

ALLEN

Scale of Influence of Substitution

in Organic Electrolytes

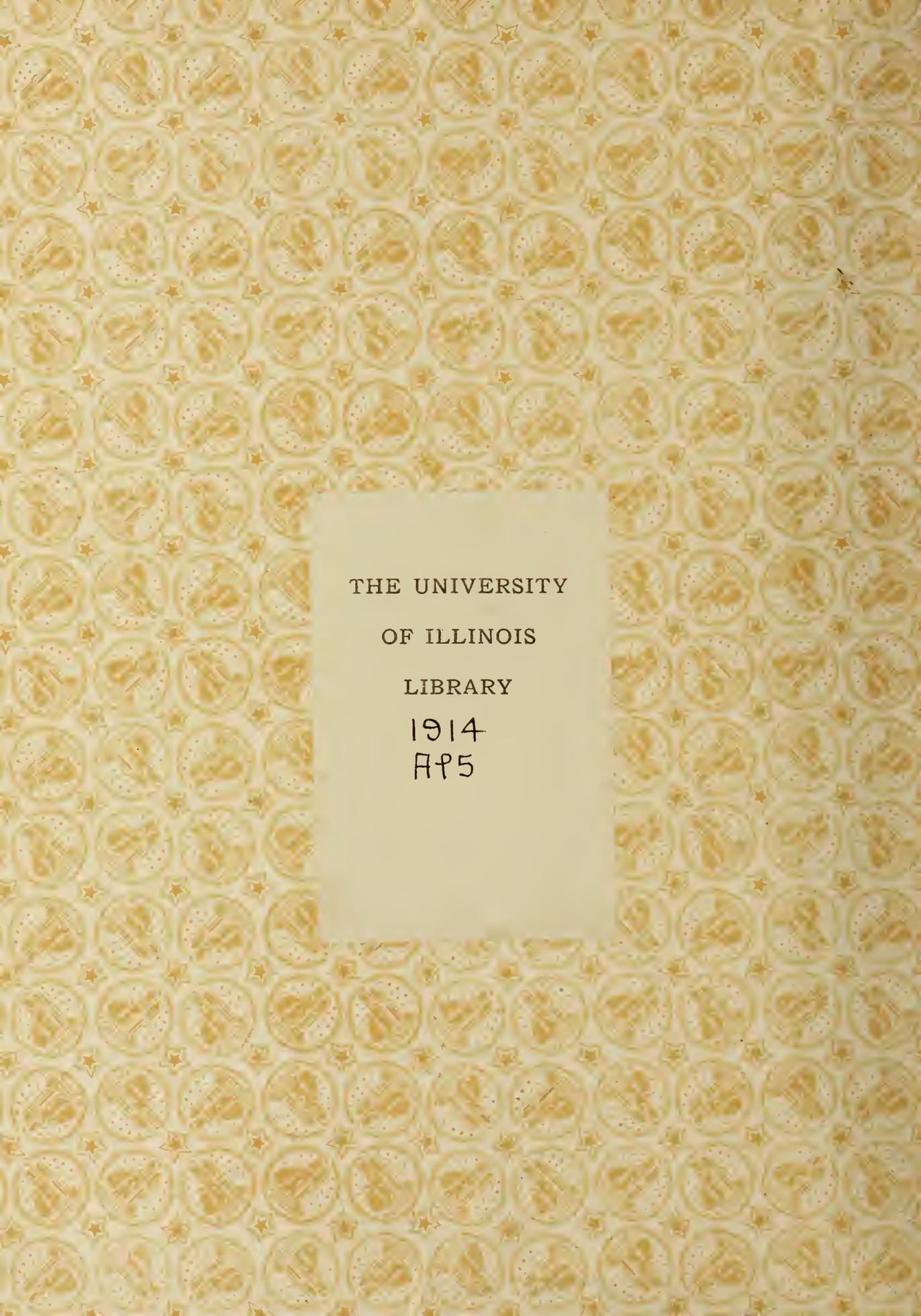
A Oxygen Place Influence in Normal

Monobasic Paraffin Acids

Chemistry

A. M.

1914

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SCALE OF INFLUENCE OF SUBSTITUTION IN  
ORGANIC ELECTROLYTES

Δ OXYGEN PLACE INFLUENCE IN NORMAL  
MONOBASIC PARAFFIN ACIDS

BY

CHESTER HARMON ALLEN  
B. A. Lawrence College,  
1912

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THESIS

Submitted in Partial Fulfillment  
of the Requirements for the  
Degree of

MASTER OF ARTS

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS <sup>U. S.</sup>

1914



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UNIVERSITY OF ILLINOIS  
THE GRADUATE SCHOOL

June 4 1914

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

CHESTER HARMON ALLEN

ENTITLED SCALE OF INFLUENCE OF SUBSTITUTION IN ORGANIC ELECTROLYTES

Δ OXYGEN PLACE INFLUENCE IN NORMAN MONOBASIC PARAFFIN ACIDS.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF

MASTER OF ARTS

*C. G. Derick*

In Charge of Major Work

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Head of Department

Recommendation concurred in:

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\_\_\_\_\_  
\_\_\_\_\_

Committee

on

Final Examination



## CONTENTS.

	Page.
Introduction and theoretical discussion .....	1
Syntheses of $\gamma$ acetyl butyric acid .....	9
Conductivity apparatus and determinations .....	17
Calculated $\kappa_0$ as a criterion of precision and as a means of determining constant errors .....	26
A critical study of the conductance data for $\gamma$ acetyl butyric acid .....	29
Calculation of the ionization constant of $\gamma$ acetyl butyr- ic acid .....	40
Calculation of the $\delta$ oxygen place factor .....	42



INTRODUCTION.



In organic chemistry the proof of the structure of compounds is one of the most important and difficult duties of the research worker. In recent years among the many methods he has used to accomplish this end, those which make use of the relationships between the physical properties and the structure of substances have been very prominent and successful. One of the especial advantages of these methods is that they usually require but a small amount of material and this can commonly be recovered.

That a relationship between the electrical conductivity of the solution of a substance and its chemical structure exists was soon realized; this, however, was not at all well understood until Arrhenius<sup>1</sup> introduced his dissociation theory in 1887. Since that time numerous workers have turned their attention to this field. Among the most prominent of those who have attempted to establish a relationship between the ionization constants, as determined by conductivity or other methods, of organic substances and their structure have been Wegscheider,<sup>2</sup> Ostwald,<sup>3</sup> Michael,<sup>4</sup> and Derick.<sup>5</sup>

It is the purpose of the present work to continue that already in progress in this laboratory in determining a relationship between the ionization of monosubstituted, n-paraffine, monobasic acids and their structure and in particular to establish the  $\delta$  position in a scale of combined influence of the doubly bonded oxygen atom when substituted into these acids.

Van't Hoff<sup>6</sup> was one of the first to recognize that the structure of a compound had a definite influence on its properties. He assumed that the influence of a substituent in a compound could be



resolved into two factors. the first of these he called the direct influence i.e. that exerted thru space and the second, called the indirect which was exerted thru the chain.

Ostwald<sup>7</sup> later announced a rule for determining the influence of substituents in organic acids. he determines his place factor from the following expression

$$a = \frac{K}{K_0}$$

in which  $K_0$  is one hundred times the ionization constant of the unsubstituted acid and  $K$  is one hundred times the constant for the substituted acid. Similarly the  $b$ ,  $c$ ,  $d$ , etc factors are determined for the  $\alpha, \beta, \gamma$ , etc positions.

This rule, however, does not conform with the more modern theories concerning chemical reactions in general. It is a generally accepted fact that the tendency for any reaction to take place is measured by the amount of free energy change. The second law of thermodynamics gives the following expression as a measure of the free energy of ionization.

$$A = R T \ln K$$

$A$  = free energy of ionization.

$R$  = the gas constant.

$T$  = the absolute temperature

$\ln K$  = the natural log of the ionization constant

Since free energy is the measure of the tendency of any reaction to occur and this is a logarithmic function any law which is not so expressed cannot be correct for the reaction ionization.

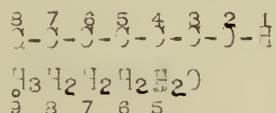
It is to be further noted that Ostwald's rule does not represent the influence of the new atom or group upon the ionization but rather



the ratio of the influence upon the ionization constant of all the atoms in the substituted molecule to that of all of the atoms in the unsubstituted molecule. It therefore does not give a general place factor which could be applied to all cases. Any rule to be generally applicable must eliminate the influence of the other atoms in the molecule and at the same time be a free energy function.

