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A PRELIMINARY STUDY OF THE CONDUCTIVITY OF CERTAIN ORGANIC ACIDS IN ABSOLUTE ETHYL ALCOHOL AT 15°, 25° AND 35°.[1]

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Introductory.

Considerable work has been done in this laboratory, especially during the past five years, on the conductivity and dissociation of organic acids in water as a solvent, over a fairly wide range of temperature and dilution. This investigation is a continuation of those in non-aqueous and mixed solvents, which have been in progress in this laboratory during the past dozen years.[2] Since, up to the present but very little has been done here with solutions of the organic acids in absolute ethyl alcohol, it was decided to extend our investigations into this field.[3]

A few rather crude measurements of the conductivity of organic acids were made comparatively early in the history of the conductivity method. Wakeman,[4] in 1893, measured the conductivities of certain organic acids in mixtures of alcohol and water, ranging from pure water to 50% alcohol. He calculated the dissociations of these acids and their dissocia-

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[1] This investigation was carried out with the aid of a grant to H. C. Jones from the Carnegie Institution of Washington.

[2] Carnegie Institution of Washington, Publication No. 170.

[3] *Am. Chem. J.*, **44**, 156 (1910); **46**, 56 (1911); **48**, 320, 411 (1912); **50**, 1 (1913).

[4] *Z. physik. Chem.*, **11**, 49 (1893).

tion constants. The dissociations decrease slowly with increase in the amount of alcohol present. The constants decrease much more rapidly for the same increase in alcohol. Wakeman plotted curves with molecular conductivities as ordinates and percentage alcohol as abscissas, and showed that, when they were extended beyond 50% alcohol in the direction of 100% alcohol, the conductivities probably approached zero as a limit. He calculated that dissociation in the mixture is much less than would be expected, and showed that the Ostwald dilution law could not be applied to the mixtures containing large amounts of alcohol.

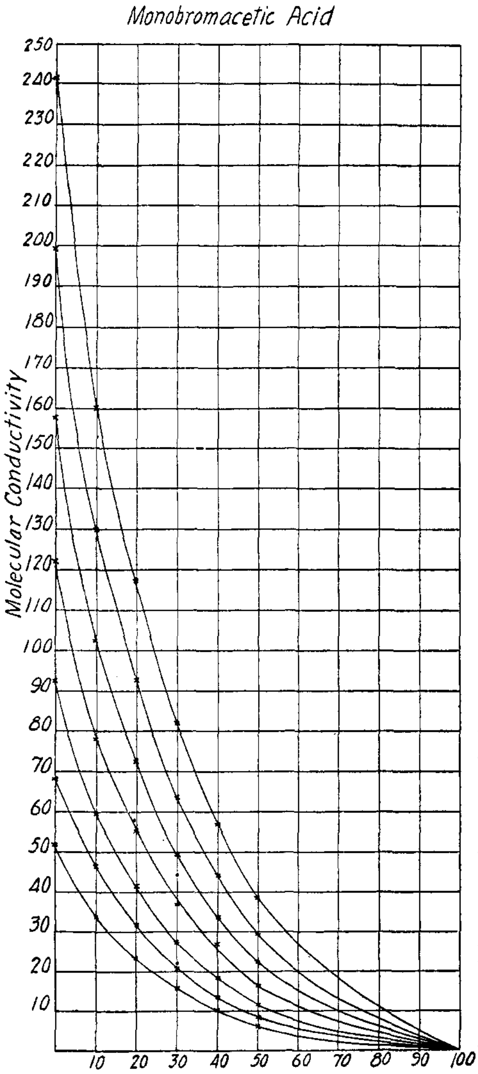

Fig. I

Schall,[1] in 1894, determined the conductivity of certain organic acids in ethyl alcohol, and in mixtures of ethyl alcohol with water. We also did some work on isobutyl alcohol. Schall concluded from his results that the molecular conductivity of organic acids is much less in the alcohols than in water, and that the acids behave very differently in alcohol-water mixtures than in the pure solvents. Some of them seem to behave just the opposite of what might be expected from their conduct in the pure solvents. For example, picric acid gives a much higher, and the others much lower, conductivity values in water-alcohol mixtures than in the pure alcohol.

A careful piece of work on the conductivity of certain organic acids in absolute alcohol at 18° seems to have been done by Wilderman[2] in

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[1] *Z. physik. Chem.*, **14,** 701 (1894).

[2] *Ibid.*, **14,** 231 (1894).

1894. A great number of precautions were taken by him in preparing the solutions and in measuring the conductivity. He does not give his results with the weaker acids, but simply states that between the volumes 10 and 160 the molecular conductivity increases approximately proportional to the volume. In summing up his work, Wilderman says that it is possible to apply the Kohlrausch method to the determination of the conductivity of strong acids in absolute alcohol, but that no reliable results could be obtained for such weak acids as acetic, monochloroacetic and succinic. He remarks that much time and patience on the part of the experimenter are required to obtain results which are at all reliable.

In a second investigation[1] Wilderman studied the same acids as in the earlier work, using in this case a precision galvanometer method and working at 25° instead of 18°. We found this method more generally applicable than that of Kohlrausch.

Considerable work[2] has recently been done in this laboratory on the conductivity of solutions in both methyl and ethyl alcohols, but this need not be discussed here.

Experimental.

