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A CONDUCTIVITY METHOD FOR THE ANALYSIS OF FORMIC ACID IN THE PRESENCE OF THE VOLATILE FATTY ACIDS PRODUCED BY FERMENTATION

By

Edmond E. Moore

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Bio-physical Chemistry

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1928

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A CONDUCTIVITY METHOD FOR THE ANALYSIS OF FORMIC ACID IN THE PRESENCE OF THE VOLATILE FATTY ACIDS PRODUCED BY FERMENTATION

INTRODUCTION

In the study of the production of chemicals by microorganisms, accurate and fairly rapid methods of analysis of the products formed are needed. In particular the work on the utilization of agricultural wastes by microbiological action has been retarded by the lack of such methods. The use of conductivity measurements in the analysis of such products will be shown in this thesis to give satisfactory results in certain cases.

REVIEW OF METHODS FOR THE ANALYSIS OF FORMIC ACID

The following methods have been used for the determination of formic acid in the presence of one or more of the other volatile fatty acids. In each case typical references precede the discussion.

Reduction of mercuric salts. Auerbach and Puddleman (1910), Auerbach and Zeglin (1922), Benedict and Harrop (1922), Finche (1913), Franzen and Egger (1911), Franzen and Greve (1910), Holmberg and Linberg (1923), Oberhauser and Hensinger (1927), Ost and Klein (1908), Pregl (1917), Riesser (1916) and Utkin-Ljubowzoff (1923).

The reduced mercury salt can be weighed or determined iodometrically. The method is accurate but time consuming. The reduction usually requires several hours of heating on a water-bath in the presence of suitable catalysts. The subsequent determination of the quantity of mercurous salt formed also requires considerable time.

Reduction of platinum chloride to metallic platinum. Bacon (1911) has used this method for the determination of small quantities of formic acid.

Reduction of iodates. Cuny (1911). The method is like that used in the reduction of mercuric salts. First, the sample is refluxed with iodic acid, the solution having been made strongly acid with sulfuric acid, then the iodine liberated is distilled off and titrated with sodium thiosulfate. The method requires as much time as that using the reduction of mercuric salts.

Reduction of potassium permanganate. Fouchet (1912), Grossman and Aufrecht (1906), Oberhauser and Hensinger (1927), Ost and Klein (1908), Whittier (1923).

If the temperature, concentration and time are properly regulated, the formates in a solution which has been made alkaline with sodium carbonate will be oxidized by potassium permanganate, while the acetates, etc. will not. The method has been modified many times, but has never become popular.

The reduction of bromine. Joseph (1912), Oberhauser and Hensinger (1927). The first method was shown to give unsatisfactory results. The second is claimed by the authors to be better. They treat the formic acid with bromine in potassium bromide, add an excess of standard sodium dihydrogen arsenite and titrate back with bromine in potassium bromide using indigo carmenstyphinic acid 2:1 as indicator. The method is time consuming.

The reduction of chromic acid. MacNair (1887), Nicloux (1897), Ost and Klein (1908), Tsiropinas (1917).

The method consists of boiling the sample with potassium dichromate and sulfuric acid and titrating back with potassium iodide and sodium thiosulfate. It has the same objections asother reduction methods.

Decomposition by concentrated sulfuric acid and measurement of the carbon monoxide evolved. Ost and Klein (1908), Wegener (1903). The method holds only for concentrated solutions.

Reduction by metallic magnesium. Fenton and Sisson (1907). The method is not accurate enough for quantitative work.

Displacement of the acetate by the formate radical. Heermann (1915). The formic and acetic acids can be converted to the sodium salts and weighed, then by treatment with formic acid the whole can be changed to sodium formate, and again this is weighed. The first weight gives the sum of the weights of sodium formate and sodium acetate, and the second weight gives the weight of the sodium formate plus that of the sodium acetate expressed as sodium formate. From these two equations the weights of the formic and acetic acids originally present can be calculated. The method has been criticized by Laufmann (1915) who reported that all the acetic acid was not expelled even after several evaporations with formic acid.

Micro analytical methods. Wohack (1921). These are based on the reduction of mercuric salts and differ from those given above mainly in the quantities used.

Separation by distillation depending on the various rates of distillation of different acids. The method was first proposed by Liebig (1849). Duclaux (1895) devised a method of analysis which was based on this principle. He distilled 110 cc. of a solution containing 1 to 2 percent of acid. 100 cc. of the distillate was collected in ten fractions of ten cc. each. The ratios between the sets of values obtained by titrating these fractions and those obtained on titrating the whole sample are known as Duclaux's constants. These constants serve to identify any particular acid. By assuming that each acid in a mixture behaves as if it were there alone Duclaux extended his method to the analysis of mixtures. This procedure has been used by many investigators but has been subject to much criticism. Richmond (1895), Upson, Plum and Scott (1917).

<u>Steam distillation</u>. Dyer (1917) introduced a method of steam distillation. He aimed at keeping the volume approximately the same by introducing steam. He regulated the source of heat and the supply of steam so that the level of the liquid in the flask did not alter appreciably. This method lessens one of the more serious errors in the Duclaux procedure in that during the distillation of an aqueous solution, unless the solute has the same rate of volatilization as the solvent, the concentration of the latter will change. Richmond (1895) found that in the case of formic, and to a less extent of acetic acid the rate of distillation is influenced by the concentration of the solution. In the case of an ordinary distillation in which the substance in solution distills at

a slower rate than the solvent, the solution will become more concentrated with the consequent alteration of constants. In an unknown mixture a correction cannot be applied with certainty in such cases. Variations in concentration, with consequent alteration of constants will be reduced if the distillation is carried out at constant volume. The limits of variation can be reduced still further if relatively large volumes of solution are distilled compared with the volume of distillate collected.

The following table gives the data upon which Dyer's method is based. It gives the comparative percentages of acid which distill over into the first 100 cc. fraction of distillate from a constant volume of 150 cc.

Table 1

Formic	Acetic	Propionic	n-Butyric
17.89	30.75	52.67	69.88

The volatility with steam increases with the addition of CH_2 groups. Dyer repeated the above, titrating 10 cc. fractions in each case and found that the percentage figure for the first 10 cc. fraction is the distilling constant for each acid, "or is that percentage of the residual acid which distills over in each successive 10 cc. fraction." He was able to show from theoretical calculations based upon the above that the percentage of any single acid distilled over at any time is a simple logarithmic function of the cc. of distillate obtained. These deductions he checked experimentally. He then was able to represent the percentage of acid distilled over for any given amount of distillate on a logarithmic chart. For each individual acid this is a straight line.

The identification of a single acid by this method is carried out as follows: The total acid present is titrated with 0.1 N alkali, the distillation is then so arranged that the amount of pure acid contained in the total 150 cc. volume in the distilling flask is about 0.5 cc. For distillation the acid is liberated with an equivalent amount of 0.1 or 0.2 N sulfuric acid. Any convenient amount of distillate, for example 100 cc., is collected. This is titrated with 0.1 N alkali and the value obtained divided by that secured in the original titration. The result will be the distilling constant of the acid for the first 100 cc. fraction of distillate. The nature of the acid distilled can be found by comparing the value obtained with the logarithmic chart.

Mixtures of acids upon distillation give curved instead of straight lines when represented on the chart. With neighboring acids these curved lines will be very flat while the further removed from each other the acids are in their relative positions on the chart, the greater will be the bulge in the curve. In the case of formic and acetic acids, since the distilling constant of each pure acid is known, and the distilling constant of the mixture is obtained, one can calculate in what proportion they are mixed. The use of the method with mixtures of acids which are not neighboring is questioned. Dyer states, "The lowest acid of the series in the mixture will be identified with certainty since it will eventually reach a point where it will begin to parallel some straight line on the chart which represents that acid. This same point indicates where the other acid of the mixture has run out and reference to a table given will indicate with a fair degree of certainty the nature of this accompanying acid". Reilly and Hickenbottom (1919) do not agree with the above; they state, "By distilling an aqueous solution of a mixture of two acids having different rates of volatilization, it becomes evident that as the distillation proceeds, the solution in the flask will become relatively richer in the less volatile acid, so that the solution gradually changes in composition with a corresponding change in vapor. It is obvious, therefore, that although a consideration of the logarithmic and other constants will give an accurate idea of the composition of the vapor at any given time, it cannot be applied with certainty to the composition of the solution distilled. The method suggested by Dyer of taking the point at which the logarithmic curve of the mixture becomes parallel to that of the less volatile component is there open to a very wide error, and can be only approximate."

Donker (1926) suggested a method of adjusting the hydrogen ion concentration so that the formic acid would distill over while the acetic acid would not. Because of the small differences in dissociation constants in these two acids the method would appear to be difficult, if at all practical.

Variations in solubility between adjacent members of the fatty acid series or corresponding derivatives are usually small and sharp separations by the solubility method are hard to obtain.

We were unable to find any reference to methods for the determination of formic acid by conductivity methods. Kolthoff (1923) gives a method for determining the total volatile fatty acids by a conductometric method. He titrated the mixture with mercuric perchlorate, and obtained a sharp change, or break, in the conductivity curve due to the formation of the slightly dissociated mercuric salts. He does not propose a method for the determination of the individual members of the series.

THEORY

For a complete discussion of this subject one should read Kolthoff (1923). We will give only a short review of the principles which one must have in mind in order to understand the method of analysis which we have developed and to distinguish it from the conductometric titration which has been reported, we believe correctly, by Kolthoff (1923) to be not applicable to this analysis.

The conductivity of an acid, or mixture of acids, of definite molarity depends upon the viscosity of the solution, temperature, dissociation of acids and mobility of ions. By using a dilute solution, about 0.0066 M at constant temperature and working with acids which are quite similar in composition we largely eliminate the first two effects so that the conductivity depends largely upon the dissociation of the acids and mobility of their ions. If a strong base, for example potassium hydroxide, is added to a dilute solution of a strong acid, for example hydrochloric acid, there is a decrease in conductivity to the neutralization point, then an increase (Table 2)(Curve I). This can be explained from the following table (Table 3).

Table 2

Data for the Neutralization Curve of 1.00 cc. of Normal Hydrochloric Acid with Potassium Hydroxide

cc. Normal Potassium Hydroxide	Bridge Reading (A)	$\frac{A}{1000-A}$	Specific Conductivity x 10^4
0.00	(A) 747.8	2.965	26.77
0.20	(B) 462.5	0.8603	23.28
0.40	420.8	0.7265	19.68
0.60	374.0	0.5974	16.18
0.80	318.0	0.4661	12.61
0.94	273.5	0.3765	10.19
0.98	259.0	0.3495	9.47
1.00	255.5	0.3431	9.29
1.02	259.8	0.3510	9.51
1.06	269.8	0.3695	10.01
1.10	281.2	0.3912	10.59
1.20	310.6	0.4505	12.23
1.40	362.5	0.5686	15.40
1.60	407.0	0.6862	18.59
1.80	446.8	0.8077	21.88

The temperature was maintained at 25° ± 0.05.

(A) In the first reading the resistance in the other arm of the bridge was 300 ohms.

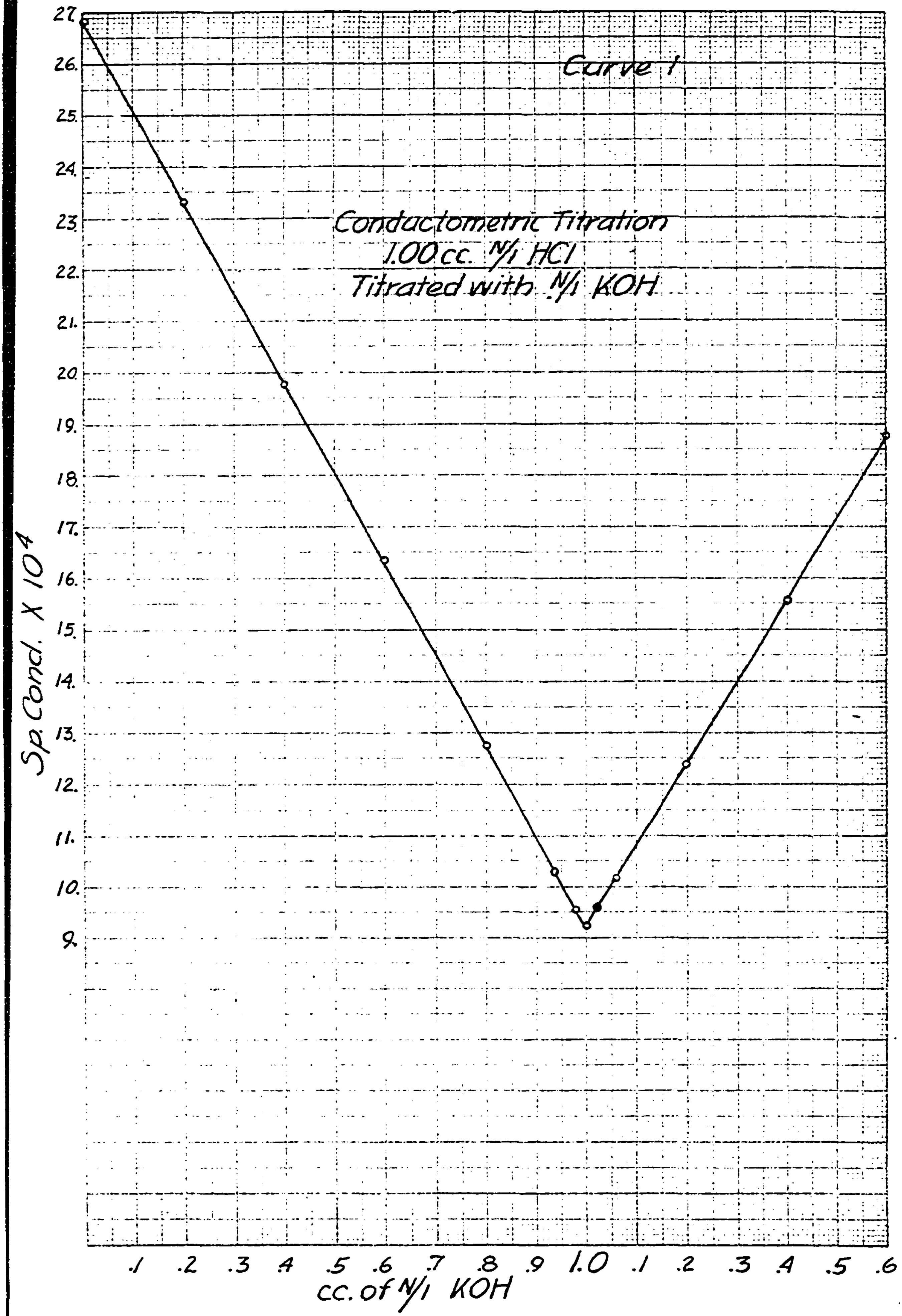
(B) In the cases of the second and all other readings, except the first, 100 ohms resistance was used in the other bridge arm.

Table 3

Mobility of the Ions at 25°C. (Kolthoff 1923)

Potassium	74.8
Chloride	75.8
Hydroxide	196.
Hydrogen	350.

All the determinations in this work were made on acids


Curve 1
Conductometric Titration
1.00 cc. N/1 HCl
Titrated with N/1 KOH
Sp. Cond. X 10⁴
27.
26.
25.
24.
23.
22.
21.
20.
19.
18.
17.
16.
15.
14.
13.
12.
11.
10.
9.
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
.1
.2
.3
.4
.5
.6
cc. of N/1 KOH

of normalities varying between 0.0055 and 0.0080 N. Hydrochloric acid of this strength will be very largely dissociated and therefore the conductivity will be high due to the large number of highly mobile hydrogen ions present. As potassium hydroxide is added the hydrogen ions are replaced by the less mobile potassium ions until neutralization is reached. The addition of more potassium hydroxide now causes an increase in conductivity, because it increases the potassium ion concentration and adds some of the highly mobile hydroxyl ions. Eastman (1925) shows mathematically that this end-point should check the true neutralization point within a few thousandths of one percent.