Michael<sup>8</sup> following Van't Hoff and Ostwald announced a scale of combined influence in the following terms, "If we number a certain carbon atom in any fatty compound with a normal chain by the figure one, our present knowledge of the combined mutual influence between this atom and the others in the molecule is expressed by the following scale of combined influence, the number indicating the degree of removal and the extent of influence decreasing in the order given: 2-3-5-6-4-7-(9-10-11)-3. It is to be strongly emphasized that the effect of any atom in the position 2 or 3 is far greater than that of any similar atom less closely connected and in the case of atoms farther removed must be largely direct i.e. spatial.

His method of numbering would be illustrated by



This rule is derived from a study of the space configurations of carbon atoms and the results of a number of chemical reactions.

Michael, however, without any justification has applied this reasoning to cases where other atoms than carbon are involved thereby assuming that these have the same space configuration which is of course untenable. He endeavors to justify these conclusions by a study of the



chemical and physical properties of the compound as for example by use of the Ostwald factor rule. It can be clearly seen that on account of these errors Michael's rule fails to give a true scale of influence for two reasons i.e. Firstly - The true measure of the influence of an atom or group on the ionizing group must be a logarithmic function of the ionization constant i.e. a free energy function. Secondly he has not succeeded in eliminating the effect of the other atoms in the molecule. The rule therefore cannot be generally applicable.

After examining the data on a large number of negatively substituted acids Derick has proposed the following method of determining the place factor for any negative atom or group substituted in a monobasic paraffine acid.

$$I = \frac{\ln K_0}{\ln K} - 1$$

$\ln K_0$  = the natural log of  $100 \times$  the ionization constant of the unsubstituted acid.

$\ln K$  = the same for the substituted acid.

$I$  = the place influence

The assumption is made that the ionization constant is the resultant of the influence of all the atoms in the molecule and that these influences additively effect the free energy of ionization.

If then we substitute an element or group into a compound the change in the ionization constant is wholly due to the difference in the effects of the displaced hydrogen and the new substituent. That the effect of a hydrogen is very small and therefore, since it occurs additively, may be neglected is seen from the following table.



Name	Formula.	K.		Place factor.
1 Pentenic acid	$C_2H_5CH=CHCO_2H$	$1.48 \cdot 10^{-5}$	-4.330	-0.007
2 Pentenic acid	$CH_3CH=CHCH_2CO_2H$	$3.35 \cdot 10^{-5}$	-4.475	+0.0095
3 Pentenic acid	$CH_2=CH(CH_2)_2CO_2H$	$2.09 \cdot 10^{-5}$	-4.690	+0.024
1 Hexenic acid	$C_3H_7=CHCO_2H$	$1.89 \cdot 10^{-5}$	-4.724	+0.0395
2 Hexenic acid	$C_2H_5CH=CHCH_2CO_2H$	$2.64 \cdot 10^{-5}$	-4.578	+0.057
3 Hexenic acid	$CH_3CH=CH(CH_2)_2CO_2H$	$1.74 \cdot 10^{-5}$	-4.753	+0.013
4 Hexenic acid	$CH_2=CH(CH_2)_3CO_2H$	$1.91 \cdot 10^{-5}$	-4.713	+0.026

In this table it is shown by the small place factors that the influence of two hydrogens is very small. We are therefore justified in neglecting the influence of a single hydrogen in formulating the rule whose derivation is given below.

The influence, I, of all the atoms in the molecule of an electrolyte Derick defines as

$$I = \frac{I}{A} = \frac{I}{R T \ln K}$$

I = Influence  
 A = the free energy of ionization  
 R = the gas law constant  
 ln K = the natural log of the ionization constant

The specific influence of a given atom as for example the  $\alpha$ Cl in  $\alpha$ -chlorobutyric acid is defined as

$$I = \frac{\log K_0}{\log K_n} - 1$$

These logarithms are the common or Briggs logarithms.

The reason for the subtraction of unity was the desire to free the influence of the given substituent from that of the other atoms in the molecule. The other atoms ( $CH_2CH_2CH_2CO_2H$ ) in  $\alpha$ -chlorobutyric acid differ from the atoms in butyric acid by a single hydrogen which is neglected. The influence of all the atoms in butyric acid according



to the above ratio is unity and furnishes the reason for subtracting unity in the above expression. The following example will make this clear.

Acid.	k	log k
Butyric	$1.56 \cdot 10^{-5}$	-4.307
$\alpha$ Chlorobutyric	$1.39 \cdot 10^{-3}$	-2.357

Influence of all the atoms in Butyric acid : Influence of all the atoms in  $\alpha$ chlorobutyric acid = -4.307 : -2.357.

Now making the value for the unsubstituted acid equal to one and subtracting we get

$$4.307 : 2.357 :: 1.632 : 1 \quad 1.632 - 1 = 0.632$$

This gives 0.632 as the  $\alpha$ chlorine place factor.

Since this method is based on the expression  $A = RT \ln K$  it is a free energy function and as such furnishes a true measure of the place influence of the new substituant. Furthermore the influence of the other atoms in the molecule has been eliminated which makes the rule perfectly general in its application. The general application of the factors can be seen from the following table.

acid	K	log K	Factor.
$\alpha$ chloroacetic	$1.55 \cdot 10^{-3}$	-2.30967	0.6330
$\alpha$ chloropropionic	$1.47 \cdot 10^{-3}$	-2.33263	0.7033
$\alpha$ chlorobutyric	$1.39 \cdot 10^{-3}$	-2.85699	0.6326
$\alpha$ bromoacetic	$1.33 \cdot 10^{-3}$	-2.88012	0.6539
$\alpha$ bromopropionic	$1.08 \cdot 10^{-3}$	-2.96658	0.8312
$\alpha$ bromobutyric	$1.06 \cdot 10^{-3}$	-2.94469	0.6159



It is at once apparent that the  $\alpha$ chlorine factor is the same regardless of the acid from which it is obtained. The variations in the values are not greater than the errors in determining the constants of the acids from which the values are derived. The same holds true for the  $\alpha$ bromine factor. These examples are but a few of the many that are at hand<sup>9</sup> to show that the place factor for a substituent is the same regardless of the acid acids which are used in its calculation.

There is another and most important correlation which can be derived from the place factors for the various substituents. This is the Rule of Thirds and is illustrated in the table below.

Acid	k	log K	place factor
$\alpha$ Chlorobutyric	$1.39 \cdot 10^{-3}$	-2.357	0.6925
$\beta$ chlorobutyric	$3.94 \cdot 10^{-5}$	-4.049	0.1873
$\gamma$ chlorobutyric	$3.00 \cdot 10^{-5}$	-4.523	0.0627
$\delta$ chlorobutyric	$2.04 \cdot 10^{-5}$	-4.690	0.0229

An inspection of the factors listed above will show that each succeeding factor is approximately one third of the one preceding it. i.e. the approximate ratio is  $\alpha : \beta : \gamma : \delta = 0.6925 : 0.1873 : 0.0627 : 0.0229 = 1 : \frac{1}{3} : \frac{1}{9} : \frac{1}{27}$ . The place factor, then, diminishes by one third for each  $\text{CH}_2$  group between the substituent and the ionizing group. This rule of thirds has been tested out for the elements and groups chlorine, bromine, iodine, hydroxyl, and phenyl and holds fairly accurately for each.

This rule gives us a simple means of determining the position of a known group in an normal chain acid. Suppose for example a new chlorinated acid had been prepared and that molecular weight and analy-



sis showed that it was a four carbon normal acid. The ionization constant could be quickly determined by means of indicators. This with the known constant for butyric acid and the  $\alpha$ chlorine place factor from any acid, could be used to determine the position of the chlorine by means of the rule of thirds. For example suppose the new acid to have a constant of  $3.00 \cdot 10^{-5}$ . The constant for butyric acid is  $1.56 \cdot 10^{-5}$  and from these the place factor is .0627. The  $\alpha$ chlorine factor is 0.6325 as shown by several determinations. Dividing this by nine we get as the factor for the new substituent the value 0.0755 which is sufficiently accurate to at once give the  $\gamma$  position to the chlorine. The new acid is then established as  $\gamma$ chloro butyric acid. If the Ostwald factor rule is used to determine the position of the substituent it is necessary to have previously determined the a, b, c, d, etc factors.



SYNTHESIS OF  $\gamma$  ACETO BUTYRIC ACID.



