.6	3.11	.48
1700	41.3	6.70	.39
3250	57	17.4	.53

(5) N. F. Hall and Y. Voge, *THIS JOURNAL*, **55**, 239 (1933).
(6) Eichelberger and La Mer, *ibid.*, **55**, 3635 (1933)

TABLE VI
LITHIUM CHLORIDE

Molarity $\times 10^4$	$10^2 \sqrt{c}$	Spec. cond. $\times 10^6$	Ac
0.608	0.779	0.0797	1.31
.909	.953	.109	1.20
1.334	1.155	.142	1.06
2.192	1.48	.195	0.890
3.244	1.80	.248	.764
4.97	2.23	.322	.648
6.81	2.61	.390	.573
24.72	4.98	.872	.353
64.45	8.04	1.596	.248
128.3	11.33	2.62	.204

TABLE VII
POTASSIUM ACETATE (FIG. 5)

Molarity $\times 10^4$	$10^2 \sqrt{c}$	Spec. cond. $\times 10^6$	Ac
1.788	1.337	0.1523	(0.852)
5.70	2.39	.281	.493
14.55	3.81	.462	.319
26.86	5.18	.654	.243
47.8	6.91	.913	.191
68.0	8.25	1.103	.162
94.4	9.72	1.373	.145
140.3	11.84	1.829	.130
177.0	13.3	2.175	.123
200	14.14	2.43	.122
400	20.0	4.46	.111
800	28.28	1.04	.129

TABLE VIII
SODIUM ACETATE (FIG. 5)

Molarity $\times 10^4$	$10^2 \sqrt{c}$	Spec. cond. $\times 10^6$	Ac
0.309	0.556	0.0281	0.910
1.19	1.09	.084	.706
8.15	2.86	.219	.268
16.80	4.10	.325	.193
32.9	5.73	.471	.143
62.0	7.88	.686	.111
117.0	10.80	1.024	.0875
163.0	12.76	1.300	.0797

been obtained with samples of solutions of perchloric acid prepared in various ways. Since the

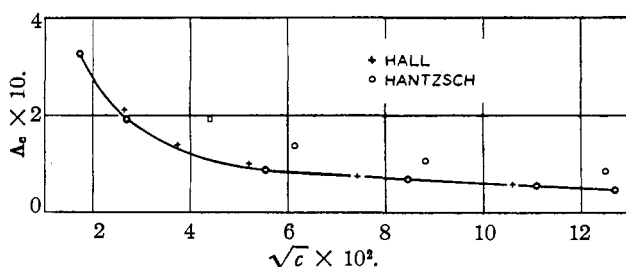


Fig. 3.—Conductance of sulfuric acid, O denotes own data.

agreement between the different series of measurements was satisfactory, it may be inferred that the data of H. and L. are slightly low.

TABLE IX
PYRIDINE

Molarity $\times 10^4$	$10^2 \sqrt{c}$	Spec. cond. $\times 10^6$	Ac
3.179	1.783	0.253	0.795
14.02	3.74	.556	.397
35.8	5.99	.949	.255
74.6	8.64	1.49	.200
514.9	22.7	9.15	.178
1277	35.7	35.32	.277
2406	49.05	139.9	.581
3976	63.1	476	1.198

Values obtained for sodium and potassium acetates are practically identical with those of

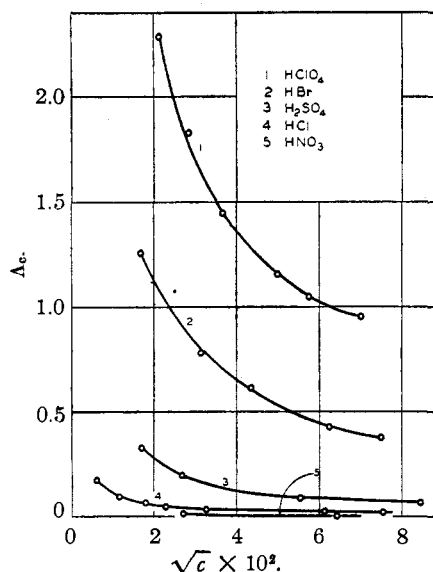


Fig. 4.—Conductances of various inorganic acids.

K. Hopfgartner⁷ except for very low concentrations where his values are lower (comp. Fig. 5). Hopfgartner, however, subtracted the conductance of the solvent in calculating the equivalent conductivity, thus neglecting the repression of the dissociation of the solvent by common ions. It should be mentioned that the solvent correction may become of importance in solutions of weak acids and bases and very dilute solutions of strong acids and bases. It is this uncertainty which makes the exactness of extrapolation to infinite dilution rather illusory. Conductivity data obtained for pyridine by A. N. Sachanov⁸ are slightly higher than ours.