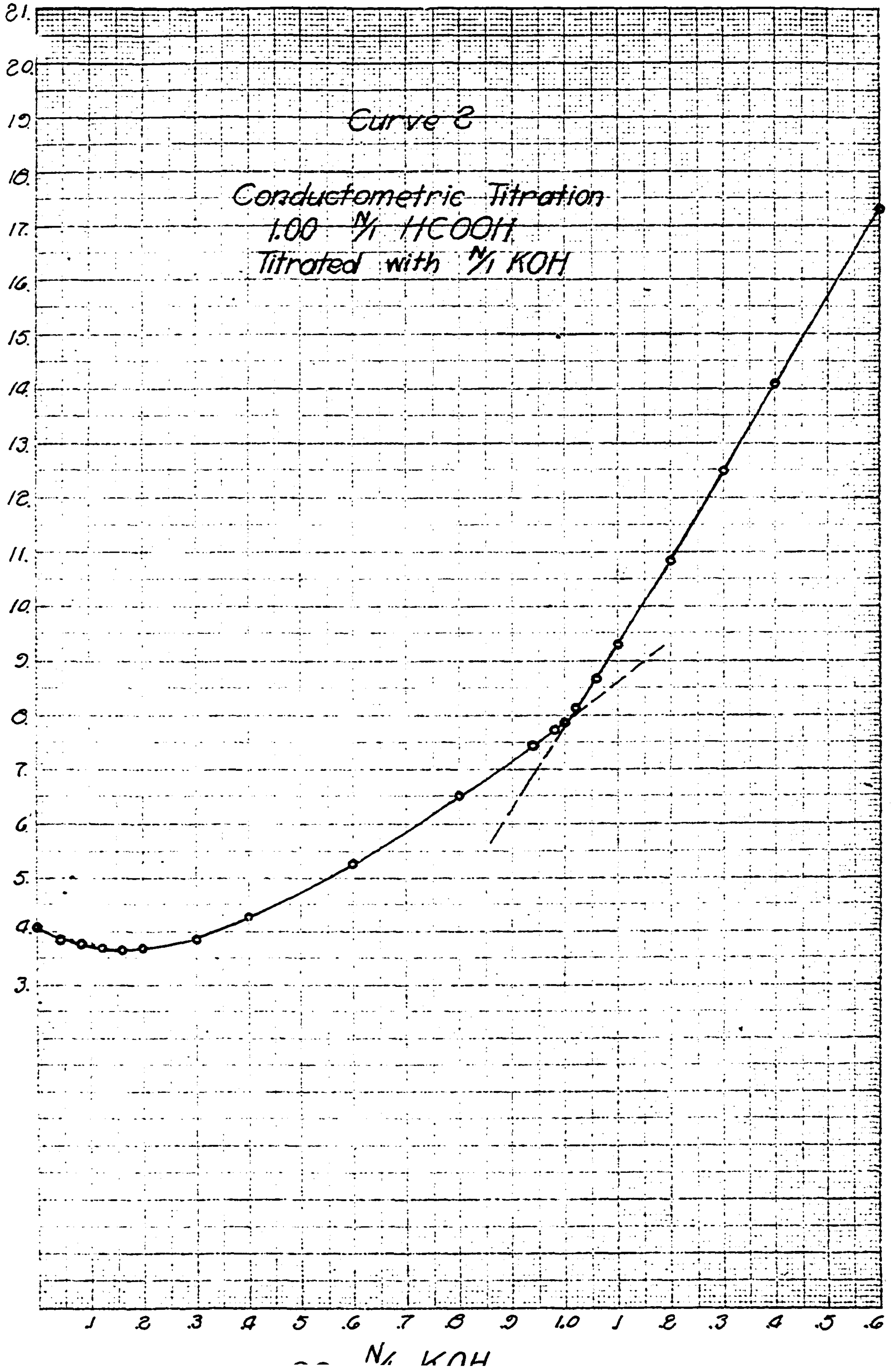
If in place of hydrochloric acid we use a weak acid, for example formic, and again neutralize with potassium hydroxide, at first the conductivity decreases as in the case of the strong acid, but it begins to increase before all of the acid is neutralized, and at the neutralization point the conductivity increase becomes still greater (Curve 2)(Table 4). The formic acid is not as highly ionized as the hydrochloric and thus the initial conductivity is less. As potassium hydroxide is added, potassium formate, which is highly ionized, is formed. This cuts down the ionization of the formic acid. A point is soon reached where the decrease in conductivity due to the decrease in hydrogen ions is less than the increase

Table 4

Data for the Neutralization Curve of 1.00 cc. of Normal Formic Acid with Normal Potassium Hydroxide

cc. Normal Potassium Hydroxide	Bridge Reading (A)	$\frac{A}{1000-A}$	Specific Conductivity ($x\ 10^4$)
0.00	310.0	0.4493	4.054
0.04	299.5	0.4275	3.861
0.08	292.2	0.4128	3.728
0.12	278.3	0.4030	3.640
0.16	285.7	0.4000	3.612
0.20	287.0	0.4024	3.624
0.30	298.7	0.4259	3.846
0.40	318.3	0.4667	4.214
0.60	367.5	0.5810	5.246
0.80	418.0	0.7181	6.485
0.94	450.8	0.8207	7.411
0.98	460.0	0.8518	7.692
1.00	465.0	0.8691	7.848
1.02	472.5	0.8957	8.088
1.06	490.0	0.9609	8.677
1.10	506.7	1.0270	9.264
1.20	545.0	1.1980	10.820
1.30	579.5	1.3780	12.440
1.40	609.0	1.5570	14.060
1.60	656.2	1.9100	17.290
1.80	693.7	2.2640	20.440

The temperature in this and other determinations in this paper was maintained at 25°±0.05. The resistance in the opposite arm was 300 ohms. Dilution water 155 cc.


Curve 2
Conductometric Titration
1.00 N/1 HCOOH
Titrated with N/1 KOH
21.
20.
19.
18.
17.
16.
15.
14.
13.
12.
11.
10.
9.
8.
7.
6.
5.
4.
3.
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
.1
.2
.3
.4
.5
.6
N/1 KOH

in conductivity due to the increase in number of potassium and formate ions. The location of this point depends upon the concentration of the acid. In a very dilute solution it would approach the neutralization point. This minimum is not a definite sharp "break" as in the case of a strong acid and strong base but a rounded "hump" which makes it unsuited for use in analytical work. When the minimum part of the curve has been passed the conductivity continues to increase evenly up to the neutralization point, where there is a "break" in the curve, the conductivity increasing more rapidly but again evenly because of the increasing numbers of the more mobile hydroxyl ions, as in the case of the strong acid and strong base.

When a weak acid, for example formic, is neutralized by a weak base, as ammonium hydroxide, the curve (Table 6) (Curve 3) at first resembles that for a weak acid and strong base. The large excess of acid present at first hinders the hydrolysis of the salt. The conductivity passes thru a minimum and then increases as in the above case. In the vicinity of the end-point hydrolysis becomes large and the conductivity increases less rapidly. When an excess of the weak base has been added the hydrolysis will be suppressed and there will be no further measureable change in conductivity.

The reactions from the beginning of the titration until hydrolysis begins to take place are the same as in the case of a weak acid and a strong base. Near the neutral point the highly ionized ammonium formate is hydrolyzed to formic acid and ammonium hydroxide both of which are but slightly ionized in the presence of ammonium formate thus slowing up the increase in conductivity. After the end-point has been passed the addition of more ammonium hydroxide will cause practically no change in conductivity as ammonium hydroxide is but slightly ionized in the presence of its salts. In the concentrations used in this work the increase in conductivity due to the presence of more base is balanced by the decrease due to the dilution of salt solution. The end-points in the last two cases may differ considerably from the true equivalence points. Where such differences affect our method they will be discussed later in this paper. For a complete discussion of the subject one should refer to Kolthoff (1923) and Eastman (1925).

It is possible to determine a strong acid and a weak acid or two weak acids of very different dissociation constants, in the same solution by a single titration with an alkali. The stronger acid is neutralized first, then the weaker, so that there are breaks in the curve corresponding to the amount of each acid present. Kolthoff (1923) shows that this method cannot be used if the ratio of the dissociation constants of the two acids is less than 1000 or if the mobilities of the anions of the two acids are nearly the same.

The volatile fatty acids have dissociation constants whose ratio at the most, in the case of formic and propionic acids, is less than 16.

Table 5

Acid	Dissociation Constant (x 10^5)
Formic	20.5 (room temperature)
Acetic	1.86 (room temperature)
Propionic	1.31 (25°)
Butyric (N)	1.48 (25°)
Valeric (N)	1.6 (25°)

The first four values are from Landoldt Börnstein (1927). The value for valeric acid is from Landoldt Börnstein (1923).

The dissociation constant for ammonium hydroxide at 25° is 1.8×10^{-5}. As stated above, if a weak acid is titrated with a weak base, a point is reached, soon after the true neutralization point, beyond which there is no further change in conductivity on the addition of more base. This point is about six percent higher than the true neutral point for the volatile fatty acids in the concentrations which we use. A correction factor has been determined to take care of this difference. Neutralization curves are given for formic acid (Curve 3)(Table 6), acetic acid (Curve 5)(Table 7) and a mixture of equal parts of the two acids (Curve 4)(Table 8). In each case we have plotted the specific conductivities

Table 6

Data for the Neutralization Curve of 1.00 cc. Normal Formic Acid with Normal Ammonium Hydroxide

cc. Normal Ammonium Hydroxide	Bridge Reading (A)	$\frac{A}{1000-A}$	Specific Conductivity $\times 10^4$
0.00	310.0	0.4493	4.057
0.05	297.8	0.4241	3.830
0.12	288.3	0.4050	3.657
0.20	287.5	0.4034	3.643
0.25	289.5	0.4074	3.678
0.40	318.7	0.4676	4.222
0.60	367.8	0.5818	5.254
0.80	417.4	0.7164	6.469
0.94	449.6	0.8169	7.377
0.98	457.6	0.8426	7.608
1.00	460.4	0.8513	7.703
1.02	461.3	0.8562	7.731
1.06	462.2	0.8593	7.759
1.08	462.6	0.8606	7.771
1.10	462.6	0.8606	7.771
1.20	462.6	0.8606	7.771

Temperature = 25°C. ±0.05

Dilution water 155 cc.

Resistance in opposite arm of bridge 300 ohms.

Table 7

Data for the Neutralization Curve of 1.00 cc. Normal Acetic Acid with Normal Ammonium Hydroxide

CC. Normal Ammonium Hydroxide	Bridge Reading (A)	$\frac{A}{1000-A}$	Specific Conductivity (x 10^4)
0.00	124.2	0.1419	1.281
0.04	115.0	0.1300	1.174
0.08	118.3	0.1342	1.212
0.10	124.8	0.1426	1.287
0.40	245.8	0.3258	2.942
0.60	320.0	0.4705	4.248
0.80	378.0	0.6077	5.592
0.94	417.0	0.7152	6.457
0.98	427.4	0.7463	6.739
1.00	430.6	0.7559	6.838
1.02	432.5	0.7590	6.853
1.06	434.0	0.7667	6.923
1.08	434.0	0.7667	6.923
1.10	434.0	0.7667	6.923
1.20	434.0	0.7667	6.923

Temperature = 25°C.±0.05

Dilution water = 155 cc.

Resistance in opposite arm of bridge = 300 ohms.

Table 8

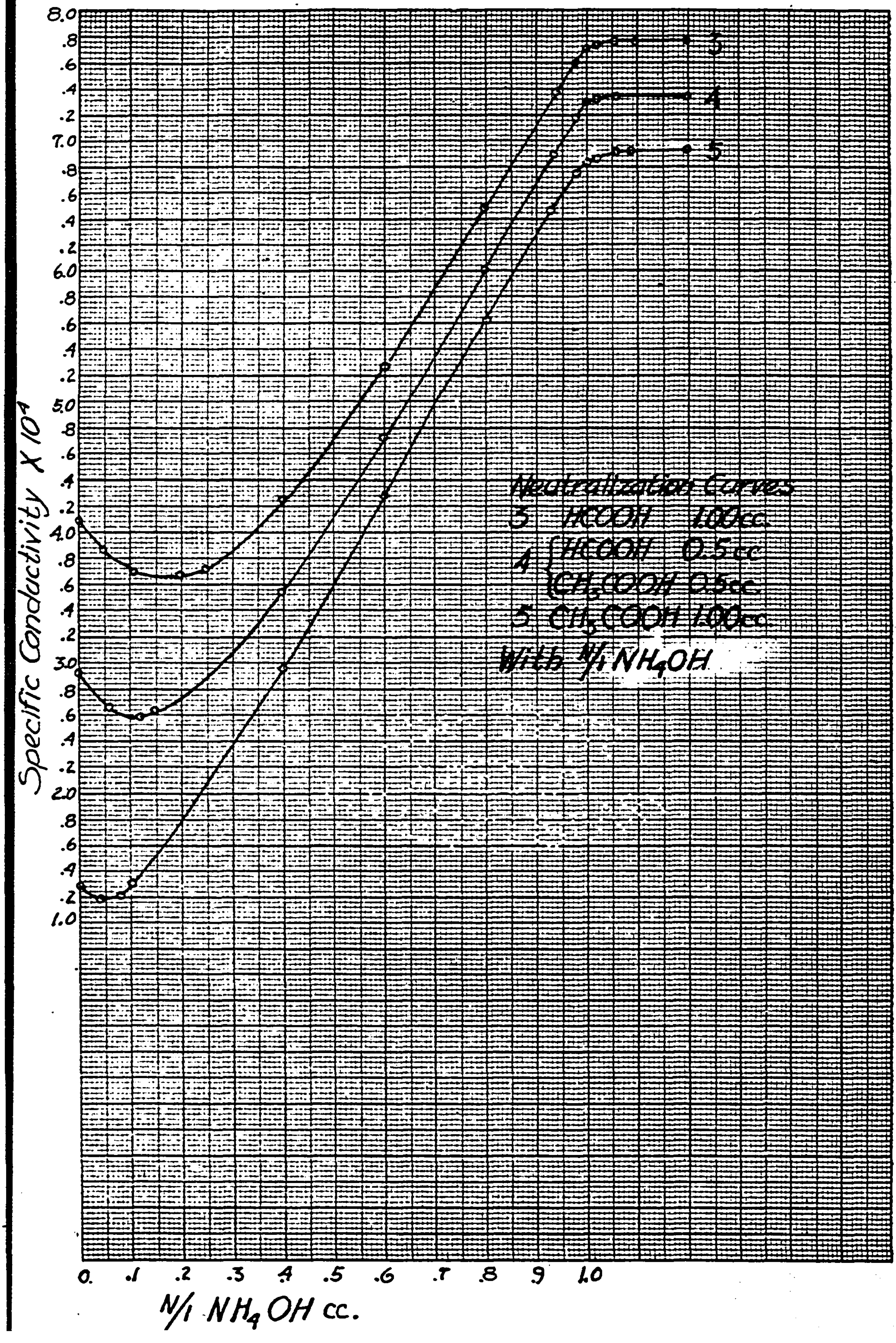
Data for the Neutralization Curve of a Mixture of 0.5 cc. of Normal Formic and 0.5 cc. Normal Acetic Acids with Normal Ammonium Hydroxide

cc. Normal Ammonium Hydroxide	Bridge Reading (A)	$\frac{A}{1000-A}$	Specific Conductivity ($x\ 10^4$)
0.00	243.0	0.3210	2.898
0.06	227.2	0.2940	2.655
0.12	221.0	0.2837	2.562
0.16	222.7	0.2865	2.537
0.40	279.5	0.3879	3.503
0.60	243.3	0.5224	4.717
0.80	299.2	0.6644	5.999
0.94	433.7	0.7626	6.868
0.98	443.2	0.7960	7.188
1.00	446.0	0.8050	7.269
1.02	447.4	0.8090	7.319
1.06	448.7	0.8140	7.350
1.08	448.7	0.8140	7.350
1.10	448.7	0.8140	7.350
1.20	448.7	0.8140	7.350

Temperature = 25°C.±0.05

Dilution water = 155 cc.

Resistance in opposite arm of bridge = 300 ohms.



Neutralization Curves
3 HCOOH 1.00cc
4 {HCOOH 0.5cc, CH$_3$COOH 0.5cc}
5 CH$_3$COOH 1.00cc
With N/1 NH$_4$OH
3
4
5
Specific Conductivity X 10^4
8.0 .8 .6 .4 .2 7.0 .8 .6 .4 .2 6.0 .8 .6 .4 .2 5.0 .8 .6 .4 .2 4.0 .8 .6 .4 .2 3.0 .8 .6 .4 .2 2.0 .8 .6 .4 .2 1.0
0. .1 .2 .3 .4 .5 .6 .7 .8 .9 1.0
N/1 NH$_4$OH cc.

against cubic centimeters of normal ammonium hydroxide added, also in each case there was present at the start one cubic centimeter of normal acid. As would be expected from the closeness of the dissociation constants it is not possible to detect any breaks corresponding to the quantities of the individual acids present (Curve 4).

It will be noted that the specific conductivity of formic acid is considerably higher than that of acetic. For a given total acid concentration the conductivity is greater the more formic acid there is present in the mixture. The specific conductivities are not straight line functions of the quantities of acid present. If the former are plotted as ordinates and the latter as abscissae, a curve is obtained which shows that the conductivity is not directly proportional to the acid concentration. This holds true in the case of pure acids as well. As we increase the concentration of the acid the percentage dissociation becomes less.

Theoretically this should be true for any acid because if we complete the curve to the point of one hundred percent acid concentration, it will reach a maximum and then decrease to zero.

A study of the data secured showed that for the concentrations used, the specific conductivity is really an antilog function of the quantity of acid present. This point will be more fully discussed in connection with the equations which we have developed for the calculation of the analytical results. Curve 6 shows the specific conductivities of various mixtures of formic and acetic acids, when the total acid concentration is two cubic centimeters of normal acid in 157 cubic centimeters of solution. Five points were determined experimentally for each curve. The point on the left shows the specific conductivity of pure formic acid of this concentration, the next point was determined using 0.50 cc. of acetic and 1.50 cc. of formic acids, the third point was determined using 1.00 cc. of each acid, for the fourth point 1.75 cc. of acetic and 0.25 cc. of formic acid were used, and for the point on the right 2.00 cc. of normal acetic acid were taken. A smooth curve was drawn thru the points obtained. Curves 7-10 were obtained in the same manner. Each point on Curve 7 refers to 1.75 cc. total normal acid, on Curve 8 each point represents 1.50 cc., on Curve 9, 1.25 cc., on Curve 10, 1.00 cc., Curve 11 shows the changes in conductivity which take place as the concentration of the formic acid is increased, and Curve 12 was determined for acetic acid in the same way. In both 11 and 12 we are dealing with the single acid only. Table 9 gives the data from Which Curves 6-12 were obtained.