This acid was first prepared by Fittig and Wolff<sup>10</sup> in 1882. They prepared it by the hydrolysis of  $\alpha$ acetyl glutaric ester. Numerous other investigators have since prepared it either directly or incidentally and references to the most important of these will be found in the bibliography. In 1889 Bentley and Perkin<sup>11</sup> prepared and carefully characterized it. Such of its properties as have been determined in the present investigation have checked theirs in every detail. Vorlander and Schilling<sup>12</sup> determined its ionization constant in 1889. Their results are tabulated later in this article.

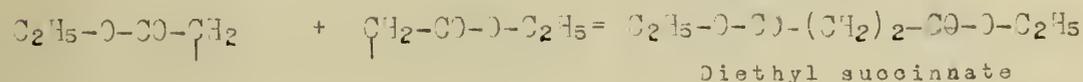
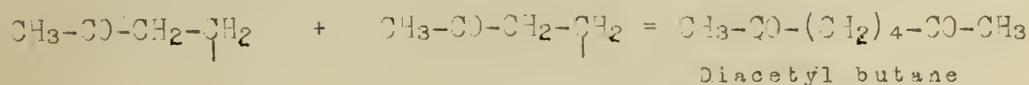
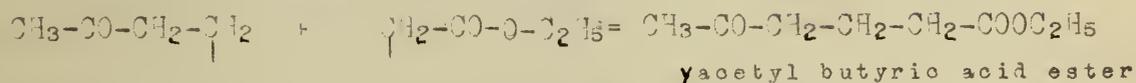
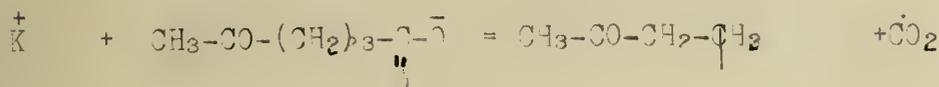
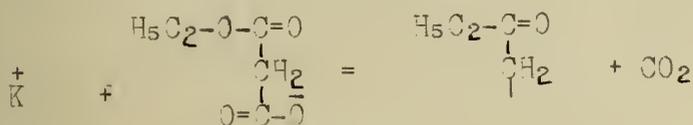
Among the methods of preparation used the most important and successful is the one described in detail below. This was the method used by all of the above mentioned investigators. It has also been prepared by the oxidation of the corresponding alcohol,<sup>13</sup> and, among other methods, by the oxidation of methyl pentanon,<sup>13a</sup>  $\text{CH}_2-\text{CH}-\overset{\text{CH}_3}{\underset{\text{C}=\text{O}}{\text{C}}}-\text{CH}_2$ , which in turn was prepared from methylene iodide and the sodium salt of acetoacetic ester.

Another method of preparation is by the hydrolysis of dihydroresorcin by long boiling with barium hydroxide. The dihydroresorcin is prepared by boiling a dilute solution of resorcin for twenty hours with two percent sodium amalgam during which time the alkalinity is kept down by passing in a slow stream of carbon-di-oxide. The product is then extracted with ether and is finally hydrolyzed. This method was attempted but as in each case either no reduction was obtained or it went too far and phenols resulted it was abandoned.

An electro synthesis using potassium ethyl malonate and the potassium salt of laevulinic acid was also attempted. The theory is



that the anions lose CO<sub>2</sub> when their charges are neutralized at the electrodes and will then unite with each other or with other radicles present. The following possibilities result.



The undesirable possibility as represented by the formation of diethyl succinate took place to a very great extent and tho the voltage, the concentration, and other factors were varied in many ways the method was abandoned as unsuccessful. Numerous interesting products were formed and some of these were studied but lack of time prevented much investigation.

#### THE METHOD OF PREPARATION OF γ ACETYL BUTYRIC ACID FOR CONDUCTANCE MEASUREMENTS.<sup>14</sup>

The steps in this preparation are;-

1. The preparation of glyceric acid by oxidation of glycerine.
2. The isolation and purification of glyceric acid by means of its lead salt.
3. The preparation of P<sub>2</sub>I<sub>4</sub>.
4. The preparation of β iodo propionic acid from glyceric acid and P<sub>2</sub>I<sub>4</sub>.



5. The esterification of the  $\beta$ iodo propionic acid.

6. The preparation of  $\alpha$ acetyl glutaric ester by an acetoacetic ester synthesis with  $\beta$ iodo propionic ester.

7. The hydrolysis of  $\alpha$ acetyl glutaric ester to form  $\gamma$ acetyl butyric acid thru the loss of  $\text{CO}_2$ .

8. The purification of  $\gamma$ acetyl butyric acid by distillation in vacuum and by the crystallization of its lead salt from absolute alcohol.

#### The Preparation of Glyceric Acid.

Glyceric acid is prepared by oxidizing glycerene with fuming nitric acid. This was done by placing 50 grams of glycerene and 50 cc. of water in a flask, mixing thoroly, cooling, and then adding 33 cc. of fuming nitric acid (Sp. Gr. 1.52) taking care that the two liquids do not mix. If mixing occurs a violent reaction accompanied by the copious evolution of  $\text{NO}_2$  results and there is considerable danger of the formation of nitro glycerene. This danger is entirely prevented by cooling. During the first ten or fifteen hours the action will be rapid if the temperature is not kept too low. It is best to not keep the temperature much lower than is necessary to prevent violent reaction as if this is done the action is likely to become violent during the night when it is inconvenient to have it taken care of. If a moderately rapid action is permitted for the first day the layers will have completely mixed by night and if then a large quantity of ice is placed in the cooling water the mixture may safely be allowed to stand over night without attention. The vigorous reaction frequently is noted the second day if ice is not added occasionally. After



three or four days all evidence of reaction will have disappeared. Larger quantities of glycerene may be used in one container and in several cases as much as 150 grams was used. It was also found convenient to use tall narrow beakers instead of flasks. Former instructions have said to allow the oxidation to continue for five days but in the present work this was not found to give increased yields.

After the oxidation is complete the mixture is diluted with about an equal volume of water and then concentrated on the water bath to a thick syrup. During this time considerable amounts of fumes are usually evolved. The acid is then diluted again and boiled with a slight excess of lead carbonate. This forms the lead salt which is moderately soluble and can be crystallized out after concentrating the solution. As this lead salt is hydrolyzed by boiling and precipitates a lead oxide which does not dissolve again it is necessary to constantly have an excess of lead carbonate present. It is necessary to avoid too great an excess, however, as the hydroxyls of the glyceric acid combine with lead giving a salt which cannot be dissolved in water. The lead glycerate can be recrystallized from water but this may be omitted if it is light brown in color. Carrero<sup>15</sup> reports the formation of considerable amounts of oxalic acid which crystallized out on standing. This was not experienced by the writer.

The lead salt was recrystallized from water and then dissolved in hot water and just enough sulfuric acid added to decompose it. After filtering off the lead sulfate the glyceric acid is concentrated to a specific gravity of 1.25. Yield, 445 cc. from 1300g of glycerene.

#### The Preparation of $P_2I_4$ .

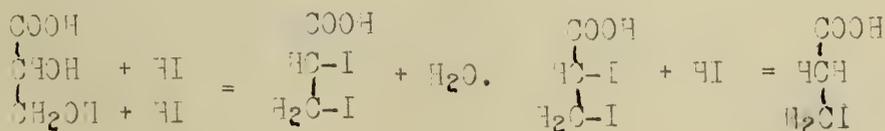
This was prepared by the union of the calculated amounts of



the elements in carbon disulfide solution. It is isolated by distilling off a part of the solvent and cooling which causes a copious precipitate of bright red plates. These can be filtered off on glass wool. It is well to remove the CS<sub>2</sub> as completely as possible as it later causes a very offensive odor when the P<sub>2</sub>I<sub>4</sub> is used. The yield is quantitative.

The Preparation of  $\beta$  Iodo Propionic Acid.