2. The dissociation of inorganic acids in acetic acid decreases in the following order

(7) K. Hopfgartner, *Monatsh.*, **33**, 123 (1912).(8) A. N. Sachanov, *Chem. Abstr.*, **6**, 179 (1912).

(see Fig. 4). At the concentration of 0.005 molar the ratio of the conductivities is 400:160:30:9:1, respectively.

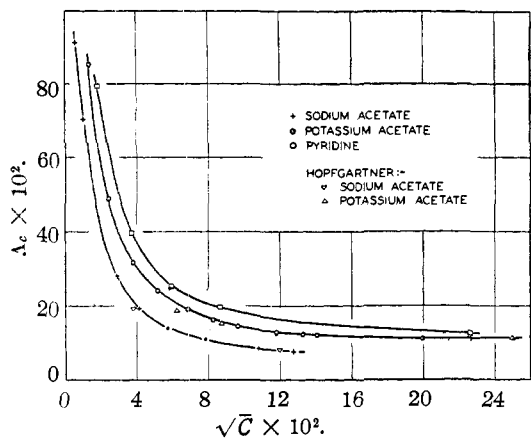


Fig. 5.—Conductances of bases, O denotes own data.

3. Although the measurements have been made at high dilutions, the Λ_c against \sqrt{c} lines are not straight as is the case in water. Straight lines are approached, however, with perchloric acid, lithium chloride and the acetates. Graphical extrapolation to an ionic strength of zero leads, even in this case, to abnormally low values of the equivalent conductivities at infinite dilutions. Hence, one is led to the conclusion that even the strongest electrolytes are partly present as ion pairs even in very dilute solutions or give rise to complex ionization, or that both occur. It is fairly certain that even the strongest bases such as pyridine, aniline and the alkali acetates are incompletely dissociated at high dilutions in acetic acid. In this connection it may be mentioned that incomplete dissociation of acetates of weak organic bases occurs even in aqueous medium as may be inferred from studies of Bartlett,⁹ Jacobs and King¹⁰ and Walden.¹¹

4. By graphical extrapolation to infinite dilution a value of 20 is obtained for the equivalent conductivity of perchloric acid. Assuming that the equivalent conductances of perchloric and acetic acids are due solely to the ions H_2Ac^+ and ClO_4^- and H_2Ac^+ and Ac^- , respectively, and both anions have the same mobility in acetic acid at infinite dilution, the ionization constant of acetic acid may be calculated from the conductivity of the pure solvent. Taking the specific conductance

of pure acetic acid equal to 1×10^{-8} (compare under Materials Used) at 25° a value of

$$K_{HAc} = [H_2Ac^+][Ac^-] = 2.5 \times 10^{-13}$$

is found. If we apply Walden's rule that $\eta\Lambda$ is constant (η being the viscosity of the solvent) (which rule certainly does not hold for the solvated proton) an equivalent conductivity of acetic acid at infinite dilution of $390 \times (0.89/1.11) = 312$ is found at 20°. On this basis a value of $K_{HAc} = 1 \times 10^{-15}$ is calculated.

Both values are much smaller than those computed from the e. m. f. measurements of N. F. Hall^{2e} of 0.05 molar diethyl-*o*-toluidine and of 0.2 molar perchloric acid solutions (Hall and Co-nant^{2a}). Assuming that both acid and base are completely ionized at these concentrations and that activities are equal to concentrations, a value of K_{HAc} of 3×10^{-10} at 25° is computed from their measurements. The discrepancy between this figure and the two reported above is to be attributed to incomplete ionization of the strong acid and base and to the difference between ion activities and concentrations.

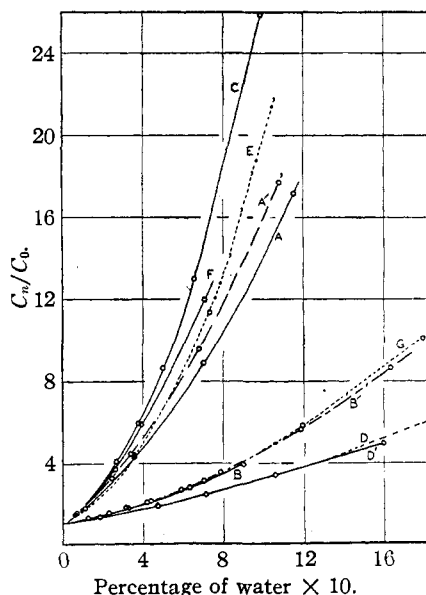


Fig. 6.—Influence of water on conductance of electrolytes.