The conductivity apparatus and method used for making the measurements were similar to that employed in previous work in this laboratory, except that on account of the high resistance offered by the alcoholic solutions of the acids, it was necessary to make use entirely of the cylindrical type of conductivity cell. The method of obtaining the constants of these cells has already been described.[3]

Since the percentage temperature coefficients of conductivity for substances dissolved in alcohol, as well as the coefficient of expansion of the alcohol itself, are so large, it is necessary to regulate the temperature as closely as possible. This was secured by the combination of a specially devised gas regulator and thermoregulator. These have already been described in earlier papers.[4]

In coöperation with Dr. P. B. Davis, of this laboratory, a new form of constant temperature bath was also designed. Its construction can be seen from Fig. II. A full discussion of the finally adopted form will be presented in a paper to be published by Davis, Putnam and Jones. In these baths the temperature ordinarily does not vary more than 0.02° which is sufficiently constant for our purpose. With special precautions as to insulation against changes in temperature, and with further modification of the thermoregulator, the variation can be decreased to a few

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[1] *Z. physik. Chem.*, **14**, 247 (1894).

[2] Carnegie Institution of Washington, Publications Nos. 80 and 180.

[3] *Am. Chem. J.*, **42**, 527 (1909); **44**, 64 (1911).

[4] *Z. physik. Chem.*, **85**, 519 (1913).

thousandths of a degree. Aside from the better temperature regulation obtained in this form of thermostat bath, there are also one or two other advantages derived from its use. The bath is made of copper which does not rust, and the stirring arrangements and the cooling coil are on the side of the bath, and are therefore out of the way. A number of minor improvements were also made.

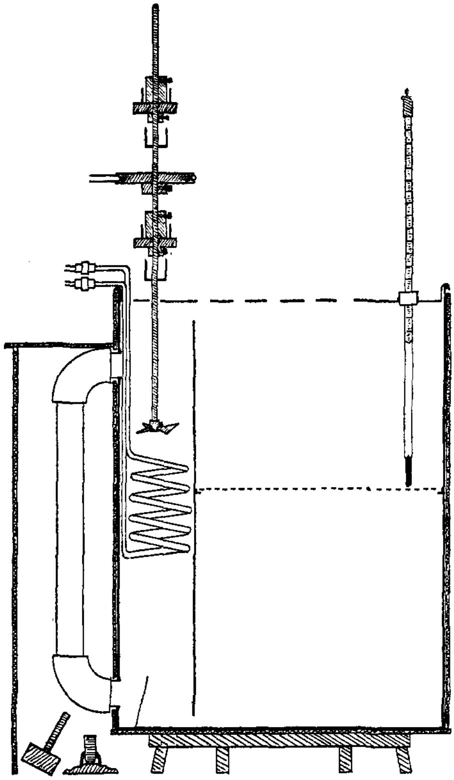

Fig. II.

Solutions were made up in 200 cc. flasks calibrated for 25°, and the measurements of the conductivities of these solutions were made at 15°, 25° and 35°. Pipets, on account of greater convenience in handling, were frequently used for measuring purposes. They were in all cases carefully recalibrated. Corrections for the expansion and contraction of the alcoholic solutions at 35° and 15°, respectively, were of course applied to the conductivity measurements.

The alcohol was prepared by heating ordinary 95% alcohol for several days with fresh lime in a copper tank, provided with a ground brass stopper and reflux condenser, and then distilling it through a block-tin condenser. The distillate was reheated with fresh lime and again distilled, the first and last portions of this distillate being discarded. A few sticks of sodium hydroxide added during the last day of heating insured the removal from the distillate of any aldehyde which might have been present, and which otherwise would have distilled over with the alcohol. By taking proper precautions, it is possible to obtain alcohol by this method having a specific gravity of 0.78506 to within the limit of error ±0.00002. According to Circular 19 of the Bureau of Standards, such alcohol is pure. The alcohol employed in the conductivity measurements varied in specific gravity from 0.78506 to 0.78517, the latter containing 99.964% alcohol. The receiver for the distillate was a 6-liter Jena glass bottle. The stopper was a three-holed paraffined cork. Through one hole passed a siphon, through another an adapter with a glass stopcock, and through the third a calcium chloride-soda lime tube, also having a glass stopcock. In this way the alcohol was well protected during distillation from impurities in the air, and small quantities sufficient for making up the solutions could be drawn off without exposing the main supply.

After weighing out the quantity of dried and purified acid necessary to make a solution of the required normality, the acid was washed off the watch glass or out of the weighing bottle into a funnel, and then into a 200 cc. Jena flask which had previously been thoroughly washed with water, and then with some of the alcohol with which the solution was to be made up. The flask was then filled to the neck with alcohol and shaken until all the acid had dissolved. It was then hung in a 25° thermostat bath until temperature equilibrium was reached, and finally filled to the mark.

In the meantime a conductivity cell, which had been thoroughly washed the day before, and in which pure alcohol had been allowed to stand over night, was dried with filtered dry air. It was then rinsed several times with portions of the solution which had just been made up, and finally nearly filled with this solution.

It was at first thought advisable to use an alcoholic solution of potassium hydroxide for titration purposes. General difficulties were, however, encountered. An approximately 0.1 *N* solution of potassium hydroxide in absolute alcohol was made up and allowed to stand for a couple of days. The carbonate settles, leaving a clear, supernatant solution. But if the bottle was opened even for a very short time, the solution became cloudy, and when poured into a buret became white with precipitated carbonate.