The glyceric acid was treated with P<sub>2</sub>I<sub>4</sub> in the ratio, 143cc. glyceric acid (Sp. Gr. 1.52), 55 cc. of water and 275 grams of P<sub>2</sub>I<sub>4</sub>. This was done in a flask with a reflux able to handle large volumes of vapor. The P<sub>2</sub>I<sub>4</sub> is added in 25 to 50 gram portions and the reaction soon becomes violent if not moderated by cooling. Occasionally during the reaction the mass becomes very black and viscous but clears to a light brown when more P<sub>2</sub>I<sub>4</sub> is added. After the iodide has all been added the flask is heated for half an hour and then allowed to cool which causes it to become semisolid with crystals of the  $\beta$  Iodo propionic acid. After filtering (using glass wool) the liquid is evaporated for another yield of crystals. This can be continued until it is practically pure phosphoric acid. The  $\beta$  Iodo propionic acid is then purified by crystallization from ligroin (B.P. up to 30°). If the crystals are already white and pure looking this may possibly be omitted if the ester is distilled later tho in every case during this work the crystallization was carried out. M.P. 32°. Yield, 200 grams recrystallized acid from 245 cc. of glyceric acid. The reaction can be illustrated



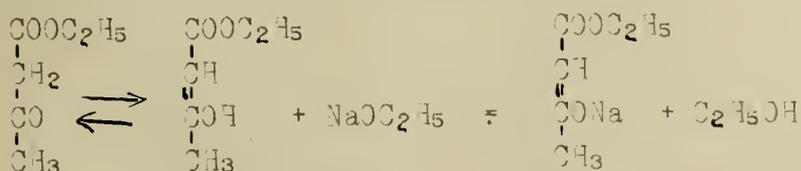


Esterification of  $\beta$  Iodo Propionic Acid.

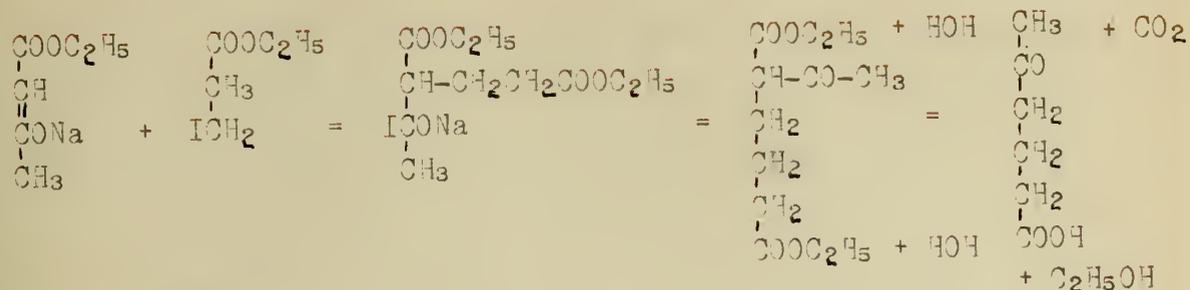
This is accomplished by dissolving the acid in absolute alcohol (100 grams in 250 cc.) and saturating the solution with dry hydrogen chloride gas. After standing half an hour it is poured into a large quantity of water after which the ester is separated and then dried with anhydrous sodium sulfate. It can be purified by distillation under reduced pressure but this was not done for the present work. Yield of ester, 96 grams from 100 grams of acid.

The Preparation of the  $\alpha$  Acetyl Glutaric Ester.

One mole of sodium (9.9 grams) is dissolved in a large excess of absolute alcohol (130 grams) under a reflux condenser. To the well cooled solution one mole (55 grams) of acetoacetic ester is added and soon after one mole (95 grams) of  $\beta$  iodo propionic ester. Heat is evolved and the liquid becomes nearly hot enough to boil. After standing half an hour the flask is placed on the water bath for an hour. A considerable precipitate of sodium iodide is formed. The reaction mixture is then poured into water which causes the  $\alpha$  acetyl glutaric ester to separate in large globules. The whole mixture is extracted with ether and the extract dried over night with sodium sulfate. After distilling off the ether the ester is distilled under reduced pressure. It distills at 165° to 170° at 23-24 mm. pressure. The yield is 60 grams of distilled ester from 100 grams of  $\beta$  Iodo propionic ester. The reactions are:-







### The Hydrolysis of $\alpha$ Acetyl Glutaric Ester.

This takes place according to the last reaction above. The purified ester is treated with twice its volume of one to two hydrochloric acid and boiled for five hours. The two layers soon disappear and considerable  $\text{CO}_2$  is evolved. After five hours, the liquid is nearly saturated, while warm, with ammonium sulfate and allowed to cool which causes the separation of considerable  $\gamma$ acetyl butyric acid. The whole mixture is extracted to exhaustion with ether, dried with sodium sulfate, the ether evaporated off, and the acid distilled in vacuum. For the distillation a Geryke pump was used and a vacuum of two millimeters maintained. The yield is 25 grams of acid from 60 grams of  $\alpha$ acetyl glutaric ester.

As distillation does not yield a pure product the whole of the constant boiling distillate was converted into the lead salt by boiling with an excess of lead carbonate. This lead salt is exceedingly soluble in water and therefore cannot be readily crystallized from it. Therefore the boiling mentioned above was, after filtering, continued in a vacuum until the volume was reduced to about 50 cc. Then a quantity of absolute alcohol was added and evaporation continued in vacuum with occasional renewal of the alcohol till nearly all of the solvent was removed. The object of adding the



alcohol was to assist in removing the water at as low a temperature as possible and at no time was a temperature higher than 75° attained. The resulting slush of crystals and alcohol was removed and sucked dry in a Buchner funnel. This lead salt was recrystallized several times from absolute alcohol taking care to wash the crystals thoroly with ether after each crystallization. The mother liquors were in each case worked up for the salt dissolved in them.

The salt was then dissolved in a small amount of water and slightly less than the required amount of sulfuric acid added to the solution. After filtering the solution was extracted with purified ether and after drying and then distilling off the ether the acid was distilled under two millimeters pressure taking care to run the distillation slowly. Considerable trouble was experienced on account of the rubber stoppers contaminating the acid. This was finally overcome by using corks. Leaks in the apparatus were closed up with a mixture prepared by dissolving old rubber stoppers in rosin till the resulting product is almost brittle when cold. For a list of boiling points of the acid see below.

Even after the above purification the acid gave a slightly cloudy 0.02 normal solution which the writer believes to be due to a non ionic impurity as will be discussed later.

#### Physical Constants and Derivatives of the Acid.

Melting point	Boiling point.	Pressure.
13°-14°.		
It readily forms a hydrate upon standing	274°-275°	760 mm
in air. This melts at 35°-36°. The ethyl	195°-200°	65 mm
ester boils at 221°. The amil melts at 114°.	170°-172°	23 mm
	150°-152°	3 mm
	122°-123°	1 mm



The oxime melts at  $104^{\circ}$ - $105^{\circ}$  and the semicarbazone at  $173^{\circ}$ - $174^{\circ}$ .

The sodium salt is reported as being an oil and the potassium salt is semisolid. All of the salts (Ca, Zn, Na, K, Pb) are very soluble in water but the silver salt, which crystallizes out on cooling.



CONDUCTIVITY APPARATUS AND DETERMINATIONS.



As it was desired to work with an accuracy of a tenth of a percent all apparatus was calibrated with this in mind. The conductivity method used was that of Kohlrausch using pipette cells, alternating current and a modified Wheatstone bridge.

#### The Glassware.

All the flasks, pipettes and other glassware used was of the best Jena glass and were steamed for at least thirty six hours before use. Most of it had been used for no other purpose for several years.

#### The Balance and Weights.

The balance was capable of weighing to a twentieth of a milligram. The weights were carefully checked against each other using the method of Richards<sup>13</sup> and then against a set calibrated by the bureau of standards. The errors were in all cases very small but were tabulated and all weights corrected for these errors.

#### The Thermostat.

This was a six liter Dwar Bulb completely open at one end. It was placed in a large glass cylinder covered with asbestos. Uniform temperature was assured by vigorous stirring with a siphon rotary stirrer actuated by a water motor. A thermometer reading to five thousandths of a degree was used to determine the temperature which was kept at 25° by means of a small electric heater made of nicrome wire wound on a strip of clay plate.

#### The Conductivity Water

The still used for the preparation of the conductivity water was built of copper and had a capacity of thirty two liters.



The condenser was a spiral coil of block tin pipe in a small copper tank provided with overflow valves and outlets to regulate the amount of water and so control the amount of condensation. The condenser was attached to the still thru a fractionating tower of sufficient length to prevent foam from being carried over with the steam. The heat was supplied by means of a closed steam coil.