Table 9

Data for Curves 6-12 Showing the Effect of Increased Acid Concentration on Specific Conductivity Also the Relative Effects of Formic and Acetic Acids

Curve	cc. Normal Acetic Acid	cc. Normal Formic Acid	Bridge Reading (A)	$\frac{A}{1000-A}$	Specific Conductivity (x 10^4)
6	0.00	2.00	395.8	0.6551	5.915
	0.50	1.50	364.3	0.5731	5.175
	1.00	1.00	322.2	0.4755	4.294
	1.50	0.50	262.8	0.3564	3.217
	2.00	0.00	168.6	0.2026	1.829
7	0.00	1.75	379.1	0.6105	5.508
	0.50	1.25	341.5	0.5186	4.683
	0.85	0.90	308.6	0.4462	4.029
	1.25	0.50	259.5	0.3504	3.164
	1.75	0.00	160.5	0.1910	1.725
8	0.00	1.50	360.2	0.5630	5.086
	0.30	1.20	335.0	0.5038	4.549
	0.75	0.75	278.8	0.4040	3.648
	1.20	0.30	218.6	0.2798	2.527
	1.50	0.00	150.2	0.1768	1.596
9	0.00	1.25	337.3	0.5090	4.596
	0.25	1.00	312.5	0.4545	4.104
	0.60	0.65	271.7	0.3731	3.369
	1.00	0.25	204.0	0.2563	2.314
	1.25	0.00	139.4	0.1620	1.463
10	0.00	1.00	310.0	0.4493	4.057
	0.25	0.75	280.6	0.3901	3.523
	0.50	0.50	243.0	0.3210	2.898
	0.75	0.25	192.3	0.2380	2.194
	1.00	0.00	124.2	0.1419	1.282
11		2.00	395.8	0.6551	5.915
		1.75	379.1	0.6105	5.508
		1.50	360.2	0.5630	5.086
		1.25	337.3	0.5090	4.596
		1.00	310.0	0.4493	4.057

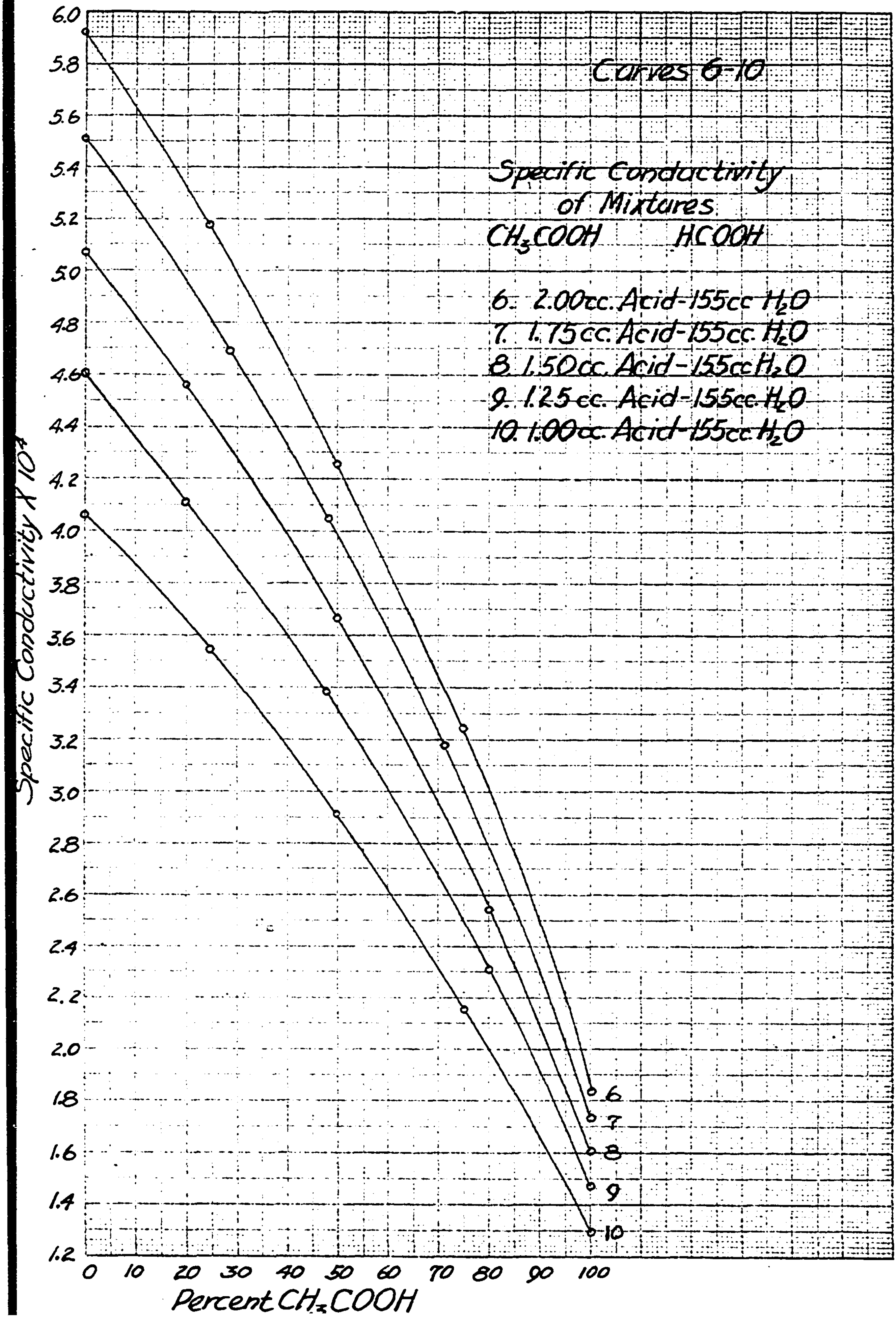
Table 9 (Continued)

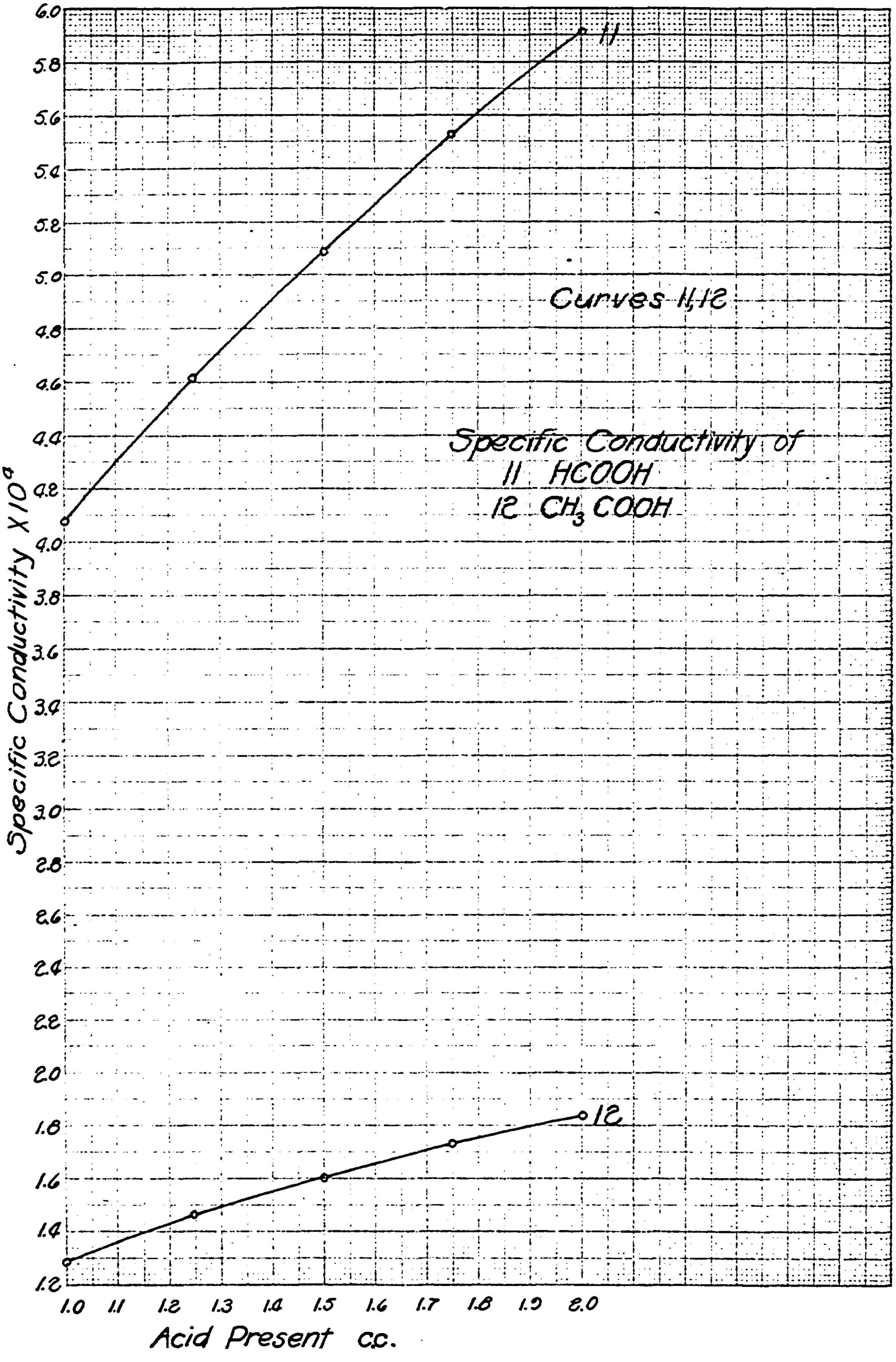
Curve	cc. Normal Acetic Acid	cc. Normal Formic Acid	Bridge Reading (A)	$\frac{A}{1000-A}$	Specific Conductivity (x 10^4)
12	2.00		168.6	0.2026	1.829
	1.75		160.3	0.1910	1.725
	1.50		150.2	0.1768	1.596
	1.25		139.4	0.1620	1.463
	1.00		124.2	0.1419	1.282

Temperature = 25°C.±0.1

Dilution water in each case = 155 cc.

Resistance in opposite arm of bridge = 300 ohms.


Curves 6-10
Specific Conductivity
of Mixtures
CH3COOH HCOOH
6. 2.00cc. Acid-155cc H2O
7. 1.75cc. Acid-155cc. H2O
8. 1.50cc. Acid-155cc H2O
9. 1.25cc. Acid-155cc. H2O
10. 1.00cc. Acid-155cc H2O
Specific Conductivity X 10⁴
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
0
10
20
30
40
50
60
70
80
90
100
Percent CH3COOH
6
7
8
9
10


Curves 11,12
Specific Conductivity of
11 HCOOH
12 CH₃COOH
11
12
Specific Conductivity X10⁴
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
Acid Present cc.

It is of interest here to compare our values for the conductivities of solutions of acetic acid in this range with those of Kendall as given by Kraus (1923). Kendall expresses his conductivities in terms of equivalent conductances in reciprocal ohms which we shall designate as E and his concentrations in terms of "dilution in liters per equivalent", which we shall designate as V. Our conductivities (Table 9) (Curve 12) are expressed in terms of specific conductivities in reciprocal ohms which we shall designate by S. Our dilutions are expressed in cubic centimeters of normal acid plus 155 cubic centimeters of water, which is obviously most easily designated by cc. To compare the two sets of values it was necessary to convert them to like units. We chose arbitrarily specific conductivity and dilution in liters per equivalent as units. The data from Kraus's work which interest us in this range are given below.

Table 10

V	E
15.816	6.561
31.63	9.26
63.26	13.13
126.52	18.30
253.04	25.60
506.01	35.67

$S = \frac{N\,E}{1000}$ (Equation 1) where N is the number of equivalents of solute present per liter of solution (By definition)

$N = \frac{1}{V}$

$S = \frac{E}{V\ 1000}$ (Equation 2)

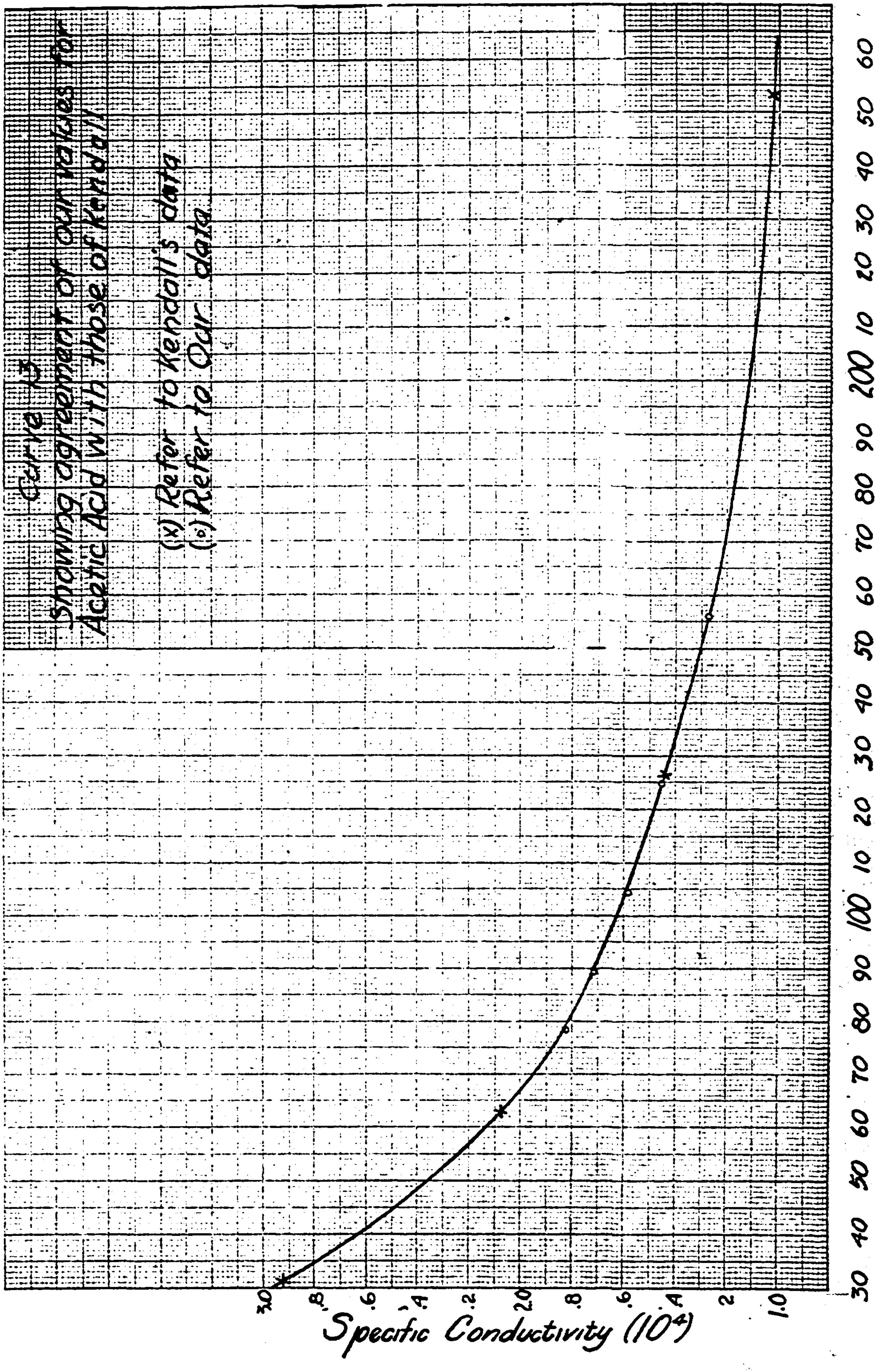
In Table 9 of our data we have the number of cubic centimeters of normal acid added to 155 cubic centimeters of water from which V may be readily calculated. Table 11 gives Kendall's data expressed in terms of specific conductivity and dilution in liters per equivalent, and Table 12 gives our data expressed in the same units. The values were plotted (Curve 13) with crosses representing Kendall's data, circles representing ours, and the agreement is very satisfactory. As we will show later, our method does not demand extreme accuracy in the measurement of conductivity in order that it may give satisfactory analytical results, the agreement shown here being far greater than that required.

Table 11

V	$S(x10^4)$
15.816	4.15
31.63	2.927
63.26	2.08
126.52	1.44
253.04	1.01
506.01	0.706

Table 12

V	$S(x10^4)$
156	1.282
125	1.463
104.4	1.596
89.5	1.725
78.5	1.829



Curve 3

Showing agreement of our values for Acetic Acid with those of Kendall

EXPERIMENTAL

Solutions

The primary standard used was hydrochloric acid which was standardized by precipitation as AgCl.

The potassium hydroxide was standardized by titrating against the standard hydrochloric acid using methyl orange as the indicator.

The volatile fatty acids used were standardized by titrating against the standard potassium hydroxide using phenolphthalein as the indicator. The solutions of volatile fatty acids were made from samples which were prepared by taking the purest acids available and fractionally distilling.

The ammonium hydroxide was standardized by titrating against the standard hydrochloric acid using methyl orange as the indicator. The volatile fatty acids and the ammonium hydroxide all had a normality of 1.00 ± 0.005.

As a further check on the concentrations the volatile fatty acids were titrated against the ammonium hydroxide potentiometrically and found to be equivalent.

All apparatus used was calibrated with the same degree of care that should be used in any exact analytical work.

Apparatus

The apparatus used consisted of, first, a thermostat which maintained a temperature of $25^\circ \pm 0.05$. As the mobilities of the ions increase from 1.5% per degree in the case of hydrogen to 2.7 % in the case of the carbonate ion, close temperature regulation is necessary. The thermostat which was made in the department shop consisted of an iron tank, painted with a lacquer on the inside and covered with asbestos board on the outside. The stirring motor and heating coils were on the same 110 volt A.C. circuit. The relay which was in the control circuit was run by two dry cells. These cells must be tested regularly because if their voltage becomes low the relay will not function properly and consequently the temperature control will be faulty. The type of relay which uses a transformer and is connected in the alternating current circuit cannot be used because of its noise. A mercury column "make and break" regulator was used. A double pole single throw switch having the motor and heating circuit on one side and the control circuit on the other was placed upon the operator's table, so that it was possible to shut off the apparatus when taking a reading. This was seldom necessary.

A Kohlrausch bridge (Leeds and Northrup 4258) was used. This bridge has a 470 centimeter wire of about 7 ohms resistance which is divided into 1000 divisions with half divisions indicated. Our readings were accurate, that is reproducible, to 0.25 divisions. The two plug controlled end coils were each adjusted to 4.5 times the resistance of the slide wire, and were accurate to 0.1 percent.