A method of filtering the solution, being a modification of one previously used in this laboratory, was then adopted, together with an arrangement for siphoning the solution out of the bottle into the buret. Fig. III shows the design of the filtering apparatus. The tower T contains sticks of sodium hydroxide, and T′ is partly filled with metallic sodium. The former acts as a protecting agent to the latter, which

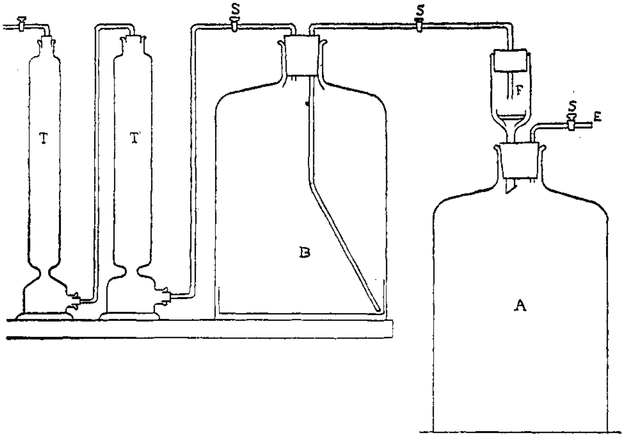

Fig. III.

serves both for removing the last traces of carbon dioxide and for drying the air. B is an empty bottle, which is later interchanged with a bottle filled with an alcoholic solution of potassium hydroxide prepared from freshly distilled alcohol. Tube E is connected with suction, so that dried, purified air passes through the whole system, including the Gooch funnel F, containing asbestos previously washed with an alcoholic solution of potassium hydroxide and then pure alcohol, and through the receiving bottle A. When the system has been thoroughly cleansed with dry air, free from carbon dioxide, the stopcocks G are closed and the bottle B is replaced by the one containing alcoholic potash. The stopcocks are then opened and suction again applied at E. When all the solution has been filtered, A is removed and, as quickly as possible, the stopper arranged to connect it by a siphon with the buret is introduced as shown in Fig. IV. A little carbonate is formed by opening in this way to the air, but it is a very small quantity, and in the course of a few days is entirely precipitated to the bottom of the bottle.

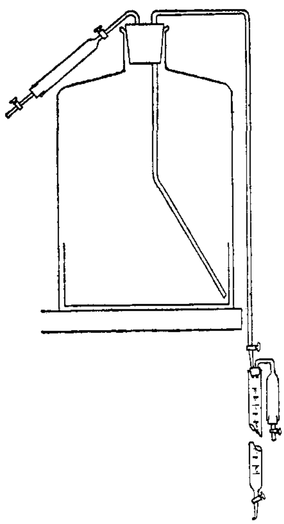

Fig. IV.

The drying flasks are filled with a mixture of calcium chloride and soda lime, to protect the alcoholic solution when the stopcocks S and S' are opened. The stoppers T and T' are of cork and are thoroughly paraffined. Such a system as this remains protected from the air for a period of several months.

The alcoholic solution, in course of time, becomes colored slightly yellow, but its alkaline concentration is apparently not changed, as can be seen by comparing titrations made against a standard acid in February and again in May.

On February 25, 10 cc. of standard acid = 8.87 cc. of alkali.
On May 7, 10 cc. of standard acid = 8.87 cc. of alkali.

The bottle containing the alkali was covered with a dark material, since, in the presence of light, the tendency of the alkaline solution to become colored is much greater than in the dark.

One of the greatest difficulties encountered in connection with the alcoholic potash method was that of temperature changes. The coefficient of expansion of alcohol is so large that even small changes in the temperature of the laboratory and consequent changes in the temperature of the solution will change quite appreciably the normality of the alkali.

It was this difficulty which led us to use an aqueous solution of ammonia with coralline as an indicator, instead of the alcoholic caustic potash with phenolphthalein as the indicator. The ammonia was prepared by heating concentrated ammonia and passing the gas which was given off, first over sticks of sodium hydroxide, which collected a large part of the water vapor and any carbon dioxide, and then over sodium, which absorbed the remainder of the water-vapor; and finally into a weighed quantity of conductivity water in a measuring flask, until the amount of the gas necessary to make a 0.1 *N* solution was dissolved. This solution was titrated against standard sulfuric acid to obtain its normality.

Coralline was used as the indicator, because it is sensitive to the organic acids, and is not sensitive to carbon dioxide, except when the latter is present in fairly large quantity. In order to test whether coralline is sensitive to small quantities of carbon dioxide, under the conditions under which we worked, another investigator in this laboratory—Mr. J. E. L. Holmes—measured out two equal quantities of a standard acid, added an equal amount of coralline to each, and then allowed carbon dioxide to bubble through one of these solutions for some minutes. Titrations of both solutions were made, and practically no effect due to the presence of carbon dioxide was found. Equal volumes of the standard acid were again measured out and carbon dioxide passed into one of the solutions for a considerable time. The two solutions were then titrated. There was, under these conditions, a small difference noted. In both cases the amount of carbon dioxide dissolved in the solutions was incomparably greater than would ordinarily be present in such solutions as we were titrating. It was found necessary to use from eight to ten drops of the solution of coralline in alcohol for each titration. Even then the end-point is not quite as sharp and distinct as with phenolphthalein.

It was found that, when calculating the concentration of the organic acid in the alcohol from the values obtained by titrating against ammonia, a slightly different value for the concentration was obtained from that formed from titrations against alcoholic caustic potash. We decided to find, if possible, the cause of this discrepancy, and to apply any necessary corrections. A known quantity of the standard sulfuric acid was titrated against alcoholic potassium hydroxide, using phenolphthalein as the indicator. Several titrations were made in every case, and then an equal quantity of the acid was titrated against the base, using coralline as the indicator. The results in the latter case did not agree with those in the former by about 0.2 cc., 10 cc. of acid being used in each case. That the difference was not due to carbon dioxide, which might have been dissolved in the sulfuric acid, can be seen from the fact that the same difference appeared in the titrations with an organic acid dissolved in absolute alcohol in which carbon dioxide is only slightly soluble.