The method of preparation was to fill the still with distilled water to which was added two hundred cubic centimeters of a solution of one hundred grams of potassium hydroxide and six grams of potassium permanganate in a liter of water. After heating to boiling the water was allowed to stand overnight. The following morning about half the contents of the still were distilled off and rejected as containing practically all of the ammonia of the original water. The remainder of the distillate was collected in bottles which had been used for no other purpose for several years. During the collection the steam was only partly condensed so the water was never exposed to the air of the laboratory but was collected in an atmosphere of steam. After filling, the bottles were covered with standard tinfoil and this covered by inverting a lipless beaker over the neck of the bottle. By these means it is usually possible to prepare water ranging from  $0.6 \times 10^{-6}$  to  $0.3 \times 10^{-6}$  in conductivity and such water was obtained at rare intervals. For some unknown reason very great difficulty was experienced in obtaining water of sufficient purity. One known difficulty was the irregularity of the steam pressure supplied which made it impossible to prevent the outside air from coming in contact with the water during collection. Also occasionally a film



of oil was noted on the water after collection indicating that some volatile impurity was present in the original distilled water. So much time was lost in ineffectual attempts to obtain pure water as to seriously delay the work.

#### The Bridge.

This was of the drum type and was constructed by the Leeds Northrup company.<sup>17</sup> The wire which was four hundred and seventy centimeters long was wound on a marble drum fifteen centimeters in diameter. The pitch of the spiral in which it was wound was exactly the same as that of the screw on which the hood carrying the contact point revolved. The contact was made by a platinum point on an especially constructed spring and was very satisfactory. The position of the contact was read by means of a graduated glass mounted in front of a graduated ridge on the revolving hood. Horizontal lines on the glass permitted reading complete revolutions. Fractions of revolutions were by means of a vertical line on the glass and the graduations on the hood. These were so arranged that it was easily possible to estimate the thousandths of a revolution. With a good minimum in the receiver it was possible to get check readings within two thousandths of a revolution or two ten thousandths of the total length of the wire.

The bridge was very carefully calibrated by checking it against especially constructed standard resistances owned by the Physics department. The minimums for this calibration were obtained by a very sensitive potentiometer and results more accurate than



a tenth of a percent were easily obtained. From twenty to twenty five points were determined for each revolution of the bridge near the center which was the point at which all readings were taken when the bridge was in use. These corrections were plotted on coordinate paper and all bridge readings referred to them for correction.

#### The Resistance Box.

This was of the traveling plug type and was composed of four banks of resistances of one, ten, one hundred, and one thousand ohms respectively, there being nine coils to each bank. By means of these any resistance from one to nine thousand nine hundred and ninety nine could be obtained. This box was checked up against standards as was described for the bridge. The errors were found to be less than a tenth percent in most cases but were tabulated and applied wherever significant.

The current was supplied by a small induction coil of high frequency. The minimums were obtained by a telephone receiver especially constructed for the purpose. Occasionally a capacity was introduced either across the cell or the box for the purpose of diminishing the noise.

#### The Cells.

These were of the pipette type. The acid cell had a capacity of about ten cubic centimeters. The electrodes were about two centimeters in diameter and a millimeter apart. They were platinized according to the method given in Tower<sup>18</sup>. This consists in thoroly cleaning the cell with nitric acid and then with hot alkali to remove grease. The cell is then filled with a three percent solution of platinum



chloride containing twenty five ten thousandths of a percent of lead acetate. The current from two storage cell is passed thru the solution and regulated by means of a reostat so that the stream of bubbles evolved does not become too rapid. A fine velvety deposit of platinum black soon makes its appearance on the cathode. The current is frequently reversed during the course of about twenty minutes so that both electrodes are covered with a firmly adhering deposit of platinum black. The cell is then washed out and filled with a dilute sulfuric acid solution and the current again passed for twenty minutes with frequent reversals. This removes occluded chlorine which would otherwise be very difficult to remove. Finally distilled water was slowly passed thru it for several days.

The constant of this cell was next determined. The constant of a cell depends upon the size and distance between the electrodes and is the ratio between these factors and those of a standard cell which would read specific conductances direct. Such a cell would have its entire volume enclosed between electrodes one centimeter square and one centimeter apart.

The constant of a cell is determined by means of a potassium chloride solution of definite strength which has been prepared from very carefully prepared potassium chloride. The actual specific conductance of such a solution has been determined by Kohlrausch.<sup>1)</sup> The conductivity of this solution is measured in the unknown cell and the cell constant determined from the equation  $\underline{L} = CL$  in which  $\underline{L}$  is the specific conductance of the solution,  $L$  is its conductance in the unknown cell and  $C$  is the cell constant.



As cell III, the constant of which had been checked many times, was at hand, this was used as a means of checking up the new cell. An approximately hundredth normal solution of potassium chloride was made and its conductivity very carefully determined in cell III. The conductance of this solution was then determined in the new cell and from the resulting data the cell constant was determined. A part of the data is tabulated below-

Cell III (known cell)			Cell IV (unknown cell)		
Bridge readings	Box readings	$\times 10^{-3}$	Bridge	Box	Cell constant.
Solution number one.					
5734			5733		
5735	33	1.407	5736	35	0.06772
5736			5735		
5582			4397		
5581	35	1.408	4393	41	0.06770
5580			4393		
5448			5221		
5446	37	1.407	5221	44	0.06777
5446			5221		
5195					
5195	41	1.407			
5193					
Solution number two.					
5711			5773		
5713	33	1.416	5774	35	0.06780
5712			5776		
5570			5573		
5570	35	1.415	5574	38	0.06776
5570			5574		
5436			5213		
5434	37	1.415	5212	44	0.06773
5432			5210		



From the above data and other determinations the constant of cell IV was determined to be 0.06776 all variations being within a tenth of a percent.

The water cell (Number I) had a capacity of about thirty cubic centimeters. The electrodes were not platinized and were about three centimeters in diameter and somewhat less than a millimeter apart. The constant of this cell was also determined by the method described for cell IV. A part of the data is tabulated below.

Known cell (III).			Unknown Cell (IV).		
Bridge.	Box	$L \times 10^{-4}$ .	Bridge	Box	Cell constants. (averages)
5424			5744	130	0.01960
5427	470	1.1179	5660	140	0.01959
5428			5390	150	0.01960
5363			5033	170	0.01964
5363	480	1.1177	Average = 0.01961		
5371					
5323					
5322	490	1.1131			
5323					

#### THE DETERMINATION OF THE CONDUCTIVITY OF ACETYLBOXYRIC ACID.

All solutions are calculated on the basis of a normal solution being one in which there is dissolved one gram molecular weight of the acid in one thousand grams of the solution. All dilutions were made by weight. A portion of the solution to be diluted was poured into a flask of known weight which had just been rinsed with it and the flask and solution weighed. The amount of water required to make the desired dilution was calculated and then weighed into the flask. In these weighings an accuracy of a tenth of a gram or



even in some cases a twentieth of a gram was maintained. The amounts required for the various solutions are given below. These are calculated from the molecular formula  $C_6H_{10}O_3$  using 1911 atomic weights. The molecular weight of the acid is 130.03.

Normality	Grams of acid required to make 1000 grams of solution.
0.02	2.6016
0.01	1.3008
0.0075	0.9576
0.0050	0.6504
0.0025	0.3252
0.0010	0.13008
0.00075	0.09756
0.00050	0.06504
0.00025	0.03252
0.00010	0.013008

In the course of a determination two 0.02 N solutions are weighed out and their conductances determined. If these checked one of them was held in reserve while the other was used to prepare two 0.01 N solutions. If these checked one was held in reserve and the other used to prepare two 0.0075 N solutions. This process was continued until 0.0001 N was reached or the solutions failed to check. In this case the reserve solution was used to prepare a third dilution. In some cases the volumes became too small to weigh accurately. In this case the reserve solutions of higher concentrations were diluted directly to lower ones thereby giving a large volume of the dilute solution. All solutions were kept in steamed Jena flasks stoppered with corks covered with tin foil. It was noted that in every case the 0.02 solution and even in some cases the 0.01 solution was slightly opalescent.



The conductance of the solutions was calculated by means of the equation

$$\underline{L} = \frac{(1 - a) K}{a \cdot R}$$

$\underline{L}$  = the specific conductance

$K$  = the cell constant

$R$  = the resistance from the standard box.

$a$  = the bridge reading

From the specific conductance can be calculated from the equation

$$\underline{L} = \frac{C \lambda}{1000}$$

$C$  = the concentration.