The Effect of Water upon the Conductivity of Electrolytes in Pure Acetic Acid.—The effect of water on the conductivity of various systems was determined and tabulated. The term C_n/C_0 denotes the specific conductance of a solution with n per cent. of water to that of the same solution in the absence of water. The results are given in Tables X to XX and graphically shown in Fig. 6.

(9) P. D. Bartlett, *THIS JOURNAL*, **55**, 741 (1933).
 (10) Jacobs and King, *J. Phys. Chem.*, **34**, 1303 (1930).
 (11) P. Walden, *Z. physik. Chem.*, **A162**, 1 (1932).

TABLE X
 CONDUCTANCE OF ACETIC ACID WITH WATER

Water content acid in %	0.0	0.0485	0.254	0.680	1.16	2.34	3.32	5.18	7.50	9.25	17.7
Spec. cond. $\times 10^7$ at 25°	.060	.065	.103	.261	0.531	2.19	5.45	20.1	59.9	111	688

In addition the influence of water upon the conductivity of pure acetic acid has been determined. The results are given in Table X. The effect of water upon the conductance of the pure solvent is relatively small.

 TABLE XI
 $\text{H}_2\text{SO}_4\text{-HAc-H}_2\text{O}$ (A IN FIG. 6)
 $C_{\text{H}_2\text{SO}_4} = 0.00065$ MOLAR

% Water $\times 10$	Spec. cond. $\times 10^6$	C_n/C_0
0	0.106	1
0.74	.18	1.70
3.53	.465	4.40
7.11	.94	8.9
11.5	1.72	16.3
21.3	4.15	39.2

 TABLE XII
 $\text{H}_2\text{SO}_4\text{-HAc-H}_2\text{O}$ (A' IN FIG. 6)
 $C_{\text{H}_2\text{SO}_4} = 0.0388$ MOLAR

% Water $\times 10$	Spec. cond. $\times 10^6$	C_n/C_0
0	1.51	1
0.632	2.36	1.56
3.34	6.8	4.49
6.7	14.6	9.6
10.7	27	17.9
15.7	47.1	31.1
25	95.5	63

 TABLE XIII
 $\text{LiCl-HAc-H}_2\text{O}$ (B IN FIG. 6)
 $C_{\text{LiCl}} = 0.0068$

% H_2O $\times 10$	Spec. cond. $\times 10^7$	C_n/C_0
0	3.96	1
0.76	4.61	1.16
1.27	5.0	1.26
2.39	6.13	1.55
3.10	6.95	1.75
4.15	8.2	2.07
6.32	10.9	2.75
9.0	15.5	3.92

 TABLE XIV
 $\text{LiCl-HAc-H}_2\text{O}$ (B' IN FIG. 6)
 $C_{\text{LiCl}} = 0.0165$

% H_2O $\times 10$	Spec. cond. $\times 10^6$	C_n/C_0
0	3.26	1
0.38	3.51	1.08
1.23	4.11	1.26
3.25	5.82	1.78
5.88	8.7	2.67
7.84	11.4	3.5
11.9	18.2	5.6
16.4	28	8.6
24	48	14.7

 TABLE XV
 $\text{HCl-HAc-H}_2\text{O}$ (C IN FIG. 6)

$C_{\text{HCl}} = 0.0106$		
% H_2O $\times 10$	Spec. cond. $\times 10^6$	C_n/C_0
0	1.65	1
0.181	1.87	1.13
.925	3.0	1.83
3.67	6.5	4.0
3.8	9.7	5.9
5.0	14.2	8.6
6.6	21.5	13.0
9.0	43	26
13	74	45

 TABLE XVI
 $\text{HClO}_4\text{-HAc-H}_2\text{O}$ (D IN FIG. 6)
 $C_{\text{HClO}_4} = 0.00058$

% H_2O $\times 10$	Spec. cond. $\times 10^6$	C_n/C_0
0	1.07	1
0.44	1.15	1.08
1.76	1.4	1.3
4.6	2.0	1.85
10.5	3.6	3.3
21	7.2	6.7
40	12.7	12
70	18.3	16
113	32	30