It was found that if the same quantity of phenolphthalein or coralline used when making the ordinary titrations were added either to pure alcohol or to water, and if these solutions of the indicators alone were titrated against the alkali, and then back against the standard acid, an appreciable quantity of the alkali was required to change the color in the one direction, and about as much of the standard acid to change it in the reverse direction, the alkali and acid being of very nearly the same strength. Corrections for the amounts of alkali and acid necessary to produce such color changes were then applied to the titration volumes of the sulfuric acid and alcoholic potash, when agreement to within the limits of experimental error between the results for the two indicators was obtained. In all of the titrations in which alcoholic potassium hydroxide was used, the temperature of the solution was recorded; and when different from 25°, which was chosen as the standard temperature, a volume correction was applied. It was found necessary to keep all of the other solutions, particularly those of the organic acids in alcohol, as well as the alcoholic potash, at the standard temperature, and this was not difficult to do.

The titration values of the ammonia and standard acid were also corrected, as just stated, for the amounts necessary to produce color change, and the concentration of the ammonia was then calculated. The normality of 1–2–4 dinitrobenzoic acid in alcohol was determined from this standardized ammonia, making the same corrections as above; and it agreed to within 0.2% with that obtained by means of potassium hydroxide. Similar corrections were therefore applied to the titrations of all the organic acids. The sulfuric acid used to standardize the alkali was made up in large quantity, and its normality determined by the usual barium sulfate method.

Owing to the large amount of preliminary work required, it has been possible, up to the present, to make conductivity measurements of only nine organic acids. The same methods of purifying the acids were employed as when the conductivities of these acids were determined in aqueous solution. In most cases the various dilutions were made up by directly weighing the acid.

In the work in alcohol it was necessary to discard all of the weaker organic acids, notwithstanding the fact that our cell constants were about eight times smaller than those of Wilderman. After trying acetic acid several times we gave up hope of obtaining satisfactory results with such weak acids. Even the strongest acids with which we worked do not give a molecular conductivity greater than unity.

Titrations of the acids against the standard alkali were made simultaneously with the conductivity measurements at every temperature. At first the alcoholic solution of the acid was not kept at constant temperature, but it was soon found that, in order to obtain comparative results, and to avoid the considerable fluctuations of laboratory temperature, it was necessary to have all the solutions continuously at one temperature, preferably at 25°.

Results.

In the following tables of conductivity, V_m is the volume for which the solutions were made up; V_c is the corrected volume. The corrections applied were both for expansion or contraction of the alcohol, and for change in the concentration of the acid due to formation of ester. Molecular conductivity, M_v, was calculated in the usual manner, as were also temperature coefficients and percentage temperature coefficients.

TABLE I.—MALONIC ACID.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	8.12	0.0190	8.13	0.0237	8.18	0.0319	0.0046	24.5	0.0079	33.9
32	32.9	0.0434	33.2	0.0555	33.7	0.0737	0.0113	26.7	0.0192	35.9
128	129.3	0.0775	129.5	0.0985	129.6	0.1351	0.0207	26.1	0.0359	36.9
512	512.8	0.2533	514.9	0.3160	518.1	0.4338	0.0613	24.2	0.1145	36.4

Specific conductivity of alcohol at 15°, 0.000254 to 0.000246; at 25°, 0.000257 to 0.000249.

TABLE II.—*o*-CHLOROBENZOIC ACID.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	8.14	0.01303	8.16	0.0159	8.28	0.0197	0.00281	21.1	0.00344	22.1
32	33.1	0.01530	33.6	0.0198	34.9	0.0271	0.00451	28.1	0.00605	31.9
128	129.5	0.0279	129.7	0.0371	129.8	0.0555	0.00903	32.8	0.0180	49.2
512	313.8	0.1330	516.5	0.1714	519.9	0.2497	0.0375	20.8	0.0759	44.6

Specific conductivity of alcohol at 15°, 0.000531 to 0.000540; at 25°, 0.000578 to 0.000622; at 35°, 0.000637 to 0.000711.

TABLE III.—*p*-CHLOROBENZOIC ACID.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	10.0	0.0017	10.08	0.0025	10.11	0.0035	0.00067	48.2	0.00086	41.7
32	33.69	0.0082	34.18	0.0117	34.9	0.0160	0.00315	40.2	0.00382	34.7
128	129.7	0.0157	130.3	0.0189	130.9	0.0270	0.00314	19.9	0.0079	42.4
512	514.8	0.1263	520.0	0.1547	522.7	0.1853	0.0368	29.3	0.0293	19.2

Specific conductivity of alcohol at 15°, 0.000585 to 0.000586; at 25°, 0.000650 to 0.000656; at 35°, 0.000752 to 0.000827.

Table IV.—*p*-Bromobenzoic Acid.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
Vm.	Vc.	μ_v 15°.	Vc.	μ_v 25°.	Vc.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	8.147	0.00264	8.24	0.00353	8.27	0.0047	0.0008	30.7	0.0012	34.9
32	32.57	0.01252	33.3	0.0147	34.33	0.0200	0.0019	15.4	0.0046	32.3
128	129.1	0.0349	129.2	0.0418	129.5	0.0559	0.0068	19.6	0.0138	33.3
512	512.8	0.1651	517.5	0.1976	518.9	0.2637	0.0307	18.6	0.0607	29.9

Specific conductivity of alcohol at 15°, 0.000217 to 0.000214; at 35°, 0.000264 to 0.000233.

Table V.—*o*-Nitrobenzoic Acid.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
Vm.	Vc.	μ_v 15°.	Vc.	μ_v 25°.	Vc.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	8.21	0.00785	8.27	0.00937	8.27	0.0120	0.00142	18.56	0.0025	27.45
32	33.19	0.0204	34.3	0.0253	34.95	0.0337	0.0040	20.31	0.0084	35.44
128	129.3	0.0460	129.5	0.0477	129.6	0.0734	0.0642	35.94	0.0413	17.00
512	512.5	0.1788	517.0	0.2452	518.5	0.2877				

Specific conductivity of alcohol at 15°, 0.000232 to 0.000227; at 25°, 0.000242 to 0.000238; at 35°, 0.000237 to 0.000232.