$\lambda$  = the molar conductance at the concentration  $C$

### Conductance Determinations on Acetyl Butyric Acid.

Normality.	$\underline{L}^u \times 10^{-4}$ .		Log.	$\underline{L}$ for the water.
0.010	1.7680	17.6640	1.247039	$0.73 \times 10^{-6}$
0.0075	1.52244	20.3252	1.303031	$0.3 \times 10^{-6}$
0.0050	1.2366	24.7320	1.393259	$0.9 \times 10^{-6}$
0.0025	0.86041	34.4162	1.536763	$0.93 \times 10^{-6}$
0.0010	0.52733	52.7330	1.722033	$0.93 \times 10^{-6}$
0.00075	0.45202	60.0363	1.773775	$1.07 \times 10^{-6}$
0.00050	0.36123	72.2543	1.853364	$0.96 \times 10^{-6}$
0.00025	0.24529	93.1167	1.971743	$1.00 \times 10^{-6*}$
0.00010	0.14146	141.4660	2.150652	$1.13 \times 10^{-6*}$

\* These values are of doubtful accuracy.



CALCULATED  $\lambda_0$  AS A CRITERION OF PRECISION AND AS A  
MEANS OF DETERMINING CONSTANT ERRORS.



The mathematical and other methods of testing the precision of conductivity measurements have been highly developed in the past. Until the present, however, there has been no method of detecting constant errors. Owing to this fact a great part of the work which has been done in the past is of little more than qualitative significance.

Derick has recently evolved a method of calculating  $\lambda_0$  from the data for any two concentrations which is capable of the widest application and serves not only as a means of detecting constant errors but also as a test of the precision of a set of measurements. Furthermore it enables one to determine the direction and approximate extent of an error in  $\lambda$  for a given solution. Used in connection with Kohlrausch's rule<sup>20</sup> for determining the  $\lambda_0$  value for weak organic electrolytes of moderately high molecular weight it furnishes a means of calculating the true value for  $\lambda$  from one which is only approximately correct.

Its derivation assumes the ideal mass law constant to hold rigorously for the electrolyte under discussion. This of course is never attained but the deviation of weak electrolytes and, for the lower concentrations, of transition electrolytes from this is in most cases less than the experimental error.

The ideal mass law expression for weak electrolytes is 
$$\kappa = \frac{c\alpha^2}{1-\alpha}$$
. As  $\alpha = \frac{\lambda}{\lambda_0}$  the expression becomes 
$$\kappa = \frac{c\lambda^2}{\lambda_0(\lambda_0 - \lambda)}$$
.

$\kappa$  = the mass law constant

$\alpha$  = the degree of dissociation

$\lambda$  = the molar conductance at the concentration  $c$ .



$\lambda_0$  = the conductance at infinite dilution.

Now since  $K$  is a constant and holds for all concentrations we may equate the values for two concentrations which gives the following expression,

$$\lambda_0 = \frac{\lambda \lambda_1 (C_1 - C, \lambda_1)}{C \lambda^2 - C, \lambda_1^2}$$

It is then possible to calculate  $\lambda_0$  from the data for any two concentrations. The customary method of determining  $\lambda_0$  by means of the sodium salt i.e.  $\lambda_{\text{RCOOH}} = \lambda_{\text{RCOONa}} + \lambda_{\text{H}^+} - \lambda_{\text{Na}^+}$  will also give a value for  $\lambda_0$ . If these values do not check the presence of a constant error, which is commonly due to an impure acid, is shown. We have then an absolute and a quick means of determining the presence of constant errors.

Since the ideal mass law constant is assumed to hold the electrolyte under discussion it is necessary to know at what concentrations this is most accurate and to what extent errors in  $\lambda$  affect it. To obtain this the logarithmic form of  $K = \frac{C \lambda^2}{\lambda_0 (\lambda_0 - \lambda)}$  is differentiated giving the following expression

$$\frac{dk}{k} = \left[ \frac{2\lambda_0 - \lambda}{\lambda_0 - \lambda} \right] \left[ \frac{d\lambda}{\lambda} - \frac{d\lambda_0}{\lambda_0} \right]$$

As the concentration of the solution increases  $\lambda$  approaches zero as its limit; as it diminishes  $\lambda$  approaches  $\lambda_0$  as its limit.

When  $\lambda$  equals zero the above expression assumes the form

$$\frac{dk}{k} = 2 \left[ \frac{d\lambda}{\lambda} - \frac{d\lambda_0}{\lambda_0} \right]$$

When  $\lambda$  equals  $\lambda_0$  the expression assumes the form

$$\frac{dk}{k} = \infty \left[ \frac{d\lambda}{\lambda} - \frac{d\lambda_0}{\lambda_0} \right]$$

Since  $\frac{dk}{k}$  is the variation i.e. the fractional error in  $k$  it can be seen at once that this error increases in value as



the concentration decreases for under these conditions the error in  $k$  is approaching infinity. Therefore as the concentration increases the effect of an error in  $\lambda$  and  $\lambda_0$  decreases. The limit in this direction is of course the highest concentration at which the electrolyte obeys the ideal mass law sufficiently for the determination in hand. This concentration is in most cases about 0.02 N.

Since  $\lambda_0$  is used as a means of detecting errors it is necessary to know at what concentration errors in  $\lambda$  and  $\lambda_1$  have the greatest and least effects as well as the extent of these effects. This can be obtained as in the case of the value for  $K$  by differentiating the logarithmic form of the expression  $\lambda_0 = \frac{\lambda \lambda_1 (C\lambda - \lambda_1 C_1)}{(C\lambda^2 - C_1 \lambda_1^2)}$  which gives,

$$\frac{d\lambda_0}{\lambda_0} = \frac{(C\lambda_1(C\lambda_1^2 + C\lambda^2 - 2C\lambda\lambda_1))d\lambda}{(C\lambda - C_1\lambda_1)(C\lambda^2 - C_1\lambda_1^2)} \frac{1}{\lambda} + \frac{C\lambda(C\lambda_1^2 + C\lambda^2 - 2C_1\lambda\lambda_1)}{(C\lambda - C_1\lambda_1)(C\lambda^2 - C_1\lambda_1^2)} \frac{d\lambda_1}{\lambda_1}$$

Let a =  $\frac{C\lambda_1(C\lambda_1^2 + C\lambda^2 - 2C\lambda\lambda_1)}{(C\lambda - C_1\lambda_1)(C\lambda^2 - C_1\lambda_1^2)}$  and b =  $\frac{C\lambda(C\lambda_1^2 + C\lambda^2 - 2C_1\lambda\lambda_1)}{(C\lambda - C_1\lambda_1)(C\lambda^2 - C_1\lambda_1^2)}$

Two cases now arise i. e. when  $\frac{d\lambda}{\lambda}$  and  $\frac{d\lambda_1}{\lambda_1}$  are of the same sign and when they are of opposite sign. In all cases so far tested a and b were of opposite sign and nearly equal to each other. If under these conditions  $\frac{d\lambda}{\lambda}$  and  $\frac{d\lambda_1}{\lambda_1}$  have the same sign the accuracy of the determination of  $\lambda_0$  will be the same at any concentration. If on the other hand  $\frac{d\lambda}{\lambda}$  and  $\frac{d\lambda_1}{\lambda_1}$  are of opposite sign the a and b values become additive and as C is a multiplying factor in each it is obvious that the effect of errors in  $\lambda$  and  $\lambda_1$  on  $\lambda_0$  is least at the lowest concentrations.



A CRITICAL STUDY OF THE CONDUCTANCE DATA FOR  
 $\gamma$  ACETYL BUTYRIC ACID.



The value 377 for  $\lambda_0$  was determined by Ostwalds rule and Kohl-  
 rauschs law being the value given for an organic acid of 10 atoms. As the value for  
 Capronic acid which is the corresponding unsubstituted acid of the  
 same number of carbon atoms and that for laevulinic acid which is the  
 next lower homologue of  $\gamma$ acetyl butyric acid is in each case 377  
 it is very likely that this value is nearly if not quite correct for  
 the value given by the salt method.

The conductance data obtained was not very accurate and the  
 calculated  $\lambda_0$  was found to be of great service in determining which  
 value out of several possibilities, differing from one to three tenths  
 percent, was the most correct. This was done by checking the several  
 values for  $\lambda$  for 0.0075 N solutions against a single 0.01 N value.  
 That value for  $\lambda$  which gave calculated  $\lambda_0$  nearest 377 was chosen as  
 most correct. The various values of  $\lambda$  for all of the other concentra-  
 tions were then checked against the best 0.01 N  $\lambda$ . In each case the  
 value chosen was the one which gave calculated  $\lambda_0$  nearest 377. The  
 series chosen is tabulated below.

Concentration.	$\lambda$	Log.
0.01	17.564	1.247039
0.0075	20.325	1.308034
0.0050	24.732	1.393259
0.0025	34.116	1.536763
0.0010	53.733	1.722033
0.00075	60.086	1.775775
0.00050	72.254	1.858304
0.00025	98.117	1.991743
0.00010	141.438	2.150352

The values obtained for calculated  $\lambda_0$  using all possible  
 combinations of concentrations for the measurement of  $\gamma$ acetyl butyric



acid are given below.