A direct current cannot be used in the determination of conductivity because electrolysis would occur and the products set free at the electrodes would set up a back E.M.F. and alter the resistance of the liquid, by interposing a layer of gas between the liquids and the electrodes; these effects are included in the term polarization. To avoid this an alternating current is used. Reilly, Rae and Wheeler (1925) give the following as the requirements which must be fulfilled if the current is to be satisfactory for this work:

(1) The alternations should be sufficiently rapid and the quantity of electricity passing at each alternation should be small so that no appreciable chemical change occurs.

(2) The quantity of electricity passing in one direction should be exactly equal to that passing in the other - if a small excess passes one way this will produce exactly the same electrode effects as a direct current of the same magnitude.

(3) The source of alternating current should give a wave of pure sine form. If this condition is not fulfilled and harmonics or overtones are present it is difficult to get a good minimum in the telephone.

Taylor and Acree (1916) have shown that with platinized electrodes appreciable differences in the value of the apparent resistance may be produced by a change in frequency of the measuring current, so that the point of balance for the fundamental frequency will not be the same as that of the overtones, with the result that a good sound minimum cannot be obtained.

The induction coil was used by Kohlrausch and Holborn (1898). The best results were obtained with small coils having few turns of wire, so that the total quantity of electricity passing at each pulse was small: the moving parts of the coil being small and light, a high note was obtained to which the ordinary telephone and ear are sensitive. This type of instrument was found to be unsatisfactory in our work; it cannot be used when accuracy greater than 0.2 % is required, since the current departs very much from the ideal requirements. Oscillograms obtained from induction coils (Taylor and Acree, 1916) contain a number of harmonics and when the area of the positive and negative loops are measured it is found that a considerable unidirectional current is present. Since the sum of the two currents in opposite directions is not zero polarization must occur.

The microphone hummer (Leeds and Northrup #9856) gave fairly satisfactory results in this work. The frequency is constant since it is maintained by a 1000 cycle tuning fork. This fork actuates the microphone and the current thru the microphone also passes thru a transformer, from the secondary of which the magnet that keeps the fork in vibration is supplied. An extra subdivided winding on the transformer has a number of terminals on the top of the case from which current at different voltages but the same frequency may be obtained. The wave form of the microphone hummer has a number of harmonics which may interfere with the precision of setting the bridge. This difficulty is somewhat lessened if a telephone receiver is used with its resonance point adjusted to the frequency of the microphone hummer. (Leeds and Northrup Catalog 10) The hummer was kept in a covered box which had a layer of cotton on the bottom and was lined with cloth to make it practically sound proof. All of the determinations which appear in this paper were made originally using this apparatus.

While the microphone hummer can be used in this work the Vreeland oscillator, Leeds and Northrup (1925), gives more satisfactory current. The apparatus is noiseless and its wave form is free from harmonics. (Taylor and Acree 1916) We have the Leeds and Northrup #9840 apparatus. This form is arranged to give frequencies of 1000 or 500 cycles per second, it is arranged to use 110 volt D.C. and consists of a mercury vapor tube provided with one cathode and two anodes. The current passes along a split circuit each arm of which includes a resistance, an inductance and a gap between the cathode and one of the anodes of the mercury vapor tube: the mercury arc thus has two symmetrical paths between the cathode and the two anodes. The circuit which produces the oscillations is shunted across the two anodes and contains two inductance coils and a capacity. A current in these coils deflects the arc to one anode more than the other: this produces a potential difference between the two anodes and a larger current passes in the inductance, charging the condenser. The latter then discharges in the opposite direction, reversing the current in the inductance and the direction of deflection of the mercury arc, and the condenser becomes charged with the opposite sign. This process continues, and the working current is taken off by two secondary coils, which may be arranged in series or parallel depending upon whether a high or low voltage is required. A further adjustment is possible from the fact that a switch is provided to change the field coils from a series to a parallel connection. Since in the latter case their inductance is one quarter of its value when the series connection is used the frequency will be doubled by changing from series to parallel, the capacitance remaining constant.

The two important types of detectors in use are the alternating current galvanometer and the telephone receiver. The former has several advantages over the latter. It is necessary to keep the current on but a short time in finding the balance point thus decreasing the chances of heating and polarization. Absolute silence is not necessary and the direction of the deflection gives at once the side of the bridge which has the larger resistance. Any creeping of the pointer after balance shows the presence of heating or polarization. For low commercial frequencies the galvanometer is preferred. For higher frequencies, especially 1000 cycles per second, the telephone receiver is twenty times as sensitive as the galvanometer. This high sensitivity is due to the characteristics of the human ear combined with those of the receiver. The sensitiveness of the telephone is so great that it is eminently satisfactory. We used a tunable telephone receiver.

To avoid or remedy stray fields, induction effects, etc., it is necessary to surround certain parts of the apparatus with earthed iron cases; for an excellent discussion of these troubles the reader is referred to Reilly, Rae, and Wheeler (1925).

The conductivity cell used was made from a 250 cc. pyrex Erlenmeyer flask by sealing two glass tubes, each having an electrode, into the sides. To increase the rigidity of the apparatus, thin pieces of glass rod were used to connect the four corresponding corners of the two electrodes. The electrodes were made of heavy platinum pieces about one-half inch square and placed about one inch apart. A clean platinum electrode gives a poor null point due to polarization; a considerable range of silence is obtained and the notes heard on the two sides of the minimum are not of the same tone. Polarization is decreased by platinizing the electrodes. Thick layers of platinum may cause changes in the solution owing to catalytic action or selective adsorption, and by making it difficult to wash out previously used solutions. By using a three percent solution of chlorplatinic acid and reversing the poles every half minute for eight minutes we secured a very satisfactory deposit. This was freed from occluded gases by electrolyzing a dilute solution of sulfuric acid in the cell for half an hour, introducing a third platinum electrode as the anode and having the two electrodes of the conductivity apparatus act as joint cathodes. The cell was hung loosely on a burette clamp in such a way that it could be shaken without removing it from its support. The level of the water in the thermostat should be above the level of the liquid in the cell.

A 2.00 cc. burette, graduated to 0.02 cc. and readable to 0.01 cc. was used. This had a long tip which was drawn out at the end so that it was possible to touch it to the surface of the solution in the cell after each addition of reagent; this insured that the reading on the burette really showed the quantity of reagent which had been added to the cell. There was negligable error due to diffusion from the finely drawn out tip which was in contact with the cell liquid only an instant.

It was found advisable to leave the conductivity cell in the bath during the run, the burette was taken from its stand, the desired amount of reagent run into the cell, the tip of the burette was allowed to touch the surface of the liquid in the cell, the burette was replaced on its stand, the cell was shaken and the bridge reading taken. The new equilibrium is reached quickly. It is not necessary to shake the cell violently or for a long time. A few twists are enough. Neither is it necessary to repeat the shaking and reading to be certain that equilibrium is reached.

Cell Constant

The cell constant was determined by using a N/50 KCl solution at 25°C. Landoldt Börnstein (1923) gives 138.65 as the value of the equivalent conductivity of this solution. The dilution water which is used to make up this standard KCl solution should be the same as that used to dilute unknowns.

From equation 1,

$$S = \frac{(138.65)(0.02)}{1000} = 2.7730 \times 10^{-3}$$

From the Wheatstone bridge equation,

$R:X = A:B$ (1)

Where X = resistance of the solution in the cell.

R = known resistance

A and B = the two parts of the bridge

$X = \frac{BR}{A}$ resistance

$\frac{1}{X} = \frac{A}{BR}$ = conductance of solution in the cell

$S = K\frac{1}{X} = K\frac{A}{BR}$ = specific conductance (3)

w = specific resistance

$X = w\frac{l}{d}$ (4)

l = distance between electrodes

d = cross section of electrodes

$$S = \frac{1}{w}$$
$$= \frac{1}{X}\ \frac{l}{d}$$
$$K = \frac{l}{d} = SX$$
$$S = \frac{K}{X}$$
$$X = \frac{BR}{A}$$
$$S = \frac{A}{B}\ \frac{K}{R}$$

The bridge has 1000 scale divisions.

$B = 1000 - A$

$$S = \frac{A}{1000-A}\,\frac{K}{R} \quad \text{(equation 5)}$$

$$K = \frac{SR}{\frac{A}{1000-A}} = S\,\frac{1}{\frac{A}{(1000-A)R}} \qquad \text{(equation 6)}$$

Table 13 gives an example.

Table 13

R	A	$\frac{A}{1000-A}$	$\frac{A}{(1000-A)R}$
100	505.8	1.023	1.023×10^{-2}
200	671.8	2.046	1.023×10^{-2}
250	719.2	2.561	1.024×10^{-2}
300	754.7	3.075	1.025×10^{-2}

$$K = \frac{(2.773)(10^{-3})}{1.0236 \times 10^{-2}} = 2.709 \times 10^{-1}$$

The cell should be checked occasionally against a standard KCl solution. If used carefully it will stay constant for a long time in the type of solutions which occur in such analyses. The constant did not change during the runs made in this work. We saturated the electrodes with hydrogen occasionally by making them the negative poles in a dilute sulfuric acid solution and connecting to a couple of dry cells. This operation appeared to aid in keeping the null point sharp but did not change the cell constant.

The glass used in conductivity work should be fairly old, as new glass is much more soluble than old.

Procedure

155 cc. of water of a specific resistance of about 2×10^5 ohms were used. This is about the quality of water which is obtained upon distillation from glass apparatus. As will be shown later the exact value of the specific conductivity of the water used need not be known in this work, nor is it necessary for other workers to use water of the same specific conductivity as that which we used. In fact, a water of higher conductivity than would be used by any reasonably careful worker, does not cause a sufficient error to vitiate the results. A quantitative study of the effects of different grades of water is given later.

The desired amount of normal acid was placed in the conductivity flask to which was added 155 cc. of dilution water from a calibrated narrow mouth flask. This gave a solution from 0.0065 to 0.013 normal in acid. When the solution is titrated with normal alkali the effect of dilution upon the conductivity is small. Another reason for using such a large cell is the rather low concentration of acids in the distillate of some of our fermentation mixtures.

To run a complete curve the bridge reading (A) was taken after each addition of alkali, from tables $\frac{A}{1000-A}$

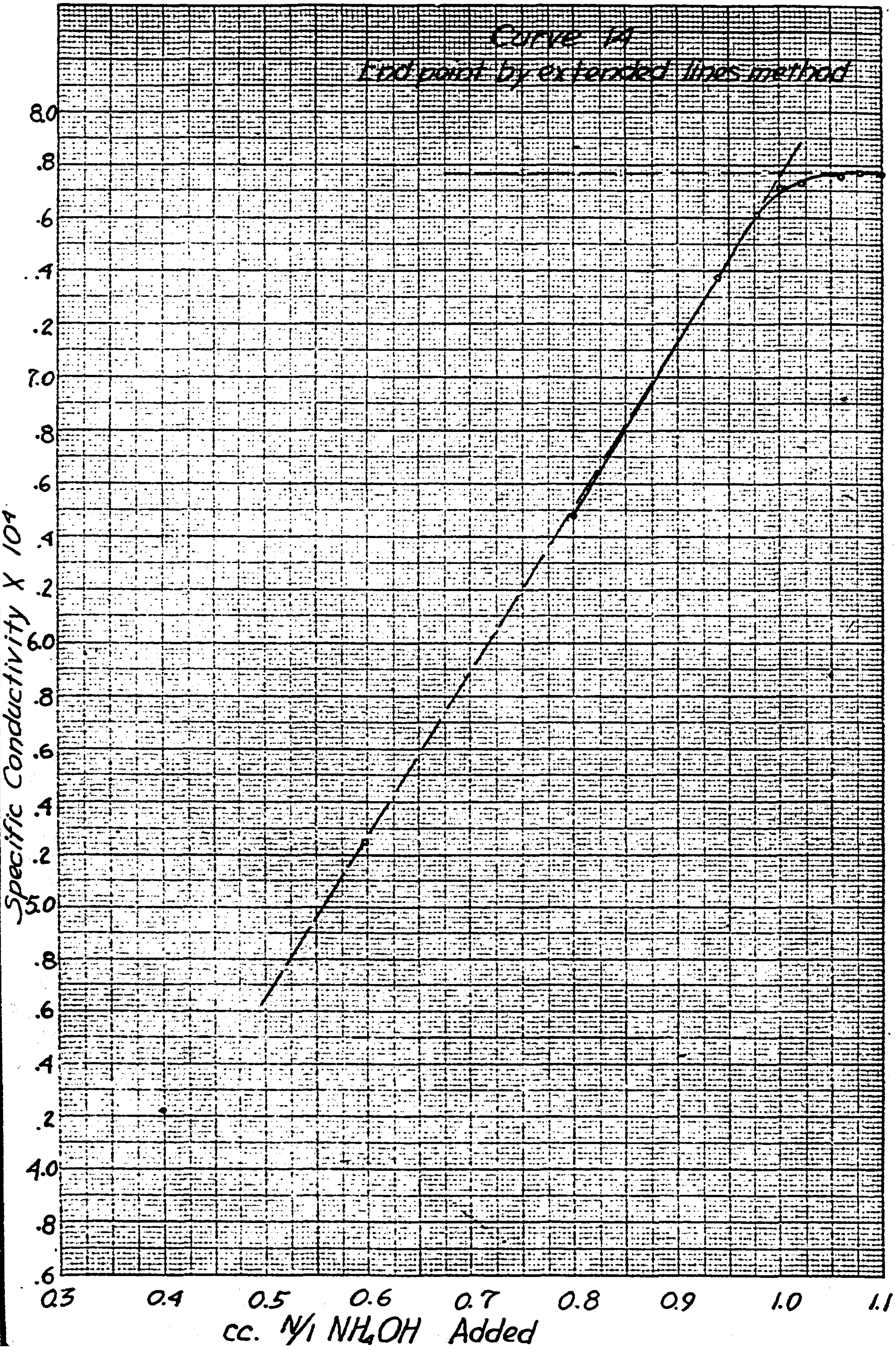
obtained and as $S = \frac{A}{1000-A} \quad \frac{K}{R}$ (equation 5)

$$K = 2.709 \times 10^{-1}$$

$R = 300$ (used unless otherwise specified)

$$S = \frac{A}{1000-A} \quad 9.03 \times 10^{-4}$$

In the ordinary analysis it is not necessary to take many points before the end-point. In fact it is not advisable to do so as normal ammonium hydroxide loses strength rather quickly when exposed to the air. The initial reading should be accurately determined, as it is from this reading that we calculate the specific conductivity of our acids. Usually the operator will know the total acid concentration, from a previous titration so the ammonium hydroxide can be run in rather quickly to this point, then added 0.05 cc. at a time until two readings check. This constant reading is used to calculate the specific conductivity of the salt. In case the operator does not know the total acid concentration it is necessary to run in the alkali about 0.02 cc. at a time until the end-point is nearly reached and then 0.01 cc. at a time until the bridge readings become constant. The end-point may be obtained in either of two ways. The values obtained may be plotted, specific conductivities against cubic centimeters of alkali added, then by extending the ascending and horizontal lines a point of intersection will be obtained which gives the number of cubic centimeters of normal acid (Curve 14)(Table 6). The extended lines referred to above are shown by the broken lines, whose intersection gives the end-point. This method has several disadvantages, First, it is time consuming, second, it is easy to make a sufficient error in drawing the lines to affect the result by several percent, and lastly, the end-point obtained, even if the work has been carefully carried out, is not the true equivalence point. (Eastman 1925) A second method which we have worked out arbitrarily gives more satisfactory results and requires much less time. If the total number of cubic centimeters of normal ammonium hydroxide which must be added before the conductivity becomes constant is divided by the factor 1.06 the result gives the number of cubic centimeters of normal acid originally present in the solution. We obtained this value, 1.06, by running a number of neutralization curves on various acid solutions of known composition and noting the quantity of normal ammonium hydroxide which must be added before the conductivity became constant. This value, 1.06, is applicable only in the range of concentrations with which we are working. The relationship between equivalence and the quantity of ammonium hydroxide which must be added before the conductivity becomes constant was discussed before in the section on theory.



Curve 14

End point by extended lines method

Accuracy of Data

The specific conductivity of a solution can be easily determined with a degree of accuracy far greater than is necessary for quantitative work. The errors, other than those incidental to any quantitative procedure, are due to instability of reagents and to the presence of substances in the solution which affect the conductivity other than those substances for which we are analyzing. We were able to check results repeatedly over intervals of several months using the same standard normal ammonium hydroxide. This was made up in quantities of several liters, and was kept stoppered at all times except when it was necessary to allow some air to enter so that the alkali could run out. The solution became somewhat clouded but its strength did not change enough to affect the results.

Table 15 gives the results of a study of the effect of the quantity of dilution water used on the specific conductivity found. In the case of acetic acid the error is negligible, the addition of more water causing enough more acid to ionize to keep the conductivity nearly constant. In the case of the formic acid which is more highly dissociated the effect is greater. The percentage error will be less the more concentrated the acid, as the ionization decreases with concentration. In the case of the salts the error is

Table 15

Errors due to Dilution

cc. Normal Solution	cc. Dilution Water	Bridge Reading (A)	$\frac{A}{1000-A}$	Specific Conductivity (X 10^4)	Average Error per cc. of dilution water (%)
(15a) 1.00 Acetic Acid	155.0	124.2	0.1420	1.282	0.08
	155.5	124.2	0.1420	1.282	
	156.0	124.2	0.1420	1.282	
	157.0	124.1	0.1418	1.280	
	158.0	124.0	0.1416	1.278	
(15b) 1.00 Formic Acid	155	310.0	0.4493	4.057	0.26
	156	309.4	0.4480	4.045	
	157	308.8	0.4466	4.032	
	158	308.4	0.4458	4.025	
	159	307.8	0.4446	4.015	
(15c) 2.00 Ammonium Acetate	155	434.0	0.7667	6.923	0.46
	156	432.7	0.7626	6.885	
	157	431.7	0.7595	6.858	
	158	430.5	0.7558	6.829	
	159	429.6	0.7527	6.797	
(15d) 2.00 Ammonium Formate	155	462.6	0.8608	7.771	0.49
	155.5	461.8	0.8580	7.747	
	156	461.0	0.8552	7.722	
	157	459.6	0.8504	7.678	
	158	458.5	0.8467	7.645	
	159	457.4	0.8430	7.612	

greater than in the case of acids as would be expected from the relative degrees of ionization of the two types of compounds.