Table VI.—*p*-Nitrobenzoic Acid.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
Vm.	Vc.	μ_v 15°.	Vc.	μ_v 25°.	Vc.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	32.96	0.0102	33.61	0.0151	34.56	0.0214	0.0045	45.5	0.0055	38.2
128	129.2	0.0516	129.3	0.0570	129.5	0.0785	0.0053	12.9	0.0212	37.5
512	512.8	0.1417	517.6	0.1814	520.5	0.2399	0.0401	28.6	0.0565	31.4

Specific conductivity of alcohol at 15°, 0.000237 to 0.000231; at 25°, 0.000237 to 0.000227; at 35°, 0.000232 to 0.000216.

Table VII.—1,2,4-Dinitrobenzoic Acid.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
Vm.	Vc.	μ_v 15°.	Vc.	μ_v 25°.	Vc.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	8.13	0.0379	8.24	0.0481	8.24	0.05879	0.0094	25.2	0.0104	22.3
32	33.62	0.0964	33.62	0.0848	33.62	0.10512	0.0171	26.9	0.0194	23.9
128	133.5	0.2556	133.5	0.1670	133.5	0.20043	0.0323	25.3	0.0359	22.4

Specific conductivity of alcohol at 15°, 0.000882 to 0.000936; at 25°, 0.000991 to 0.000935; at 35°, 0.001133 to 0.00123.

TABLE VIII.—1,2,4-DIHYDROXYBENZOIC ACID.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	9.99	0.0080	10.06	0.0098	10.10	0.0126	0.0014	20.9	0.0023	28.3
32	33.0	0.0155	33.01	0.0197	33.01	0.0254	0.004	26.5	0.0054	28.3
128	129.1	0.0171	129.3	0.0272	129.6	0.0391	0.100	59.1	0.0117	43.4
512	514.9	0.1008	517.5	0.1464	520.2	0.2018	0.044	44.3	0.0539	37.2

Specific conductivity of alcohol at 15°, 0.000551 to 0.000613; at 25°, 0.000631 to 0.000682; at 35°, 0.000735 to 0.000791.

TABLE IX.—TETRACHLOROPHTHALIC ACID.

Molecular Conductivity.							Temperature Coefficients of Conductivity.			
							15–25°.		25–35°.	
V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.	Cond. units.	Per cent.	Cond. units.	Per cent.
16	16.08	0.0543	16.21	0.0639	16.21	0.0770	0.0045	16.9	0.0064	18.9
64	64.06	0.1011	64.06	0.1198	64.06	0.1461	0.0093	18.5	0.0131	21.9
256	258.9	0.1294	259.3	0.1541	260.0	0.1813	0.0121	18.1	0.0171	22.5
512	..	..	..	..	..	..	..	..	..	..
1024	1027.0	0.3208	1036.0	0.3860	1043.0	0.4960	0.0309	19.3	0.0527	27.6

Specific conductivity of alcohol at 15°, 0.000543 to 0.000554; at 25°, 0.000616 to 0.000637; at 35°, 0.000711 to 0.000742.

The rate at which the organic acids combine with alcohol can be seen from the following data. The times at which the titrations were made are given, and the percentage decrease in normality shows the rate of ester formation.

TABLE X.—MALONIC ACID.

Changes in Concentration.

Time.	Observed normality.	Calculated normality.	Per cent. decrease in normality.
12.40 P.M.	0.1232	0.1250	1.44
2.30 P.M.	0.1229	0.1250	1.68
4.00 P.M.	0.1222	0.1250	2.24
12.50 P.M.	0.03039	0.03125	2.75
2.30 P.M.	0.03008	0.03125	3.75
4.10 P.M.	0.02966	0.03125	5.09
12.00 M.	0.00773	0.007812	1.05
2.30 P.M.	0.00772	0.007812	1.18
4.00 P.M.	0.00771	0.007812	1.31
12.10 P.M.	0.001950	0.001953	0.16
2.40 P.M.	0.001942	0.001953	0.51
4.10 P.M.	0.001930	0.001953	1.18

TABLE XI.

o-CHLOROBENZOIC ACID. *p*-CHLOROBENZOIC ACID.

Changes in Concentration.

Time.	Observed normality.	Calculated normality.	Per cent. decrease in normality.		Time.	Observed normality.	Calculated normality.	Per cent. decrease in normality.
10.00 A.M.	0.1228	0.1250	1.76		12.30 P.M.	0.0996	0.1250	20.32
12.15 P.M.	0.1225	0.1250	2.00		2.00 P.M.	0.09919	0.1250	20.65
4.15 P.M.	0.1210	0.1250	3.20		4.15 P.M.	0.0989	0.1250	20.90
4.40 P.M.	0.1208	0.1250	3.36		12.40 P.M.	0.0297	0.03125	5.09
11.00 A.M.	0.03018	0.03125	3.43		2.00 P.M.	0.0292	0.03125	6.40
11.50 A.M.	0.02976	0.03125	4.77		4.30 P.M.	0.0286	0.03125	8.42
3.30 P.M.	0.02914	0.03125	6.76		12.30 P.M.	0.00771	0.007812	1.31
4.30 P.M.	0.02862	0.03125	8.42		2.20 P.M.	0.007691	0.007812	1.55
11.40 A.M.	0.00772	0.007812	1.18	2 days later	3.30 P.M.	0.00767	0.007812	1.77
12.30 P.M.	0.00771	0.007812	1.31		4.10 P.M.	0.00766	0.007812	1.99
2.30 P.M.	0.00770	0.007812	1.44		5.00 P.M.	0.00763	0.007812	2.25
4.00 P.M.	0.00769	0.007812	1.57		12.35 P.M.	0.001942	0.001953	0.57
11.35 A.M.	0.001946	0.001953	0.36		3.15 P.M.	0.001923	0.001953	1.54
12.30 P.M.	0.001936	0.001953	0.88	2 days later	12.30 P.M.	0.001916	0.001953	1.97
2.50 P.M.	0.001932	0.001953	1.08		3.30 P.M.	0.001913	0.001953	2.05
4.45 P.M.	0.001923	0.001953	1.54		4.15 P.M.	0.001903	0.001953	2.57