Concentrations	Calculated $\lambda_0$
0.01 and 0.0075	401.8
0.0050	374.5
0.0025	346.6
0.0010	340.7
0.00075	353.4
0.00050	351.6
0.00025	363.6
0.00010	339.2
0.0075 and 0.0050	359.2
0.0025	337.3
0.0010	335.9
0.00075	349.4
0.00050	347.4
0.00025	363.3
0.00010	361.7
0.0050 and 0.0025	329.3
0.0010	333.3
0.00075	319.0
0.00050	349.0
0.00025	369.2
0.00010	661.8
0.0025 and 0.0010	335.1
0.00075	356.4
0.00050	353.4
0.00025	374.6
0.00010	364.3
0.0010 and 0.00075	334.3
0.00050	333.6
0.00025	330.1
0.00010	359.6
0.00075 and 0.00050	434.6
0.00025	333.3
0.00010	364.3



0.00050 and 0.00025	404.3
0.00010	368.5
0.00025 and 0.00010	354.7

Much information develops from a critical study of the above data. In the first place all values, since all electrolytes of this type are known to approximate the mass law in the form given, should be constant. The lack of this regularity shows that the data is neither constant nor accurate to the desired degree. The fact that the values for the 0.001 N solution are lower in each series and that all values in the 0.001 series are irregular and unusual shows at once that this solution is in error and is probably of too low a concentration. The fact that in only a few cases do the values rise above 365 and that the average is considerably below this clearly indicates that there is a constant error which renders the solutions poorer in ionizing material than should be the case for solutions of their supposed concentrations. This fact taken in connection with the opalescent solutions mentioned earlier in this paper may be taken as an indication that there is a rather difficultly soluble non ionic impurity present in the acid. Another possible explanation is that possibly the acid may have taken up some water thus forming the hydrate which of course has a higher molecular weight. Every precaution was taken to prevent this. Still a third possibility is that the anion may be hydrated thus increasing its molecular weight and decreasing its conductivity.

An attempt was made to settle the question of the formation of the hydrate in the following manner. A portion of the acid was brot to 25° and then as quickly as possible dissolved in water which



was also at 25°. the solution was placed in a cell at once and its conductance determined as quickly as possible. The total time elapsed between solution of the acid and the completed determination of the conductivity being one and a half minutes. The conductivity was redetermined at intervals for several hours. There was a very slight decrease in the conductivity during the first two minutes but as this was not greater than the experimental error of the experiment as performed in this way it was decided that if the hydrate formed at all its rate of formation was practically instantaneous.

Another modification of the calculated  $\lambda_0$  values which is of great service in determining the extent and direction of errors in  $\lambda$  is illustrated in the following table. This data was obtained by adding one tenth of a percent of its value to each  $\lambda$  and calculating a series of  $\lambda_0$  values using the 0.01 N  $\lambda$  to which first one tenth percent was added and again from which one tenth percent had been subtracted. Then a second set of values was calculated using  $\lambda_s$  from which one tenth percent had been subtracted calculating these as before against the 0.01 N value to one tenth percent had been added and from which it had been subtracted. Finally a third set was calculated using the true  $\lambda$  for the 0.01 N solution and the others to which one tenth percent was added and again with this amount subtracted. These six series of  $\lambda_0$ s are tabulated below.

(See next page).



Calculated  $\lambda_0$  Values Using  $\lambda$ 's With Plus and Minus 0.01% Variations.

N. 1.	True $\lambda_0$ 2.	0.01N $\lambda$ + 0.01%		0.01N $\lambda$ - 0.01%		0.01N $\lambda$ (unchanged)	
		3. +0.01%	4. -0.01%	5. +0.01%	6. -0.01%	7. +0.01%	8. -0.01%
0.0075	401.3	376.4	262.8	791.7	391.1	406.5	311.7
0.0050	374.5	374.6	313.3	461.7	330.3	414.3	341.3
0.0025	346.6	346.7	322.5	377.4	344.4	439.9	333.9
0.0010	340.7	340.5	329.2	350.5	333.6	345.9	334.4
0.00075	333.4	333.9	329.9	347.0	337.3	343.4	334.0
0.00050	331.6	331.9	330.4	427.0	330.2	355.5	347.3
0.00025	363.6	369.9	364.3	373.3	363.2	372.3	366.7
0.00010	339.2	326.2	324.0	363.4	365.1	363.1	362.7

It was shown that if the errors in  $\lambda$  and  $\lambda_1$  are in the same direction they practically neutralize each other and calculated  $\lambda_0$  is determined with the same accuracy regardless of the concentration. If, on the other hand, they are in opposite directions their effect on the calculated  $\lambda_0$  is greatly magnified and is much greater at higher concentrations.

In column seven the  $\lambda_0$  value obtained from 0.01N $\lambda$  unchanged and the 0.0075 $\lambda$  + 0.01% is 406.5 while the actual  $\lambda_0$  is 401.3. This shows a very small change which would indicate that the errors were in the same direction i.e. the actual error in the 0.0075 N $\lambda$  is a positive error. In the next column is shown the effect of errors in opposite direction. Here the value 311.7 is obtained this being a decrease of ninety for a tenth of a percent variation. This very plainly shows the great effect of errors in opposite directions at high concentrations and is fully in accord with the theoretical discussion on page 23. The other possibility with errors in opposite directions is shown in column five where for a variation of a tenth percent in each  $\lambda$  with the errors in opposite directions the very high value 791.7 is obtained which is again in accord with the theory. The



very small effect of errors at the lower concentrations is shown by the small variations in the calculated  $\lambda_0$ 's for the 0.0001 solution. The values here show scarcely any variation even when the errors are made in opposite directions as in columns five, six, seven, and eight. This again agrees with the deductions on page 23. A further illustration of the diminished sensitivity at lower concentrations is given in the table below. The a and b values here are the ones developed on page 23 by differentiating the expression for  $\lambda_0$ . The differential takes the form  $\frac{d\lambda_0}{\lambda_0} = a \frac{d\lambda}{\lambda} + b \frac{d\lambda_1}{\lambda_1}$  and the values given below are calculated by evaluating the respective expressions for a and b which are given on page 23.

$\lambda$ .	a.	b.
0.0075	-275.50	273.93
0.0050	- 90.623	87.632
0.0025	- 36.325	37.321
0.0010	- 15.965	16.965
0.00075	- 13.362	14.413
0.00050	- 9.9755	10.976
0.00025	- 7.147	3.2313
0.00010	- 3.2620	4.1960

The large values for a and b at the higher concentrations show the sensitivity of the  $\lambda_0$  calculation for these concentrations. It can be seen at once that if  $\frac{d\lambda}{\lambda}$  and  $\frac{d\lambda_1}{\lambda_1}$  were of opposite sign, the a and b would be added which would give calculated  $\lambda_0$  a far greater sensitivity for errors in opposite directions at the high concentrations.

If however  $\frac{d\lambda}{\lambda}$  and  $\frac{d\lambda_1}{\lambda_1}$  are of the same sign the fact that a and b are of opposite sign makes them practically neutralize each other which causes the sensitivity of calculated  $\lambda_0$  to be nearly



the same at all concentrations.