The degree of care required in making dilutions is no greater than that required in any exacting analytical procedure of the laboratory. In those cases where it is necessary to know only the specific conductivity of the acid or acids and not the change in conductivity upon neutralization only ordinary care need be taken in diluting.

Errors due to using different kinds of dilution water in analysis. In order to use the diagrams and equations developed in this paper an investigator should use water of about 2 X 10^5 ohm resistance. This is the quality of water distilled from pyrex. The same quality of water should be used for diluting unknowns that is used in making the standard potassium chloride solution with which the cell constant is determined.

A dilution water of the above quality was kept in this laboratory in a tin container which had a loose cover for a month. During this time it did not change enough to affect our results in an appreciable degree.

Ex. (1.00 cc. of Normal Formic Acid with 155 cc. of dilution water)

Date	Specific conductivity (X 10^4)
7/31/28	4.054
8/31/28	4.057

(2 cc. of Normal Ammonium Acetate with 155 cc. of dilution water)

Date	Specific Conductivity (X 10^4)
7/31/28	7.771
8/31/28	7.771

Table 16

Specific Conductivities of Ordinary Laboratory Dilution Waters

Water	Resistance in opposite arm	Bridge (A)	$\frac{A}{1000-A}$	Specific Resistance	Specific Conductivity ($X10^6$)
1	9000	110.0	0.1263	268,000	3.720
	18700	204.0	0.2563	269,000	3.716
2	9000	142.5	0.1673	198,000	5.032
	18700	257.5	0.3468	198,000	5.023
3	9000	157.0	0.1862	178,000	5.604
	18700	280.0	0.3890	175,000	5.640

Water #1 was prepared by redistilling tap distilled water from pyrex containers.

Water #2 was prepared by distillation of tap water from pyrex containers.

Water #3 was ordinary tap distilled water.

The values given above were secured with our apparatus without any modifications. As this set-up was not designed for high resistance work the above values do not check very well and they may be off further than the lack of agreement would indicate. However, we are not interested in the absolute values of resistance for this water but rather in the effect which waters of different resistances have on our results. Using the above dilution waters the specific conductivities of a solution of 1.00 cubic centimeters of formic acid in 155 cc. dilution water were as follows (Table 17):

Table 17

Errors Due to Use of Different Grades of Dilution Water

Water	R	A	$\frac{A}{1000-A}$	Sp. Cond. (X 10^4)	Maximum Error
1	300	309.7	0.4485	4.050	0.35%
2	300	310.0	0.4493	4.057	
3	300	310.4	0.4501	4.064	

Dilution waters #1 and #3 above have the extreme values for specific conductivity which will be met with. No trouble will be experienced in obtaining water which falls between these two values. New conductivity water has a very low specific conductivity. Water that has stood a long time in new glass or which has been exposed to the air, will show a relatively high conductivity so that either of these would cause an appreciable error, if used. A correction can be made for the conductivity due to the water but if ordinary care is taken in following the procedure this is not necessary. It must be remembered that we are proposing a method for the analysis of acid mixtures and that we are not interested in slight errors in physical constants insofar as these errors do not affect our analytical results.

DIAGRAMS

Construction of Diagrams

The data for Diagrams 1 and 2 were obtained from solutions in which the total acid content was known, so that all that was needed was the initial and final specific conductivities.

On Diagram 1 we have plotted on the vertical planes, as ABCD, the specific conductivities of the various mixtures of formic and acetic acids as ordinates, the percentage composition, total acid being taken as 100 in each case, is shown by the abscissae. Each vertical plane represents a definite total acid composition. The front plane ABCD gives the specific conductivities of various mixtures of formic and acetic acids where the total acid concentration is one cubic centimeter of normal. We may consider this either as secured from the data in Table 9 , or as Curve 10 on the front face of the three dimensional figure, ABRQTDCD. The next vertical plane EFGH (Table 9)(Curve 9) represents 1.25 cc. total normal acid; the next IJKL (Table 9)(Curve 8) 1.50 cc; the next MNOP (Table 9)(Curve 7) 1.75 cc.; the rear plane QRST (Table 9)(Curve 6) 2.00 cc. The left side of each plane represents pure formic and the right side pure acetic.

Each profile plane represents the same ratio of acids but different total acid composition, that is, the mol

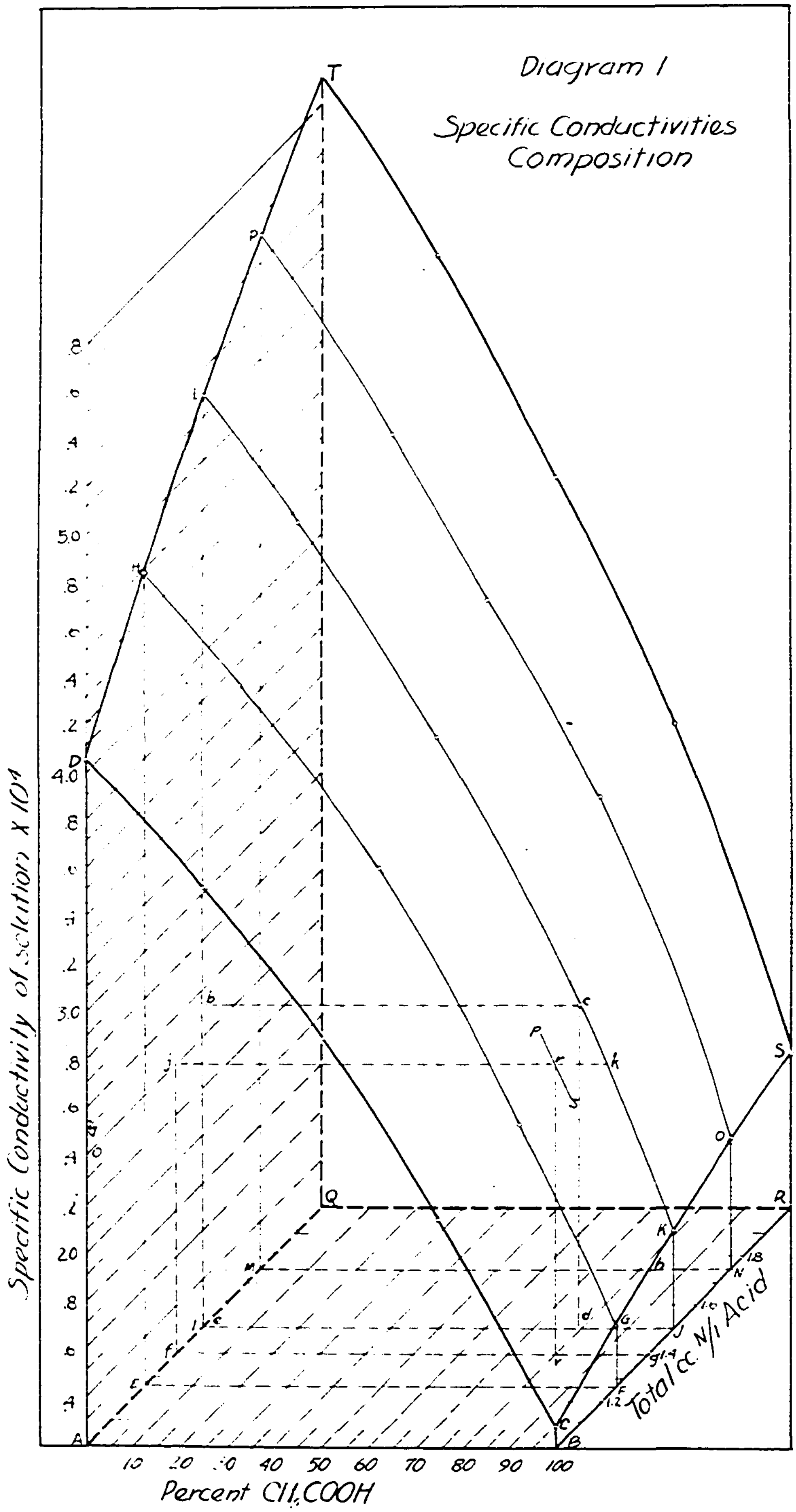


Diagram 1

Specific Conductivities
Composition

fraction is a constant for each plane but the sum of the cc. N. varies from one to two. The profile plane on the left, AQTD (Table 9)(Curve 11), shows the specific conductivities of different quantities of pure formic acid, from one to two cc. of normal, with 155 cubic centimeters of water. The profile plane on the right, BRSC (Table 9)(Curve 12), refers to pure acetic. Those profile planes between the above two represent different mixtures as indicated. For example, a plane parallel to the above two and midway between them would show the specific conductivities of mixtures of the two acids in which the quantities of each are equal.

On the horizontal plane, ABRQ, the Z axis represents the total quantity of acid present, the X axis the ratio of the two acids.

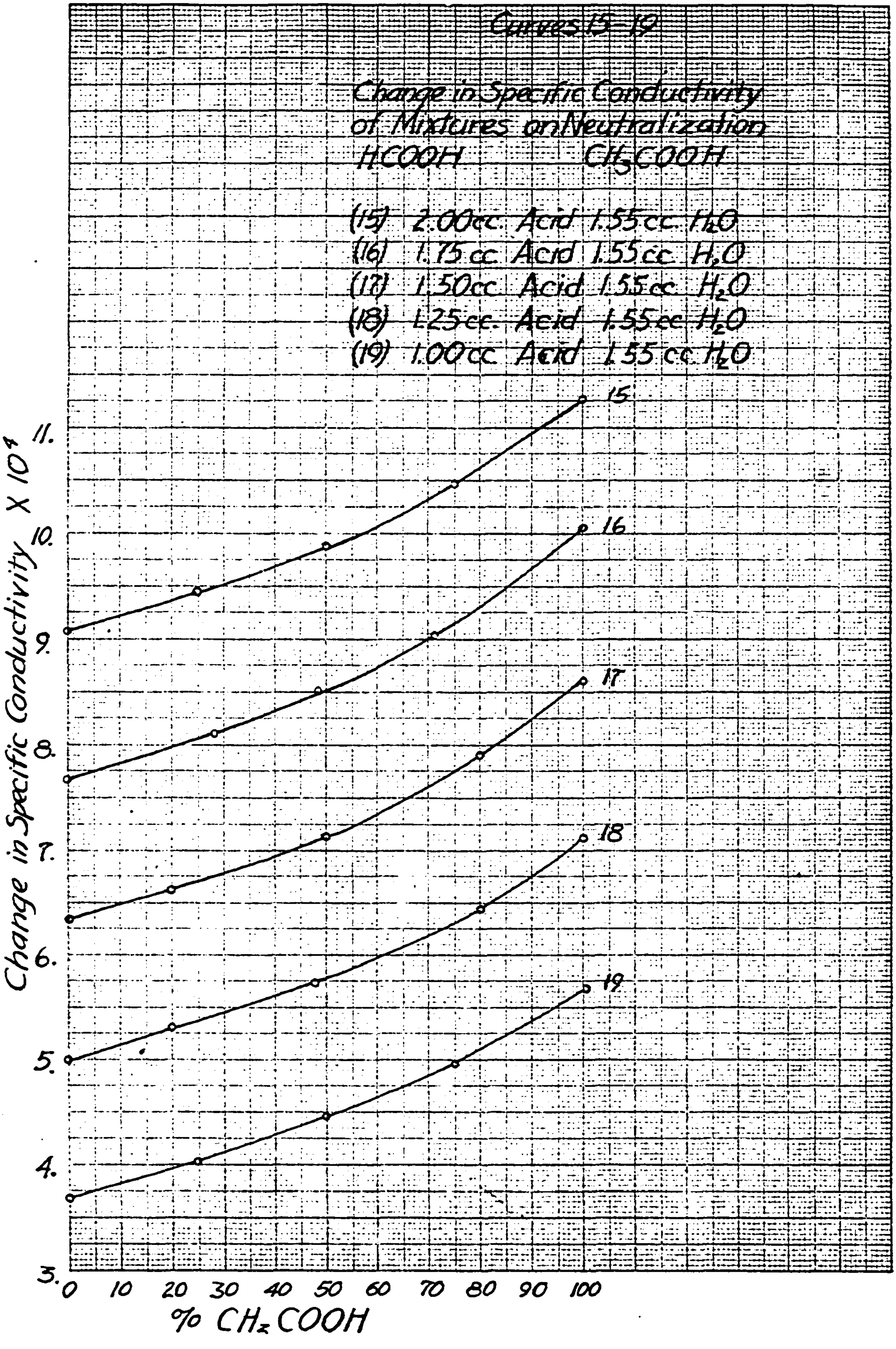
Diagram 2 is similar to Diagram 1 except that here the vertical axes represent not the specific conductivity of the acid or acids present in the original solution, but the change in specific conductivity which takes place upon neutralization. This diagram gives us one more value for each acid mixture. Its accuracy is of about the same order as that of the specific conductivity diagram, certain errors creep in due to extra operations and calculations required while certain other errors cancel or are diminished. Unless there is an acid or a base present in the solution as an impurity, the change in conductivity should be practically independent of small variations in procedure, such as temperature, volume of solution, conductivity of dilution water, all of which should affect the conductivities of the acids and resulting salts in the same direction. The effect while it is in the same direction is of a different degree, so that the accuracy is of about the same order as that in the case of Diagram 1. Either has a sufficient degree of accuracy for analytical work. Table 14 and Curves 14-20 show the component parts from which Diagram 2 is made. As the method is exactly similar to that used in Diagram 1 we will not discuss it further.

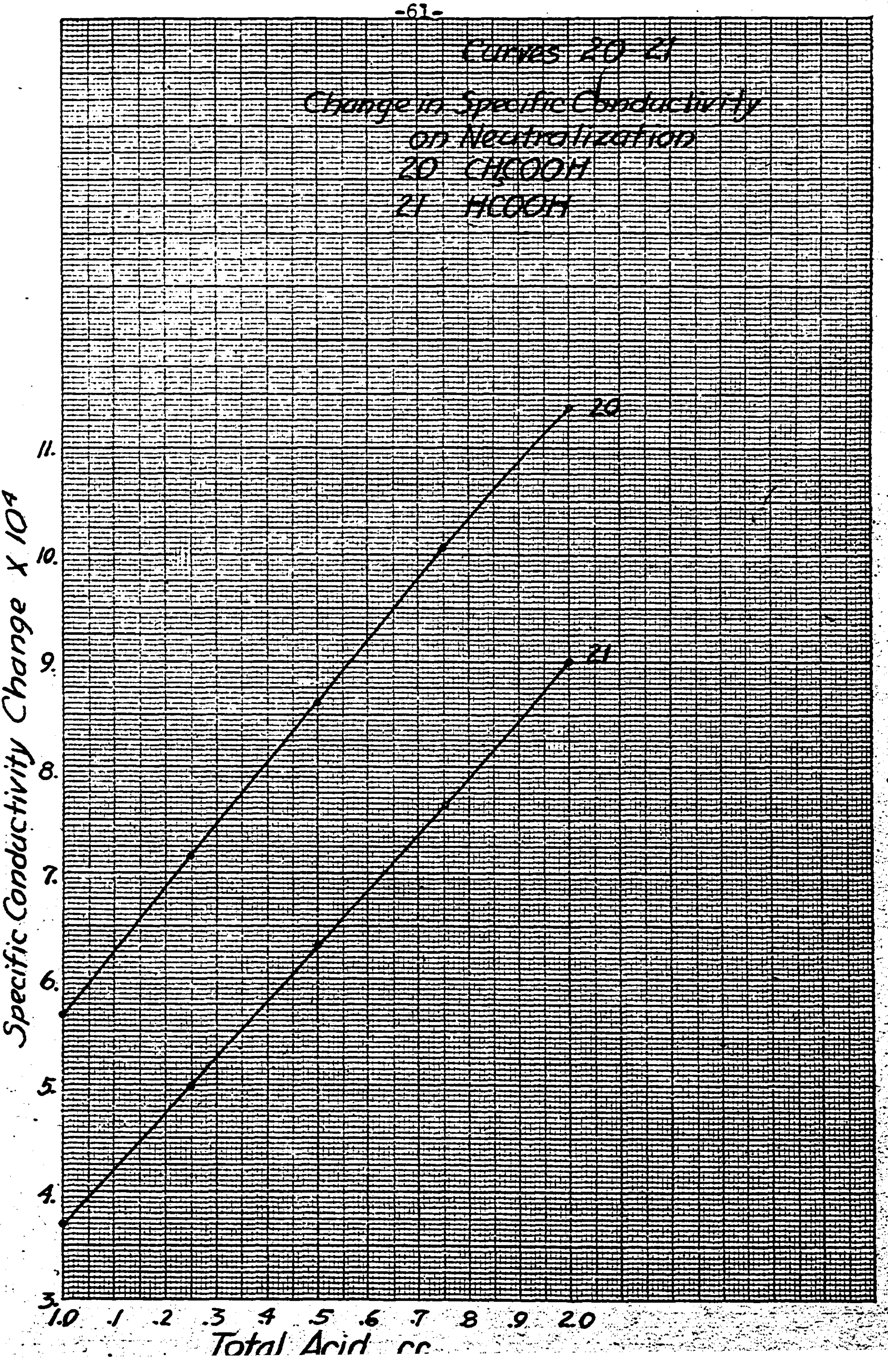
The use of three component diagrams would seem to deserve wider use than it has received in cases where it is not possible to derive simple equations and where equations are derived with certain assumptions which may not be fully legitimate. In our case we have proven that our assumptions are legitimate. The diagram is constructed from a number of points which are determined experimentally, every line on it being determined by these points, so that no assumptions are made in its construction. The diagrams which we propose will be criticised on the grounds that they are not drawn to scale, that in the front planes ten centimeters represents only 1.00 cubic centimeters of total normal acid while in the rear