TABLE XII.

p-BROMOBENZOIC ACID. *o*-NITROBENZOIC ACID.

Changes in Concentration.

Time.	Observed normality.	Calculated normality.	Per cent. decrease in normality.	Time.	Observed normality.	Calculated normality.	Per cent. decrease in normality.
11.30 A.M.	0.12275	0.1250	1.80	12.15 P.M.	0.12176	0.1250	2.60
2.45 P.M.	0.12129	0.1250	2.97	12.30 P.M.	0.12088	0.1250	3.30
4.40 P.M.	0.12088	0.1250	3.30	4.30 P.M.	0.12088	0.1250	3.30
11.40 A.M.	0.03070	0.03125	1.76	12.30 P.M.	0.03013	0.03125	3.59
2.50 P.M.	0.03007	0.03125	3.76	2.30 P.M.	0.02914	0.03125	6.77
4.50 P.M.	0.02914	0.03125	6.76	4.30 P.M.	0.0286	0.03125	8.45
11.00 A.M.	0.00774	0.00781	0.89	12.00 M.	0.00773	0.00781	1.03
12.15 P.M.	0.00773	0.00781	1.00	2.30 P.M.	0.00772	0.00781	1.17
4.00 P.M.	0.00771	0.00781	1.22	4.00 P.M.	0.00771	0.00781	1.29
11.10 A.M.	0.001950	0.001953	0.16	12.10 P.M.	0.001951	0.001953	0.11
12.25 P.M.	0.001932	0.001953	1.08	2.40 P.M.	0.001934	0.001953	0.98
4.10 P.M.	0.001927	0.001953	1.34	4.10 P.M.	0.001928	0.001953	1.28

TABLE XIII.

Changes in Concentration.

p-NITROBENZOIC ACID.

Time.	Observed normality	Calculated normality.	Per cent. decrease in normality.
12.00 M.	0.03034	0.03125	2.93
2.30 P.M.	0.02976	0.03125	4.77
4.45 P.M.	0.02893	0.03125	7.43
12.00 M	0.007738	0.007812	0.95
2.30 P.M.	0.007734	0.007812	1.00
4.45 P.M.	0.007721	0.007812	1.17
12.00 M.	0.001950	0.001953	0.16
2.30 P.M.	0.001932	0.001953	1.08
4.30 P.M.	0.001921	0.001953	1.64

1,2,4-DINITROBENZOIC ACID.

Time.	Observed normality.	Calculated normality.	Per cent. decrease in normality.
12.30 P.M.	0.1230	0.1250	1.60
2.30 P.M.	0.1213	0.1250	2.96
4.30 P.M.	0.1213	0.1250	2.96
12.20 P.M.	0.02974	0.03125	4.83
4.00 P.M.	0.02974	0.03125	4.83
5.00 P.M.	0.02974	0.03125	4.83
12.35 P.M.	0.00749	0.007812	4.13
2.30 P.M.	0.00749	0.007812	4.13
1 day later } 10.00 A.M.	0.00764	0.007812	2.21

This titration was made with the solution after it had stood in the cell over night.

TABLE XIV.

Changes in Concentration.

1,2,4-DIHYDROXYBENZOIC ACID.

Time.	Observed normality.	Calculated normality.	Per cent. decrease in normality.
11.15 A.M.	0.10008	0.1250	19.94
12.30 P.M.	0.09940	0.1250	20.50
2.30 P.M.	0.09899	0.1250	20.82
4.30 P.M.	0.09873	0.1250	21.02
12.25 P.M.	0.03034	0.03125	3.09
12.45 P.M.	0.03029	0.03125	3.09
2.30 P.M.	0.03029	0.03125	3.09
4.30 P.M.	0.03013	0.03125	3.59
12.00 M.	0.00774	0.007812	0.89
2.30 P.M.	0.00773	0.007812	1.03
4.15 P.M.	0.00771	0.007812	1.27
12.10 P.M.	0.00194	0.001953	0.51
2.40 P.M.	0.00193	0.001953	1.08
4.30 P.M.	0.00192	0.001953	1.59

TETRACHLOROPHTHALIC ACID.

Time.	Observed normality.	Calculated normality.	Per cent. decrease in normality.
11.50 A.M.	0.06218	0.0625	0.52
12.50 P.M.	0.06168	0.0625	1.32
3.20 P.M.	0.06168	0.0625	1.32
4.30 P.M.	0.06168	0.0625	1.32
12.00 M.	0.04561	0.01566	0.32
1.00 P.M.	0.04561	0.01566	0.32
3.30 P.M.	0.04561	0.01566	0.32
4.30 P.M.	0.04561	0.01566	0.32
12.15 P.M.	0.00386	0.00391	1.08
2.00 P.M.	0.00385	0.00391	1.28
4.00 P.M.	0.00384	0.00391	1.54
12.25 P.M.	0.000973	0.000976	0.31
2.10 P.M.	0.000965	0.000976	1.13
4.10 P.M.	0.000958	0.000976	1.85

Discussion of the Results.