 TABLE XVII
 $\text{HClO}_4\text{-HAc-H}_2\text{O}$ (D' IN FIG. 6)
 $C_{\text{HClO}_4} = 0.00246$

% Water $\times 10$	Spec. cond. $\times 10^6$	C_n/C_0
0	2.86	1
1.32	3.42	1.20
7.14	6.7	2.34
16.0	14.1	4.93

 TABLE XVIII
 $\text{HNO}_3\text{-HAc-H}_2\text{O}$ (E IN FIG. 6)
 $C_{\text{HNO}_3} = 0.17$ MOLAR

% H_2O $\times 10$	Spec. cond. $\times 10^7$	C_n/C_0
0	0.67	1
1.01	1.19	1.8
3.4	2.88	4.3
7.3	7.65	11.4
12.0	18.9	28.2
19.5	57.5	85.8

Discussion of the Results

1. The effect of water upon the conductivities of solutions of acids was found to be virtually independent of the concentration of the acid, except with traces of water (comp. curves A

TABLE XIX

p-TOLUENE SULFONIC ACID-HAC-H₂O (F IN FIG. 6)

% Water × 10 ²	$C_{\text{ACID}} = 0.008$ Spec. cond. × 10 ⁷	C_n/C_0
0	2.15	1
0.47	3.18	1.48
2.6	8.07	3.75
7.1	25.8	12.0
14	75.4	35
21	158	73.5
40	499	232

TABLE XX

NaAc-HAC-H₂O (G IN FIG. 6)

% Water × 10 ²	$C_{\text{NaAc}} = 0.016$ Spec. cond. × 10 ⁸	C_n/C_0
0	1.3	1
0.36	1.37	1.05
.91	1.5	1.15
2.2	1.9	1.46
4.3	2.7	2.08
7.0	4.04	3.11
12.3	7.6	5.8
18.8	14.4	11.1
26	25	19.2
46	71	54

and A', Fig. 6). This is easily explained by the fact that the final concentration of water after reacting with the solvated proton is a function of the concentration of the acid. With neutral salts (curves B and B', Fig. 6) and inorganic acetates, the effect of water is entirely independent of the electrolyte concentration.

2. The conductivities of neutral salts (B and B') and acetates (curve G, Fig. 6) are affected in the same way by water. This was to be expected since the acetate ion is a much weaker base than the hydroxyl ion. The relatively large influence of water in both cases has to be attributed to an increased ionization as a result of an increase of the dielectric constant of the medium. The behavior of the acid solutions depends upon the kind of acid present. The smallest effect of water is noticed with perchloric acid (curves D and D', Fig. 6). This acid behaves as a strong electrolyte in acetic acid; it is partially dissociated into H₂Ac⁺ and ClO₄⁻ and partly present in the form of "ion pairs" CH₃C(OH)₂ClO₄. Water being a stronger base than

acetic acid causes the transformation of acetonium ions into hydronium ions. The increase of the dissociation of the acid on addition of water is of the same order as that produced in neutral salts and in alkali acetates; a smaller mobility of H₃O⁺ as compared with that of H₂Ac⁺ would explain why the relative increase of the conductivity of perchloric acid solutions is less than that of neutral salts and acetates. The other acids studied behave no longer as strong electrolytes in acetic acid, and a very large increase of the conductivity upon addition of water is found. In addition to the effects which occur with perchloric acid, the base water displaces the equilibrium between the un-ionized part of the acid and its ions comparable to the effect of addition of ammonia to an aqueous solution of a weak acid. Consequently the addition of water to a solution of a weak acid in acetic acid gives rise to a much larger increase in the number of ions than is the case with other electrolytes.

Summary

1. The strength of inorganic acids in acetic acid decreases in the following order



2. The ionization product of acetic acid, $K_{\text{HAc}} = [\text{H}_2\text{Ac}^+][\text{Ac}^-]$ is of the order of 2.5×10^{-13} at 25°.

3. Perchloric acid behaves like a strong electrolyte in acetic acid. It is partly present as ions and partly in the form of ion-pairs, CH₃C(OH)₂ClO₄. Other acids studied are weak acids; they are partly dissociated, partly present in the form of ion-pairs, and partly in the un-ionized state. The influence of water upon the conductivities of solutions of various acids could be interpreted with the above assumptions.

4. Alkali acetates and lithium chloride behave like strong electrolytes in acetic acid. The relative increases of the conductances upon addition of water to solutions of both types of electrolytes are identical, the effect being interpreted by an increase in the dissociating power of the medium.

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