Table 14

Data for Change in Conductivity Diagram 2

Normal Acid (cc)		Bridge Reading (A)		$\frac{A}{1000-A}$		Specific Conductivity ($X\ 10^4$)		Change in Specific Conductivity ($X\ 10^4$)
CH_3COOH	HCOOH	Initial	Final	Initial	Final	Initial	Final	
	1.00	310.0	462.6	0.4493	0.8606	4.057	7.771	3.714
	1.25	337.3	515.2	0.5090	1.063	4.596	9.599	5.003
	1.50	360.2	558.9	0.5630	1.266	5.086	11.422	6.336
	1.75	379.1	592.8	0.6105	1.456	5.508	13.147	7.639
	2.00	395.8	623.4	0.6551	1.655	5.915	14.945	9.030
1.00		124.2	434.0	0.1419	0.7667	1.282	6.923	5.642
1.25		139.4	488.3	0.1620	0.9544	1.463	8.618	7.152
1.50		150.2	530.0	0.1768	1.128	1.596	10.185	8.589
1.75		160.3	566.1	0.1910	1.305	1.725	11.784	10.059
2.00		168.6	592.0	0.2026	1.451	1.829	13.102	11.273
2.00	0.00	168.6	592.0	0.2026	1.451	1.829	13.102	11.273
1.50	0.50	262.8	602.5	0.3564	1.516	3.217	13.689	10.472
1.00	1.00	322.2	610.8	0.4755	1.570	4.294	14.177	9.883
0.50	1.50	364.3	617.9	0.5731	1.617	5.175	14.602	9.427
0.00	2.00	395.8	623.4	0.6551	1.655	5.915	14.945	9.030
1.75	0.00	160.3	566.1	0.1910	1.305	1.725	11.784	10.059
1.25	0.50	259.5	574.5	0.3504	1.350	3.164	12.191	9.027
0.85	0.90	308.6	581.2	0.4462	1.387	4.029	12.525	8.496
0.50	1.25	341.5	585.3	0.5186	1.412	4.683	12.760	8.077
0.00	1.75	397.1	592.8	0.6105	1.456	5.508	13.147	7.639
1.50	0.00	150.2	530.0	0.1768	1.128	1.596	10.185	8.589
1.20	0.30	218.6	535.2	0.2798	1.153	2.527	10.412	7.885
0.75	0.75	278.8	543.7	0.4040	1.191	3.648	10.755	7.107
0.30	1.20	335.0	552.8	0.5038	1.236	4.549	11.1611	6.612
0.00	1.50	360.2	558.9	0.5630	1.266	5.086	11.422	6.336
1.25	0.00	139.4	488.3	0.1620	0.9544	1.463	8.618	7.152
1.00	0.25	204.0	491.9	0.2563	0.9684	2.314	8.745	6.431
0.60	0.65	271.7	502.7	0.3731	1.011	3.369	9.129	5.760
0.25	1.00	312.5	510.3	0.4545	1.042	4.104	9.409	5.305
0.00	1.25	337.3	515.2	0.5090	1.063	4.596	9.599	5.003
1.00	0.00	124.2	434.0	0.1419	0.7667	1.282	6.923	5.642
0.75	0.25	192.3	440.9	0.2380	0.7886	2.149	7.121	4.972
0.50	0.50	243.0	448.7	0.3210	0.8140	2.898	7.350	4.452
0.25	0.75	280.6	455.9	0.3901	0.8378	3.523	7.565	4.042
0.00	0.00	310.0	462.6	0.4493	0.8606	4.057	7.771	3.714


Curves 15-19
Change in Specific Conductivity of Mixtures on Neutralization
HCOOH CH₃COOH
(15) 2.00cc Acid 1.55cc H₂O
(16) 1.75cc Acid 1.55cc H₂O
(17) 1.50cc Acid 1.55cc H₂O
(18) 1.25cc Acid 1.55cc H₂O
(19) 1.00cc Acid 1.55cc H₂O
15
16
17
18
19
Change in Specific Conductivity X 10⁴
3.
4.
5.
6.
7.
8.
9.
10.
11.
0
10
20
30
40
50
60
70
80
90
100
% CH₃COOH



Curves 20-21

Change in Specific Conductivity on Neutralization

20 CH_3COOH

21 HCOOH

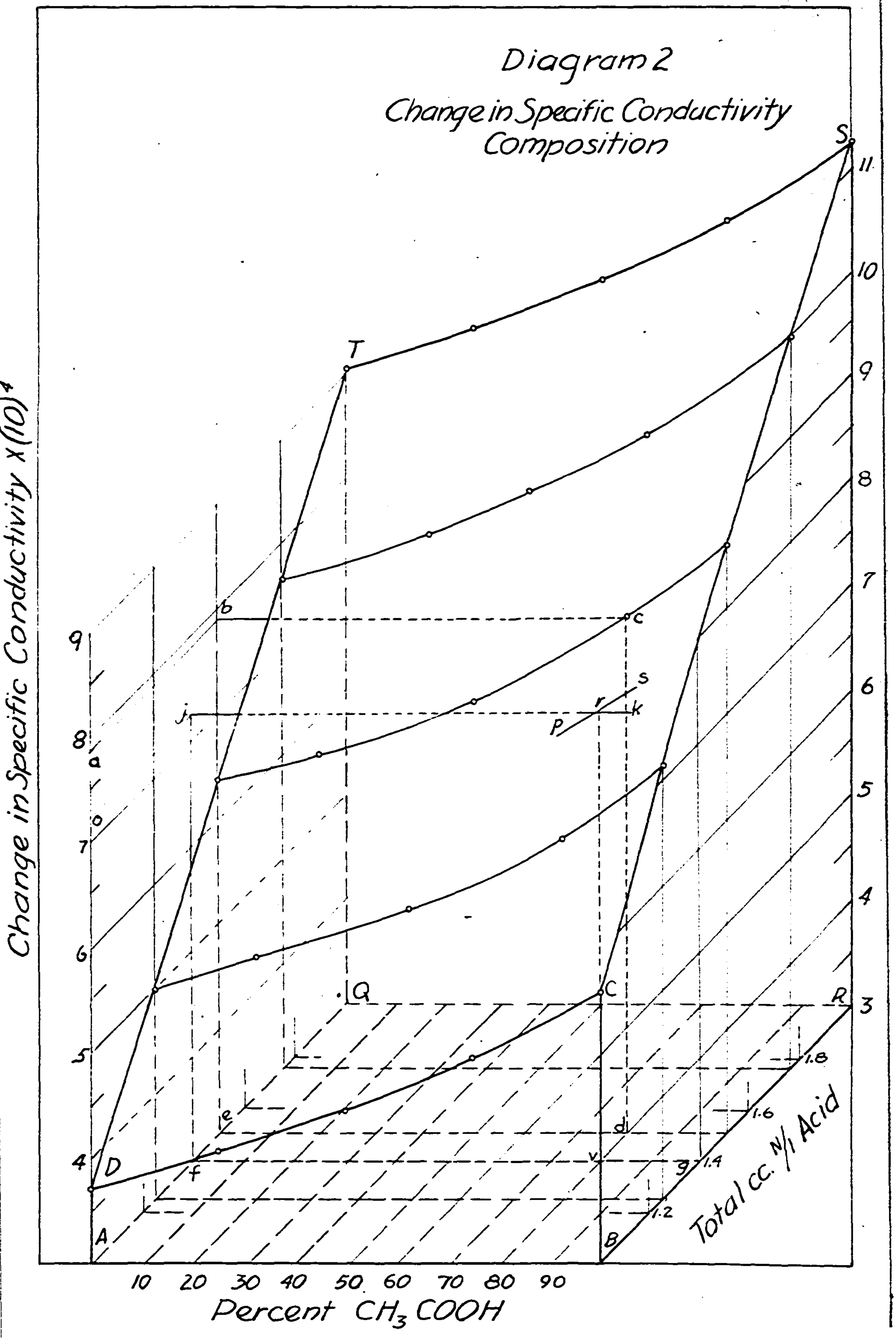


Diagram 2

Change in Specific Conductivity Composition planes it represents 2.00 cubic centimeters. It is true that our diagrams do not give as good a picture of the actual conditions as one drawn to scale by making the X axis of the front plane half the length of the corresponding axis of the rear plane (Diagrams 3 and 4). Such diagrams are however more difficult to read than 1 and 2. Furthermore, no assumption, and therefore no error, has been made in constructing 1 and 2 in the manner that we did. Each profile plane represents a certain mol fraction, each vertical plane a certain total acid composition and the horizontal plane has its values clearly marked so that each datum plotted has the same significance that it would have if plotted on diagrams 3 and 4.

Use of the Diagrams in Analysis

This is perhaps most readily shown by examples. The distillate which is known to contain acetic and formic acids, should be stoppered as soon as it has distilled over. A one-hole rubber stopper fitted with a soda-lime tube is used. The latter is bent so that the part of the tube which contains the soda-lime hangs down beside the flask. This is done to eliminate the danger of any of the reagent getting into the distillate. An aliquot part of the distillate is now taken and titrated with standard potassium hydroxide using phenolphthalein as an indicator. One can now calcu-

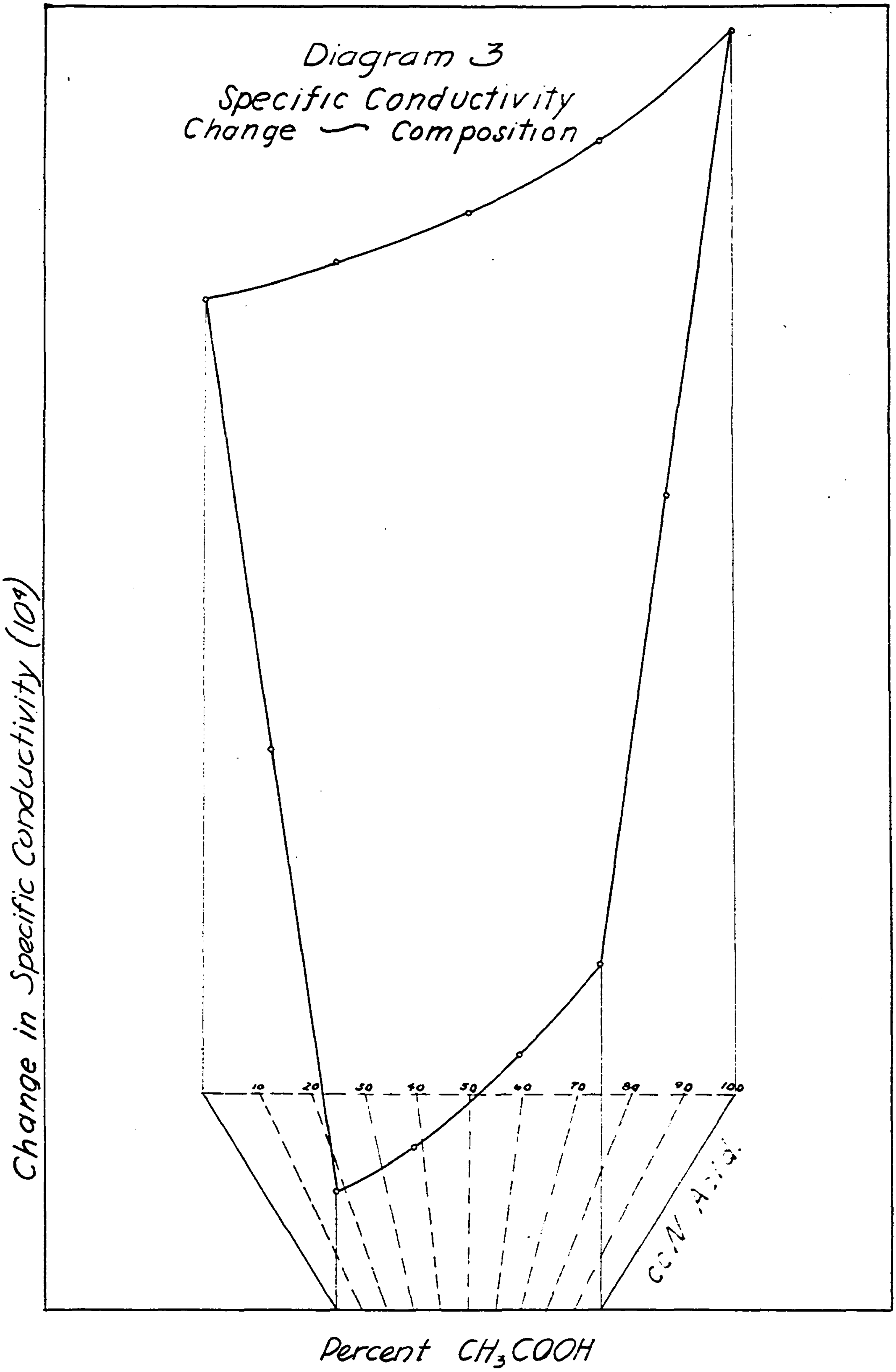
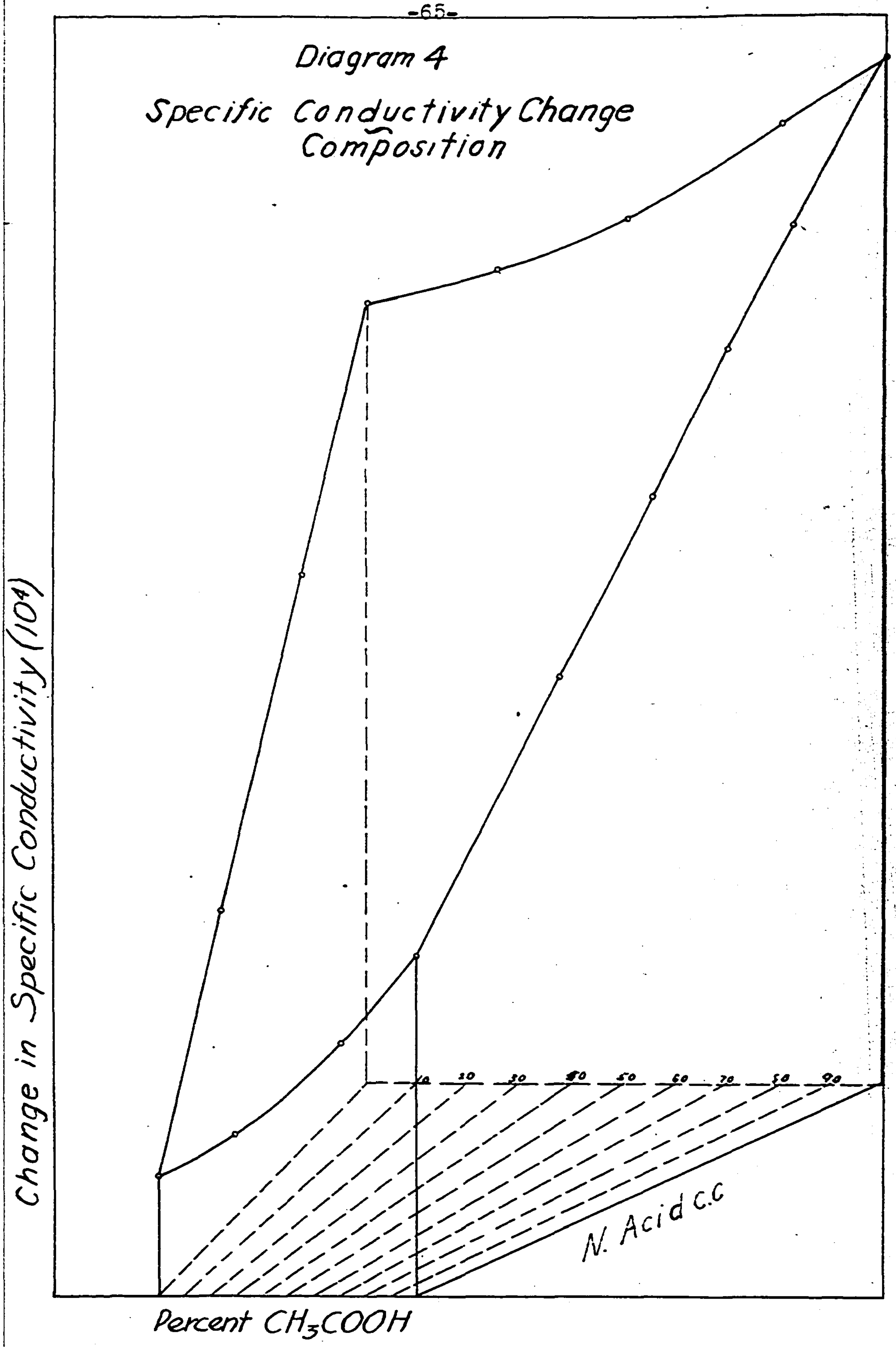


Diagram 3
Specific Conductivity
Change ~ Composition

Diagram 4

Specific Conductivity Change
Composition



late the number of cubic centimeters of this acid which must be added to the dilution water in order that 156.5 cc. of the resulting mixture shall contain approximately 1.50 cc. of N/1 acid. The quantity, 1.50 cc., of normal acid is taken because its conductivities are plotted in the center of the diagram and a considerable error in the quantity of dilution water added would not throw the results so far off that the diagram could not be used. An acid 33 percent stronger or weaker than that specified could still be determined, as the total acid present will be found by the titration. The acid is made up to 156.5 cc. as this was the volume of the total solution which we had when we determined the specific conductivities of the various mixtures of acids whose total acid concentration was 1.50 cc. of normal. As stated above, when we were securing the values for the construction of the diagram we added 155.0 cc. of dilution water to different quantities of the acid, from one to two cubic centimeters of normal. We found that this method was easier to carry out in this work than the usual one of making up to a constant volume each time and that the values checked those obtained by the latter method well within the limits of other experimental errors. As will be seen from the section above on the effect of the quantity of dilution water used the error of the greatest magnitude will occur in the change in conductivity of formic acid upon neutralization. If instead of 1.50 cc normal acid we had 2.00 cc., then on neutralization we would have 158.5 cc. of salt solution instead of 158.0 cc. An error of 0.50 cc. in dilution in the case of sodium formate would cause an error of 0.25 percent in the result (Table 15d). The same would hold if we had only 1.00 cc. of normal instead of 1.50 cc.