It will be noted in the above tables that 1,2,4-dinitrobenzoic acid shows an irregularity in its titration values. The conductivity of this acid was determined before we began to keep the solutions used in titration at a constant temperature. In the case of all the other acids the results show that with increase in time a greater amount of esterification has taken place; that is, the normality of the acid has become less. The amount of ester formed in a given time depends upon the nature of the acid.

Since each dilution was made up independently of the others, that is, by direct weight, it is interesting to note that the proportion of ester formed in the less dilute solutions, is much greater than in the more dilute solutions. Indeed, in some cases there is practically no ester formed in the $N/128$ and $N/512$ solutions. As has already been stated none of the conductivities is greater than unity, and consequently, the molecular conductivity of the alcohol for each dilution is relatively quite large, the correction for this factor being in some cases as much as 70% of the total conductivity. It can be seen from the tables that the conductivity of the alcohol alone varies considerably, usually increasing appreciably with time. Some of the conductivities of the alcohol increase with rise in temperature, some actually decrease, while others remain very nearly constant. We can offer no explanation for this lack of uniform variation, except to call attention to the several factors which might affect the conductivity of the pure solvent. One might be the absorption by the alcohol of traces of various gases or water-vapor from the atmosphere. This, however, ought to be a negligible factor, since our cells were very nearly filled, and were tightly closed with ground-glass stoppers. The decomposition effects brought about by the platinum electrodes may be an important factor. Compare here the work of Wilderman and others on this question. It is evident that the electrodes do have some effect, since fresh alcohol just taken from the bottle does have a fairly uniform conductivity. Part of the effect, with alcohol which stood in the cell over night, might be due to the solubility of the glass cell. This, however, is not at all probable, since our cells have been in constant use in this laboratory for several years, and hard glass is only very slightly soluble in alcohol.

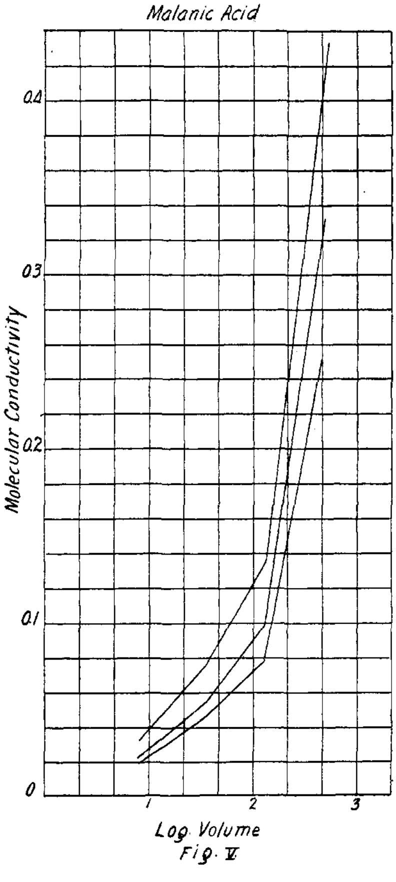

Fig. V

The conductivities of some of the solutions, and curiously enough of the more dilute solutions, vary to a much smaller extent with time, than does the conductivity of the pure alcohol.

It will be recalled that Wakeman plotted curves of conductivity of the organic acids against percentage alcohol (see Fig. I) and on extending the curves in the direction of 100% alcohol they apparently approached zero conductivity as a limit. As can be seen from our results, the conductivities do not actually approach zero, but a number less and usually very much less than unity.

One of the most interesting facts which came out in this work is the extraordinarily large percentage temperature coefficients of conductivity of the organic acids in alcohol. These range from fifteen to fifty per cent.

There is often a rapid increase in the conductivity of the organic acids with increase in dilution, yet certain of the acids behave in just the opposite manner; *e. g.*, *o*-chlorobenzoic acid and *p*-nitrobenzoic acid.

Our results seem to suggest the following possibilities, if we take into account the work done here on the organic acids in aqueous solutions:[1] that there is much greater alcoholation than hydration, and this is decreased with rise in temperature. The work already done in this laboratory renders this highly improbable. The alcoholates may be more unstable with rise in temperature than the hydrates; but water seems to have, in general, far more power to combine with dissolved substances than alcohol.

If dissociation in alcoholic solutions increased with rise in temperature, it might account for the large temperature coefficients of conductivity in such solutions, but this again seems highly improbable.

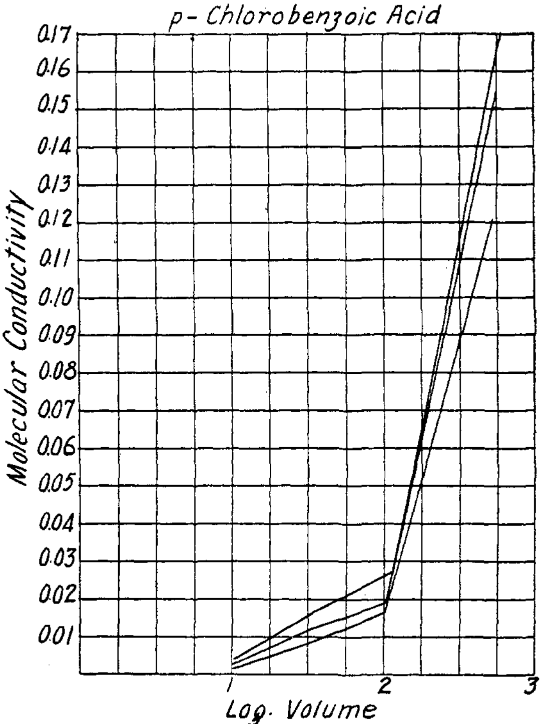

Fig. VI.