A narrow neck flask was calibrated to deliver 152.5 cc. of liquid. The calculated amount of acid solution was placed in this flask and enough dilution water was added to make up to volume. The whole was poured into the conductivity cell. The flask was then rinsed with two portions of dilution water of 2.0 cc. each, the rinse water being added to the flask to bring the total volume up to 156.5 cc. The specific conductivity of the mixture was taken, the normal ammonium hydroxide added, at first quickly up to as near the neutralization point as one can safely go. If the initial titrations and dilutions are made carefully it is safe to add 1.50 cc. of alkali at once, after which it should be added 0.01 cc. at a time until the bridge reading becomes constant. The number of cubic centimeters of alkali which must be added divided by 1.06 gives the number of cubic centimeters of normal acid present. The use of the factor 1.06 was explained above in the section on theory. If care was taken in the original titration with potassium hydroxide the subsequent dilution, when one divides by 1.06, the number of cubic centimeters of normal ammonium hydroxide required to bring the conductivity to a constant value, the result obtained will be 1.50 ± 0.02 cc. In fact we found that, unless we were somewhat doubtful as to the accuracy of our dilution, it was not necessary to get the exact end-point. We took 1.50 cc. as the total normal acid present. To get the change in specific conductivity we ran in 1.50 cc. of normal alkali, found the bridge reading and then we added alkali 0.01 cc. at a time until two bridge readings checked. By this method it is necessary to take but four or five readings for an analysis which speeds up the work.

The following is a typical example: 9.95 cc. of an unknown required 1.20 cc. of 1.159 N sodium hydroxide, using phenolphthalein as indicator, to neutralize. Therefore, 9.95 cc. contained 1.391 cc. of normal acid. Thus it was necessary to add 10.73 cc. of the acid solution in order to have 1.50 cc. of N acid present in the 156.5 cc. This was added to 145.80 cc. of dilution water. The bridge reading was 218.6 which corresponds to a specific conductivity of 2.527 X 10^{-4} (Resistance in opposite arm of bridge 300 ohms).

1.59 cc. of ammonium hydroxide were added before the bridge reading became constant. Using the factor 1.06 mentioned above it was found that there were 1.50 cc. of normal acid present. The final bridge reading was 535.2 which corresponds to a specific conductivity of 10.412×10^{-4}.

From the facts that there were 1.50 cc. total normal acid present, and that the specific conductivity was 2.527×10^{-4}, it is possible by referring to Diagram 1 to find the ratio of the two acids present. The acid mixture which we have must be represented by a point on the vertical plane which shows the specific conductivities of various mixtures of acid whose total normal acid content is 1.50 cubic centimeters. The point on the curve in this plane which represents a specific conductivity of 2.527×10^{-4} is directly above the 0.8 point on the base line of this plane, which signifies that the acid was made up of eight parts of acetic and two of formic.

To locate the point on the diagram one can mark off on the vertical edge of a card a distance (Aa) corresponding to a specific conductivity of 2.527×10^{-4} on the diagram, then slide the lower horizontal edge of the card along the 1.50 cc. line (ed) in the horizontal plane until the length marked off on the edge of the card corresponds to the distance (cd) from the line to the 1.50 cc. curve. This point (d) on the horizontal plane represents a definite composition which can be read directly from the diagram. When one has become more familiar with the use of the diagram a pair of dividers or a compass will be found to be more satisfactory in locating points.

The change in specific conductivity was 7.885×10^{-4}. From diagram 2 it will be seen that the point (c) on the 1.50 cc. curve in the vertical plane, which represents a change in specific conductivity on neutralization of 7.885×10^{-4} as shown by Aa or eb, is directly above the 0.80 point (d) on the 1.50 cc. line in the horizontal plane which again signifies that the acid present is twenty percent formic and eighty percent acetic.

There were present in the original 10.73 cc. of acid 1.50 X 0.80 = 1.20 cc. of normal acetic acid and 1.50 X 0.20 = 0.30 cc. of normal formic acid. The sample was therefore 0.112 normal in acetic acid and 0.0279 normal in formic acid.

In case the number of cubic centimeters of acid present, as found by the conductivity titration, does not come out exactly 1.50 cc. of normal the diagrams can still be used. They hold for any values of total normal acidity between one and two. It must be remembered that the exact volume of the aliquot taken from the original sample must be known.

Let us assume that in the above case the analyst took 10.00 cc. of the unknown with the following results:

Initial specific conductivity 2.401 X 10^{-4}

Final specific conductivity 9.645 X 10^{-4}

Change in specific conductivity 7.244 X 10^{-4}

1.47 cc. of alkali was required to bring the specific conductivity to a constant value.

1.47 divided by the factor 1.06 gives 1.39 as the number of cubic centimeters of normal acid present in 10.00 of the original.

The positions which the 1.39 cc. lines occupy on the profile and horizontal planes are given by (fj), (gh) and (fg). Its position in the vertical plane may be drawn in, with sufficient accuracy, as we have the 1.25 cc. and 1.50 cc. lines in their respective vertical planes, by assuming that each point on this line will occupy a position $\frac{14}{25}$ of the distance between the 1.25 and 1.50 cc. lines from the 1.25 cc. line. This is not absolutely correct as lines which represent equal differences in total acid concentration are not equal distances apart, but become closer together as the acid concentration increases. A correction factor may be secured for each point by reading from the diagram the ratio of the distances between two adjacent sets of lines which represent equal differences in total acid concentration. We have made such corrections and found that the effects were not appreciable.

In an actual determination it is not advisable to draw in the whole vertical plane curve. In the case that we are considering, one should draw a horizontal line (jk) a distance above the 1.39 line on the horizontal plane which corresponds to a specific conductivity of 2.401×10^{-4} on the diagram as shown by (Ao) or (fj). It is not necessary to draw this line across the whole diagram, if one remembers that the point which we seek must lie $\frac{14}{25}$ of the distance between the 1.25 and 1.50 cc. vertical curves from the 1.25 cc. line, as well as on the horizontal line. Two points (p and s) on the 1.39 cc. vertical curve can now be drawn in near the point where this curve will intersect the above horizontal line. These points will determine with sufficient accuracy the direction of the curve in this region. The point (r) where this 1.39 cc. vertical plane curve intersects the horizontal line represents a specific conductivity of 2.40×10^{-4}. The point (Diagram I) at which the 1.39 cc. line in the vertical plane represents a specific conductivity of 2.4×10^{-4} is directly over the 0.8 point (v) on the 1.39 cc. line in the horizontal plane, indicating that the acid present is made up of eight parts of acetic to two of formic. Using diagram 2 in the same way the point (r) in the 1.39 cc. vertical line which corresponds to a change in conductivity of 7.244×10^{-4} as shown by (Ao) or (fj), is directly above the 0.8 point (v) on the 1.39 cc. line (fg) in the horizontal plane.

There are: (1.39)(0.8) = 1.11 cc. of N/1 Acetic acid
(1.39)(0.2) = 0.278 cc. of N/1 Formic acid

in 10.00 cc. of original. Therefore the original was:

0.0278 normal in formic acid and 0.111 normal in acetic acid.

Effect of the Presence of Higher Fatty Acids Other Than Acetic upon the Accuracy of the Diagram

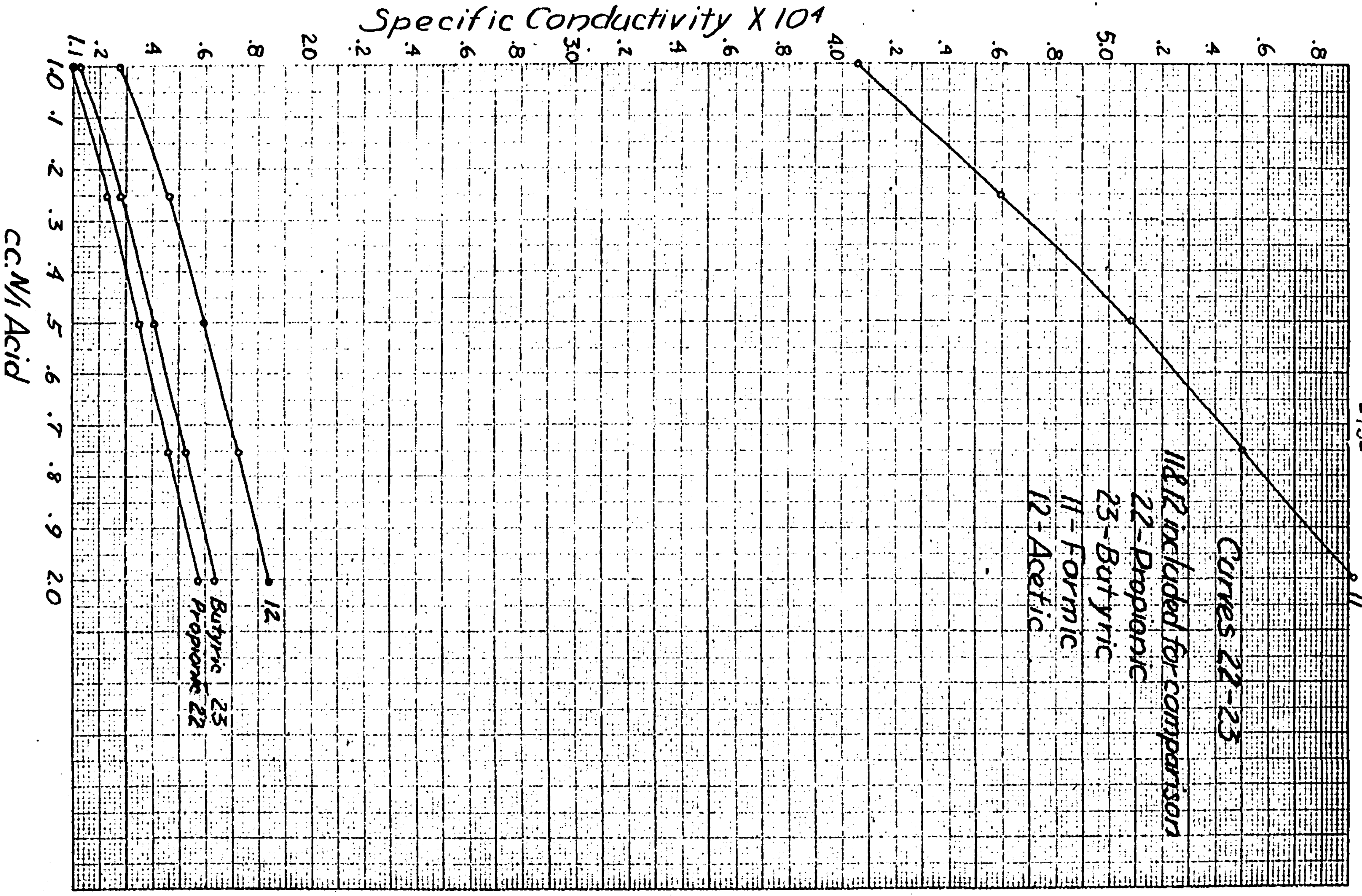
The above diagrams were constructed from data obtained with formic and acetic acids and mixtures of these two. The question naturally arises as to the accuracy of the method if in place of pure acetic we have mixtures of acetic, propionic and butyric acids present with the formic, or in extreme cases if acetic acid were not present at all but merely a mixture of formic and propionic, which combination would appear reasonable. Propionic is taken because its conductivity differs from that of acetic more than does that of the other fatty acids above formic. Admittedly we had better use a formic-propionic acids diagram in a case of this kind, for, as will be seen from Table 18, Curves 22-23, the maximum error would be nearly five percent in this case. This error would increase from zero in the case of pure formic to five percent in the case of pure propionic. A method for calculation of the above error is given later.

The above example is an improbable maximum, as it is very unlikely that any investigator would assume that a sample of pure propionic acid was a mixture of formic and acetic acids. It is given to show the maximum possible error. As an organism which produces formic acid is quite unlikely to produce more than one other acid in large quantities the probable error in the above case becomes small, especially if one uses the diagram or equation which was derived for the higher acid present in greatest quantity. As we have reasonably satisfactory qualitative tests for the volatile fatty acids (Dyer (1917)) it is not difficult to choose the proper equation.

Table 18

Specific Conductivities of Various Concentrations of (a) Propionic and (b) Butyric Acids
(155 cc. water in each case)

(a) cc. Normal Propionic	Bridge (A)	$\frac{A}{1000-A}$	Specific Conductivity (X 10^4)
1.00	107.8	0.1282	1.092
1.25	119.4	0.1356	1.224
1.50	130.0	0.1494	1.349
1.75	139.0	0.1615	1.458
2.00	148.0	0.1737	1.568
(b) cc. Normal Butyric			
1.00	111.5	0.1254	1.131
1.25	124.2	0.1419	1.281
1.50	134.7	0.1557	1.406
1.75	144.2	0.1685	1.522
2.00	153.2	0.1809	1.634


Specific Conductivity X 10^4
1.1
.2
.4
.6
.8
2.0
.2
.4
.6
.8
3.0
.2
.4
.6
.8
4.0
.2
.4
.6
.8
5.0
.2
.4
.6
.8
1.0
.1
.2
.3
.4
.5
.6
.7
.8
.9
2.0
cc. N/1 Acid
12
Butyric 23
Propionic 22
11
Curves 22-23
11 & 12 included for comparison
22-Propionic
23-Butyric
11-Formic
12-Acetic

The above diagrams are presented as a new method of examining data. We have developed a method by which a datum taken with conductivity apparatus can be converted into percentage composition by use of a three dimensional diagram. The biggest value of our diagram, at least in our present work, is not in the interpretation of data but in proving the validity of the equations which we develop to fit these data.

EQUATIONS

It is usually more satisfactory to substitute values in an equation and solve for results, than it is to read results from a diagram. This is especially true when the diagram represents three components. For the above work we have developed an equation which holds very well for a mixture of formic acid with any one other volatile fatty acid and a modification of this which may be used for formic acid in mixture with several other volatile fatty acids with a maximum error of four percent.

Let us assume a mixture of formic and acetic, remembering in this case that no error is made if we take propionic, butyric or valeric acid in place of acetic.

Let F = cc. of normal formic acid present

A = cc. of normal acetic acid present

T = total cc. of normal acid present

$F + A = T$ (Equation 7)

When Curves 6-11 and Diagram 1 are examined it is seen that the specific conductivities of the mixtures are not the sum of individual specific conductivities. It was necessary to find some simple function of the specific conductivity which would straighten out these curves. We found that if we expressed each conductivity as a number times 10^{-3}, Ex. $(0.7107)(10^{-3})$, then took the antilog of the first factor and plotted this against cubic centimeters of normal acid we changed these curves to lines which were nearly straight (Table 19)(Curves 23-28). This is really the same as taking the logarithm of the number of cubic centimeters and plotting that against specific conductivity, but while the latter is the more usual method the former was better suited to our purpose.

With the aid of this antilog function we developed the next equation:

$$\text{Antilog } S' = \frac{F}{T}\left(\text{Antilog } S'_{FT}\right) + \frac{A}{T}\left(\text{Antilog } S'_{AT}\right) \quad \text{(Equation 8)}$$

S' is that number which multiplied by 10^{-3} gives the specific conductivity of the mixture.

S'_{FT} is that number which multiplied by 10^{-3} will give the specific conductivity which a sample of this total acid concentration would have if it were pure formic acid.

S'_{AT} is that number which multiplied by 10^{-3} will give the specific conductivity which a sample of this total acid concentration would have if it were pure acetic acid.

S' is determined. S'_{FT} and S'_{AT} are read from the diagram (1).