The greater expansion of the alcohol with rise in temperature would allow a freer movement of the ions, and this is doubtless of some significance. A method for determining the dissociation of the organic acids in alcohol, somewhat similar to that used with aqueous solutions, will, it is hoped, be worked out in the investigation of this subject which is to follow this preliminary one. It will involve the study, in alcohol, of the conductivity

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[1] Carnegie Institution of Washington, Publication No. 170.

of some salts of the acids, as well as of hydrochloric acid and the chlorides corresponding to these salts.

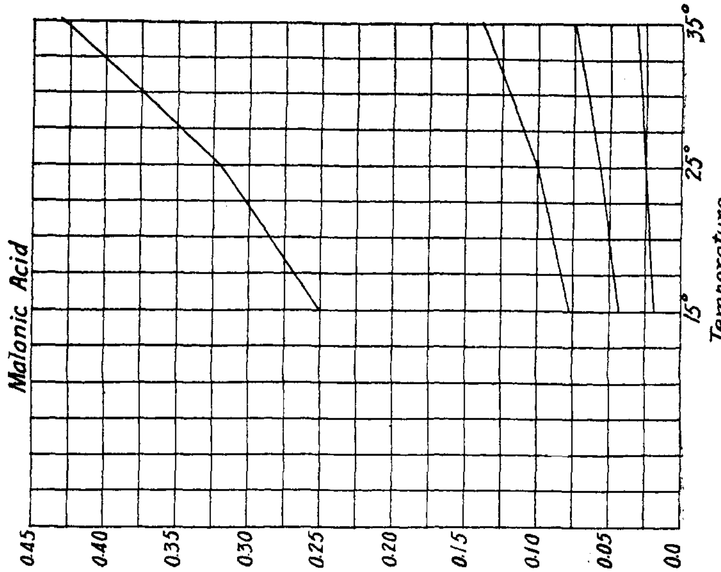
Fig. VII.

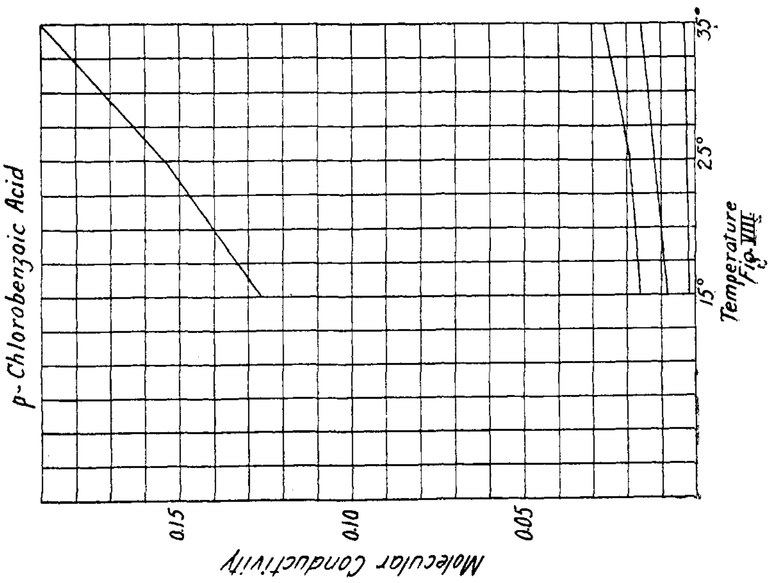
Fig. VIII.

The increase in conductivity with increase in volume is shown graphically in Figs. V and VI. The increase in conductivity with rise in temperature can be seen from Figs. VII and VIII. In the latter case the curves have very much the appearance of those in aqueous solutions. This suggests the thought that perhaps the increase in molecular conductivity in alcohol with rise in temperature, is a parabolic function, as in aqueous solutions; and that the Euler equation

$$\mu v = \mu o + \alpha t + \mu t^2$$

applies to both.

This will be tested in the later work by determining the conductivities of some of the acids at temperatures other than the three already named, and comparing the results obtained, with those calculated from this equation. The most striking feature of the conductivities of the organic acids in alcohol, as compared with the conductivities of the same acids in water, is *their very small value.* When we consider the relative powers of alcohol and water to dissociate salts, the above fact does not at present seem to admit of any very satisfactory explanation. Alcohol has from one-fourth to one-fifth the dissociating power of water, as shown by their dissociation of salts. With the organic acids the conductivities in alcohol are often several hundred times smaller than in water. It is hoped that the further work which is now in progress in this laboratory on this problem may throw some light on this relation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF IODINE COMPOUNDS.

BY GILBERT N. LEWIS AND MERLE RANDALL.

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Elementary Iodine.

The elementary forms of iodine which we shall consider are solid and liquid iodine, I_2 in aqueous solution, and the two gaseous modifications, I_2 and I. Solid iodine is taken as the standard state.

I(s) = I(l).—The free energy of liquid iodine is obtained directly from the melting point of solid iodine, which was found by Ramsay and Young[1] to be 114°, a value which is in good agreement with those given by Regnault and by Stas. From the vapor pressure measurements of Ramsay and Young the heat of vaporization of liquid iodine has been calculated by Baxter, Hickey and Holmes[2] and shown to be 5250 cal. per g. atom. From their own measurements, which we shall presently discuss more fully, the heat of sublimation of I(*s*) at the same temperature, 114°, is 7270 cal. Subtracting, we find in round numbers for our reaction[3] $\Delta H = 2000$ cal.

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[1] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

[2] Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907).

[3] Favre and Silbermann obtained the value 1500 cal., but only made one determination.