Combining equations 7 and 8 above:

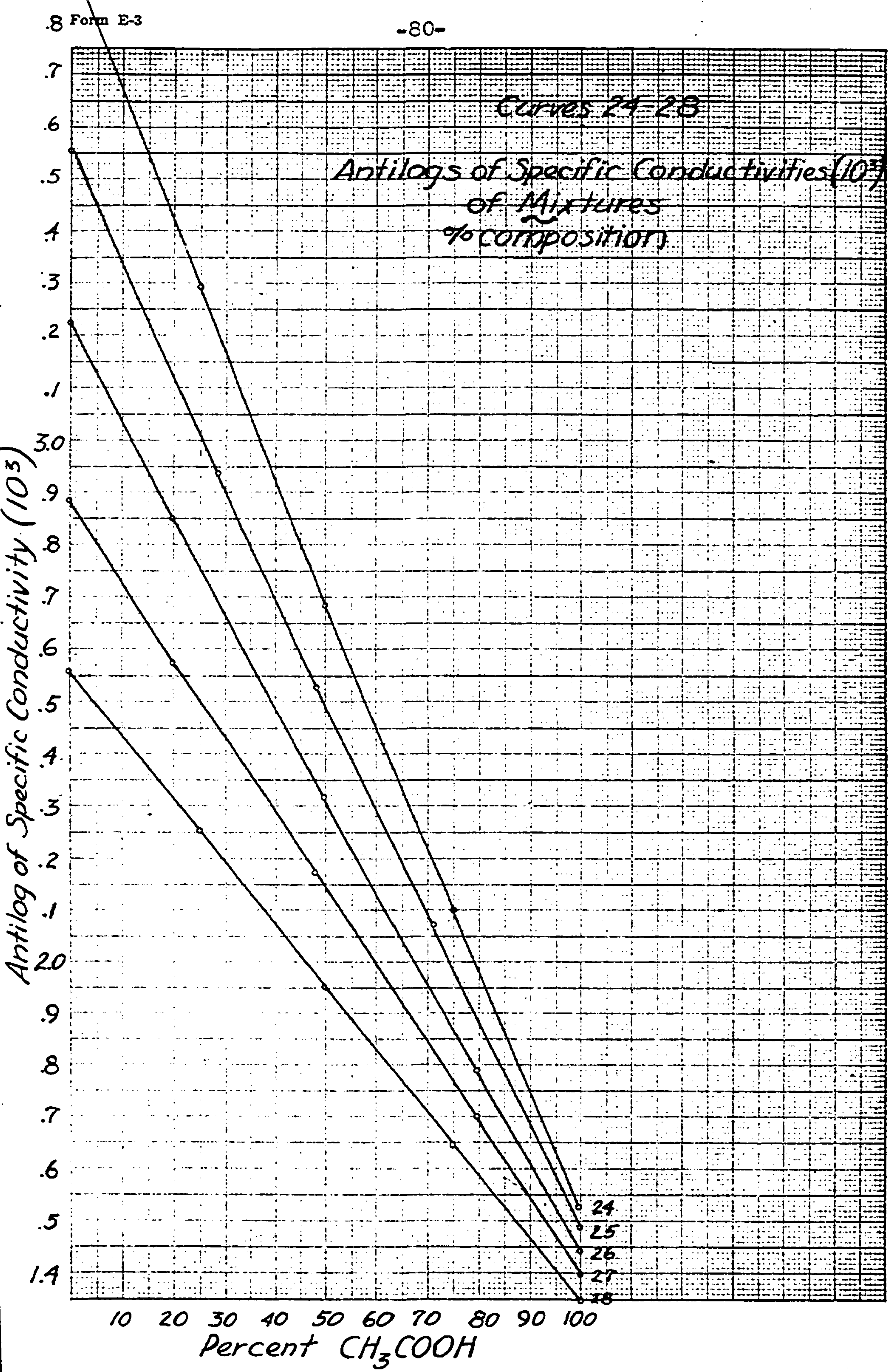
$$\begin{aligned} \frac{F}{T}\text{ Antilog } S'_{FT} &= \text{Antilog } S' - \frac{A}{T}\left(\text{Antilog } S'_{AT}\right) \\ &= \text{Antilog } S' - \frac{T-F}{T}\left(\text{Antilog } S'_{AT}\right) \end{aligned}$$

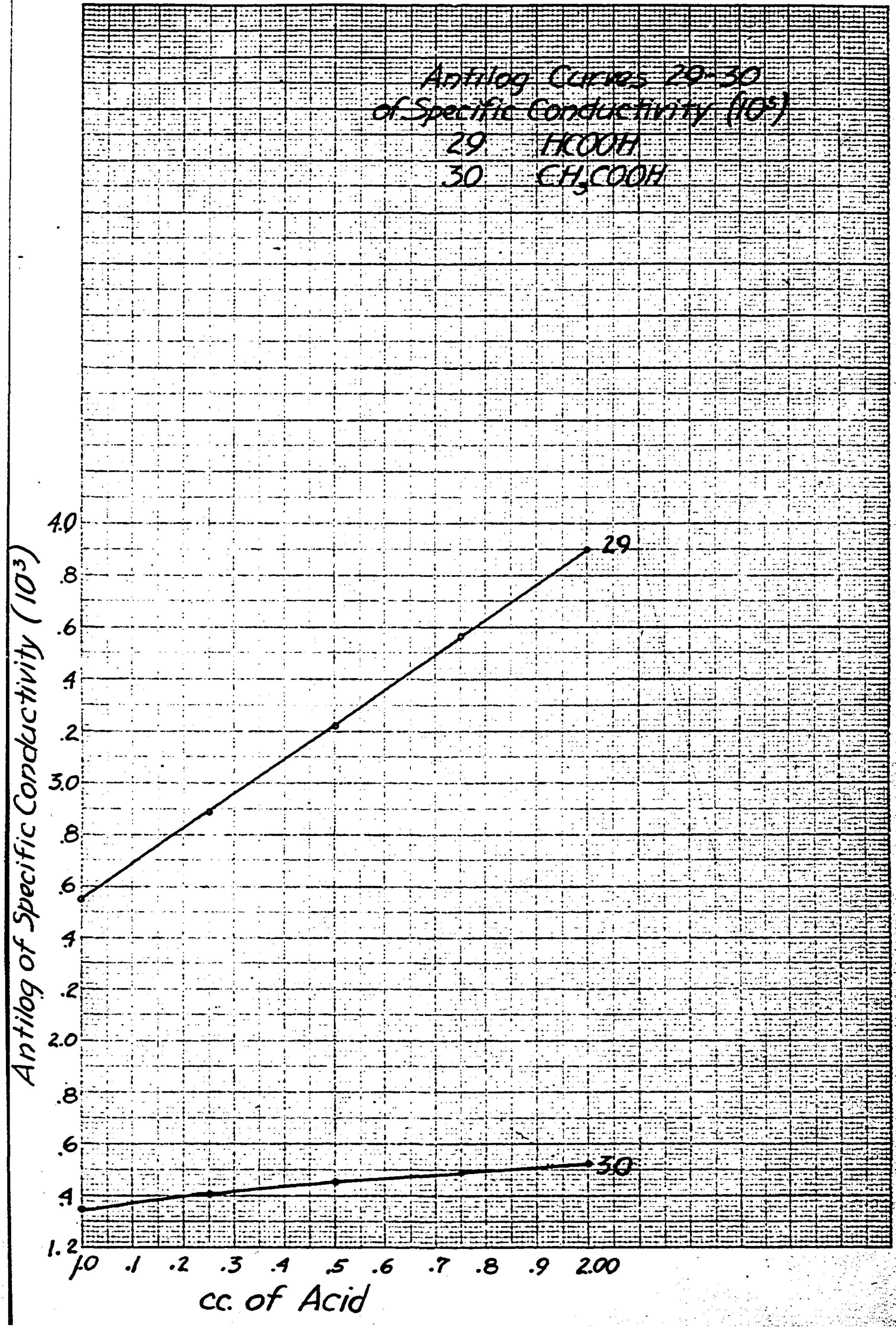
Table 19

Antilog Data for Equations 2-4 and for Curves 24-30

cc. Normal Formic	cc. Normal Acetic	Specific Conductivity ($X 10^{+3}$)	Antilog of First Factor
2.00	0.00	0.5915	3.904
1.50	0.50	0.5175	3.292
1.00	1.00	0.4294	2.688
0.50	1.50	0.3217	2.097
0.00	2.00	0.1819	1.524
1.75	0.00	0.5508	3.555
1.25	0.50	0.4683	2.940
0.90	0.85	0.4029	2.529
0.50	1.25	0.3164	2.072
0.00	1.75	0.1725	1.488
1.50	0.00	0.5086	3.226
1.20	0.30	0.4549	2.850
0.75	0.75	0.3648	2.316
0.30	1.20	0.2527	1.790
0.00	1.50	0.1596	1.444
1.25	0.00	0.4596	2.882
1.00	0.25	0.4104	2.575
0.65	0.60	0.3369	2.172
0.25	1.00	0.2314	1.704
0.00	1.25	0.1463	1.401
1.00	0.00	0.4075	2.556
0.75	0.25	0.3523	2.251
0.50	0.50	0.2898	1.949
0.25	0.75	0.2149	1.614
0.00	1.00	0.1282	1.343

Form E-3


Curves 24-28
Antilogs of Specific Conductivities (10³) of Mixtures
% composition
Antilog of Specific Conductivity (10³)
.8
.7
.6
.5
.4
.3
.2
.1
3.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
2.0
.9
.8
.7
.6
.5
1.4
10
20
30
40
50
60
70
80
90
100
Percent CH₃COOH
24
25
26
27
28


Antilog Curves 29-30
of Specific Conductivity (10³)
29 HCOOH
30 CH₃COOH
Antilog of Specific Conductivity (10³)
4.0
.8
.6
.4
.2
3.0
.8
.6
.4
.2
2.0
.8
.6
.4
1.2
1.0
.1
.2
.3
.4
.5
.6
.7
.8
.9
2.00
cc. of Acid
29
30

$$= \text{Antilog } S' - \text{Antilog } S'_{AT} + \frac{F}{T} \text{ Antilog } S'_{AT}$$

$$F = \frac{T\,(\text{Antilog } S' - \text{Antilog } S'_{AT})}{(\text{Antilog } S'_{FT} - \text{Antilog } S'_{AT})} \quad \text{(Equation 9)}$$

As we usually desire to know the percentage of the total acid which is formic rather than the number of cubic centimeters of normal present we can omit the T in the above equation and we have,

$$\text{Percent formic} = \frac{\text{Antilog } S' - \text{Antilog } S'_{AT}}{\text{Antilog } S'_{FT} - \text{Antilog } S'_{AT}} \text{ (X 100) (Equation 10)}$$

Equation 10 was tested using various mixtures of the two acids, and the values obtained were compared with those given by the diagram. The following table shows the agreement.

Table 20

Total Acid	Specific Conductivity (X 10^4)	Percent Formic	
		Diagram	Equation
1.50	1.596	00.0	00.0
1.25	3.000	40.0	40.2
1.75	2.401	12.1	12.1
1.25	4.200	82.5	82.9
1.50	2.527	20.0	19.4

To illustrate the method of calculation we will take the last example above.

$T = 1.50$

S'_{FT}(Table 9) = $(0.5086)(10^{-3})$ Antilog of first factor 3.226.

S'_{AT} (Table 9) = $(0.1596)(10^{-3})$ Antilog of 1st factor 1.444

S' (measured)$(0.2527)(10^{-3})$ Antilog of 1st factor 1.789

$$\text{Percent formic} = \frac{1.789 - 1.444}{3.226 - 1.444} \times 100 = 19.36$$

In case T is not one of the values for which S'_{FT} and S'_{AT} were determined, the latter values can be obtained from Graphs 11 and 12.

In case propionic or butyric acid is present in place of acetic S'_{PT} or S'_{BT} can be obtained from Table 18 or Graphs 22 and 23.

The above equation was developed for a mixture of formic acid with one other volatile fatty acid. It has been shown above that the presence of other volatile fatty acids than those sought would cause considerable error. The next equation developed applies to those cases where the operator is uncertain as to what acids he has present.

For the volatile fatty acids above formic, the greatest difference in specific conductivity occurs between acetic and propionic, the conductivity of butyric and valeric acids approaching that of acetic. If we take the average (S'_{Tav}) of S'_{AT} and S'_{PT} as a value to be substituted for S'_{AT}, S'_{PT}, S'_{BT} in Equation 10 we should cut down the chances of a large error.

From the values for S'_{AT} (Table 9) and S'_{PT} (Table 18) we obtain the following:

Table 21

T	1.00	1.25	1.50	1.75	2.00
S'_{Tav}	0.1186	0.1344	0.1472	0.1592	0.1698

The maximum error that could be caused by using the above values, or intermediate values from Curve 31, would occur in the cases where the sample contained pure acetic or pure propionic acids. It is very improbable that an investigator would have a pure acid and yet have no idea as to the composition of his sample, but we give this example to show the maximum error which is approached if this general formula is used.

Using this formula,

$$\text{Percent formic} = \frac{\text{Antilog } S' - \text{Antilog } S'_{Tav}}{\text{Antilog } S'_{FT} - \text{Antilog } S'_{Tav}} (100)$$

(Equation 11)

for 1.00 cc. pure acetic:

$S' = 0.1282$ (Table 9)

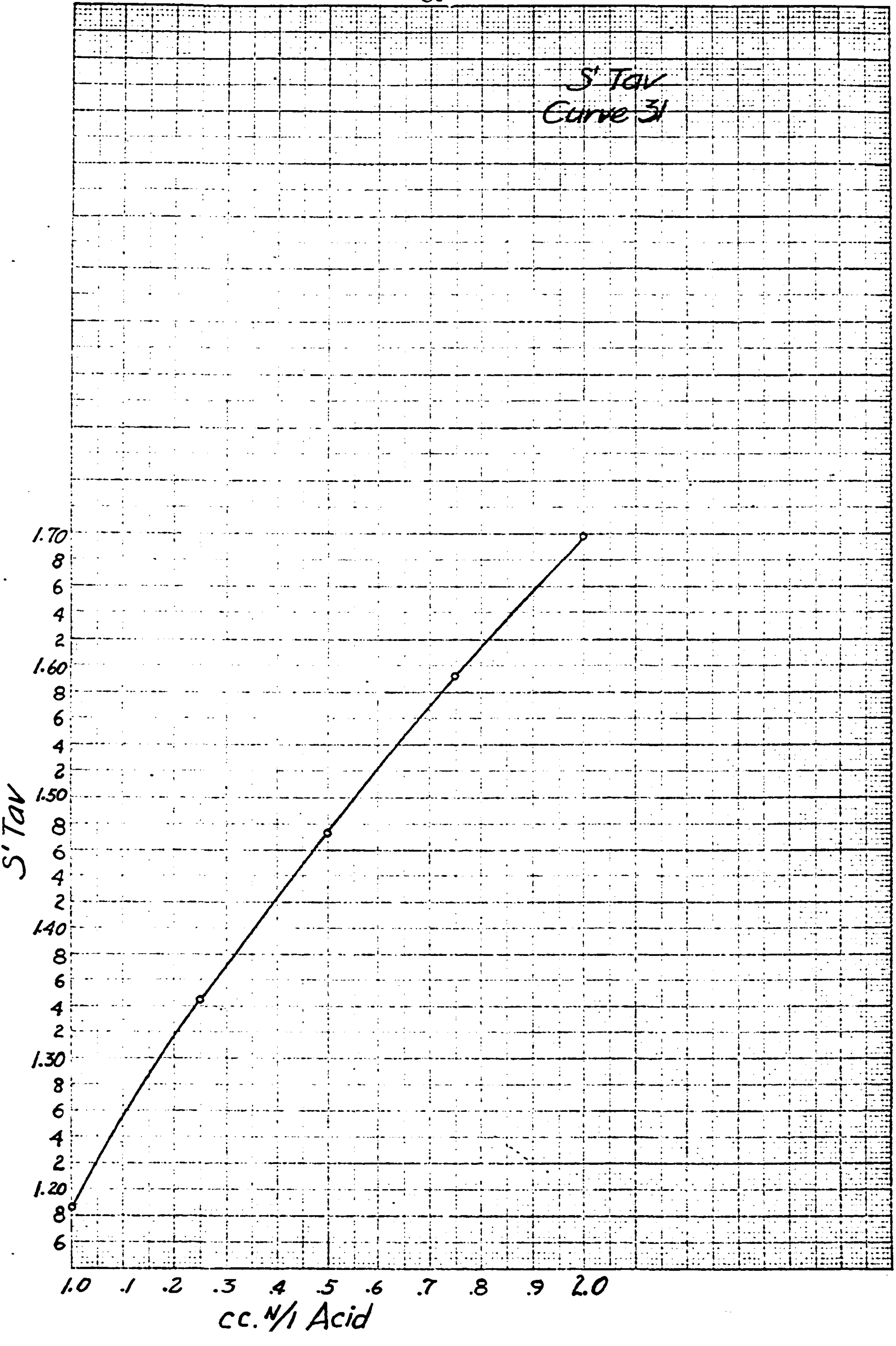
$S'_{Tav} = 0.1186$ (Table 21 or Curve 31)

$S'_{FT} = 0.4057$ (Table 9)

Percent formic would be calculated as:

$$\frac{\text{Antilog } 0.1282 - \text{Antilog } 0.1186}{\text{Antilog } 0.4056 - \text{Antilog } 0.1186} (100) = + 2.3\%$$

Pure propionic acid would give the same error in percent with opposite sign.


S' Tav
Curve 31
1.70
8
6
4
2
1.60
8
6
4
2
1.50
8
6
4
2
1.40
8
6
4
2
1.30
8
6
4
2
1.20
8
6
S' Tav
1.0
.1
.2
.3
.4
.5
.6
.7
.8
.9
2.0
cc. N/1 Acid

Every factor in the analysis tends to cut down the above error. The presence of formic acid, or of other acids, cuts it down. A mixture of equivalent quantities of acetic and propionic acids would give correct results. Pure butyric acid or valeric acid would give fair results.

For 1.00 cc. of pure butyric:

$S' = 0.1131$ (Table 18b), $S'_{Tav} = 0.1186$, $S'_{F} = 0.4057$

Percent formic would be calculated as:

$$\frac{\text{Antilog } 0.1131 - \text{Antilog } 0.1186}{\text{Antilog } 0.4057 - \text{Antilog } 0.1186} \times 100 = 1.2\%$$

If one had a mixture containing formic, one other volatile fatty acid in considerable quantity, and others in small amounts he should use formula 10 as developed for the higher fatty acid which he has present in largest amount. An idea of the composition of the acid unknown could be obtained by using the qualitative tests proposed by Dyer (1917).

If the above procedure is followed carefully the results obtained and time required compare very favorably with those of any of the present methods.

SUMMARY AND CONCLUSIONS

A quick accurate method, using either the specific conductivity of the acid mixture, or the change in conductivity upon neutralization with ammonium hydroxide, has been developed for the analysis of mixtures of formic acid with acetic and other volatile fatty acids.

The two factors are quite unlike in that the more highly ionized the acid, the greater its specific conductivity and the less its change in specific conductivity upon neutralization.

Three dimensional diagrams have been constructed for the interpretation of the data. From a study of these diagrams equations have been developed for the calculation of the percentage of formic acid in a mixture.

The percentages so calculated are less in error than those obtained by the methods ordinarily in use at the present time.

The method promises to be valuable with mixtures other than those already tested.

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