Since the true value for  $\lambda_0$  is known to be 377 from the salt method (Ostwald's rule) it is possible to calculate the actual errors in the various  $\lambda$  values from the expression  $\frac{d\lambda_0}{\lambda_0} = a \frac{d\lambda}{\lambda} + b \frac{d\lambda_1}{\lambda_1}$ . This is done as follows: Let  $\frac{d\lambda}{\lambda}$  be the error in 0.01 N  $\lambda$  and  $\frac{d\lambda_1}{\lambda_1}$  be the error in the  $\lambda$  for the 0.005 N solution. Similarly let  $\frac{d\lambda_i}{\lambda_i}$  be the errors in each of the  $\lambda$ s below 0.01 N successively. It is possible to get the value of the error in  $\lambda_0$  at once by dividing the difference between the true  $\lambda_0$  (377) and the one obtained, by 377. It is possible in this way to get an equation which has two unknowns in it. By using the next concentration i.e. 0.0025 we obtain another expression involving one of the unknowns but at the same time introduce a third unknown i.e. the error in the 0.0025 solution. The third expression necessary for the solution of these three unknowns is obtained by calculating the values of a and b for the combination 0.0050 and 0.0025 and making the third expression from them by use of the  $\lambda_0$  calculated from them. The calculations are given below

0.01 and 0.005

$$\frac{d\lambda_0}{\lambda_0} = \frac{377-374.2}{377} = -0.006514 \text{ the negative sign is given because}$$

the value of  $\lambda_0$  was too low and because when substituted later it was found to be the correct sign.

$$a = -96.628 \quad b = 97.632 \quad (\text{see page 34})$$

$$\text{Let } X = \frac{d\lambda}{\lambda} \quad \text{and } X_2 = \frac{d\lambda_1}{\lambda_1}$$

Substituting these values into the expression at the top of the page we

$$\text{get } -0.006514 = -96.623X + 97.632X_2$$



Similarly we get for the combination 0.01 and 0.0025 the expression

$$-0.030637 = -36.325X_1 + 37.321X_3 \quad X_3 = \text{error in } 0.0025 \lambda$$

Now making use of the combination 0.0050 and 0.0025 and the a and b calculated for it we get as the third expression

$$-0.12520 = -53.703X_2 + 59.702X_3$$

We now have three simultaneous equations and can solve for the three unknowns. In a similar manner using the values of a and b for the 0.01 series (page 34) and the corresponding  $\lambda_0$  values we can obtain the errors in all of the  $\lambda$ s. These are the actual errors and their calculation is made possible by the assumption of the accuracy of the Ostwald rule in calculating  $\lambda_0$ . (see page 29).

Actual Errors in  $\lambda$ .

N.	$\lambda$	Errors.
0.010	17.664	+ 0.022152
0.0075	20.3252	+ 0.022100
0.0050	24.732	+ 0.021323
0.0025	34.4162	+ 0.01943
0.0010	52.733	- 0.027077
0.00075	60.0363	+ 0.016133.
0.00050	72.2513	+ 0.013903
0.00025	93.1167	+ 0.021504
0.00010	141.466	+ 0.014336

It is at once noticeable that the 0.001 solution which has been irregular in every calculation is now shown to have its error in the opposite direction which explains its anomalous behavior.

There is another way in which the expression  $\frac{d\lambda_0}{\lambda_0} = a \frac{d\lambda}{\lambda} + b \frac{d\lambda_1}{\lambda_1}$  can be used to indicate the extent and direction of errors in  $\lambda$ .

This is done by making the errors in  $\lambda$  and  $\lambda_1$ , which are expressed by  $\frac{d\lambda}{\lambda}$  and  $\frac{d\lambda_1}{\lambda_1}$  respectively, equal to first plus and then



minus a tenth of a percent and from the resulting equation calculating the value of  $\frac{d\lambda_0}{\lambda_0}$ . The value which this gives for the error will be the same as the error calculated from the value 377 for  $\lambda_0$  if the error in the work is actually a tenth of a percent. If this is not the case the extent and direction of the variations will be an indication of the errors in the work. There are four pairs of calculations. The first is made assuming an error of + 0.1% in the 0.01M  $\lambda$  and an error of + 0.1% in the remaining  $\lambda$  s. The second is assuming a plus error in the 0.01M  $\lambda$  and minus errors in the other ones. Similarly two calculations are made when 0.01 is given a minus error. The results of these calculations appear in the columns headed  $\frac{d\lambda}{\lambda}$ . The results in the columns headed 'actual' are derived by dividing the difference between the calculated  $\lambda_0$  for that concentration in the 0.01 series and the true  $\lambda_0$  value by the value of true  $\lambda_0$  which is 377, i.e. they are the actual fractional errors in  $\lambda_0$ .

N.	0.01M + 0.1% and other -0.1% $\frac{d\lambda}{\lambda}$	actual	0.01M + 0.1% and other -0.1% $\frac{d\lambda}{\lambda}$	actual
0.0075	0.00382	-0.0632	-0.55434	-0.346
0.0050	0.00100	0.0028	-0.19426	-0.162
0.0025	0.00099	0.0041	-0.07365	-0.695
0.0010	0.01697	0.0007	-0.0329	-0.334
0.00075	0.00108	-0.0407	-0.0273	-0.066
0.00050	0.00100	0.0003	-0.0209	+0.025
0.00025	0.00108	0.0035	-0.0154	-0.0114
0.00010	0.00093	-0.0383	-0.0075	-0.0449

(for the remainder of the table see next page)



N.	0.01% - 0.1% and other +0.1%	0.01% - 0.1% and other -0.1%.
	$\frac{d\lambda}{\lambda}$ actual	$\frac{d\lambda}{\lambda}$ actual
0.0075	0.5543 0.971	-0.00362 -0.0266
0.0050	0.19426 0.231	-0.00100 -0.0147
0.0025	0.07365 0.0744	-0.00099 0.214
0.0010	0.03293 0.0288	-0.001695 -0.0062
0.00075	0.02773 -0.0131	-0.00106 -0.0442
0.00050	0.02095 0.1360	-0.00100 0.0711
0.00025	0.01533 0.0141	-0.00103 -0.0016
0.00010	0.00746 0.0731	-0.00093 0.0700

The above data would give much information if a critical study could be made of it. There is however some uncertainty concerning the choice of the sign of the error as worked out by this and the method given before this and therefore a discussion of the above is omitted. These tables are inserted here more as a suggestion for future study than as a statement of fact.

#### The Water Correction.

This is a much debated question and until more data is available it cannot be settled. If the impurity in the conductivity water is carbon dioxide as it probably is then it seems likely that this correction ought not to be subtracted from the conductivity of an acid but should be subtracted from the conductivity of a salt.

In the work presented above the correction has not been applied as in every case it would make the conductivity <sup>less</sup> and therefore  $\lambda$  and  $\lambda_0$  smaller and they are already too small. Also Kendal's work<sup>21</sup> seems to



indicate that this correction should not be applied to electrolytes of this type. This conclusion is further confirmed by the work done in this laboratory<sup>22</sup>. It has however been recorded and can be applied later if necessary. The calculated  $\lambda$  will be of great service in determining whether or not to apply the correction as the values can be calculated both ways and the one which is most correct can thus be determined.



CALCULATION OF THE IONIZATION CONSTANT OF  
YACETYL BUPIRID ACID.



The ionization constant is calculated by means of the formula  $K = \frac{C \lambda^2}{\lambda_0(\lambda_0 - \lambda)}$ . If the electrolyte is weak enough and the solutions are not more concentrated than two hundredths normal this value should be a constant for all concentrations. The results obtained are tabulated below. The mean error is  $\pm 0.009$

Concentrations.	$\lambda$	$K \times 10^{-5}$ .
0.010	17.664	2.303
0.0075	20.325	2.304
0.0050	24.732	2.298
0.0025	34.416	2.293
0.0010	52.733	2.275*
0.00075	60.036	2.230
0.00050	72.254	2.272*
0.00025	93.117	2.239
0.00010	141.466	2.257**

\*These solutions were shown by means of the calculated  $\lambda_0$  to be inaccurate.

\*\*Solutions of as low a concentration as this are not expected to be accurate. This is also usually true of 0.00025 N solutions.

This table demonstrates the inefficiency of the ionization constant as a test of the accuracy of data. These values are more consistent than those customarily obtained but when the data is subjected to the far more exacting test of the calculated  $\lambda_0$  the errors in it are made apparent.

As stated earlier in this paper the ionization constant of this acid was measured in 1839 by Vorlander and Schilling. Their



data is tabulated below. The mean error is  $\pm 0.012$ .

Dilution	Concentration.	$\kappa$	$\gamma \times 10^{-5}$ .
16	0.0625	6.96	2.13
32	0.03125	9.87	2.21
64	0.015624	13.84	2.20
128	0.007813	19.41	2.20
256	0.003906	27.16	2.19
512	0.001954	37.66	2.13
1024	0.000977	52.12	2.13
2048	0.0004833	71.46	2.13

The work was done at 25°. The cell constant was determined by means of 0.02 N KCl using 0.002765 as its conductance. The specific conductance of the water was 2.1 to 3.4  $\times 10^{-6}$ . In the calculations the water correction was not applied.  $\kappa_0$  was given the value 376.

The  $\kappa_0$  values were calculated for this data and are tabulated below.

Concentrations.	$\kappa_0$	Concentrations	$\kappa_0$
0.0625 and 0.03125	- 7.03	0.015624 and 0.007813	252.7
0.015624	603.2	0.003906	364.3
0.007813	455.2	0.001954	335.3
0.003906	420.1	0.000977	352.5
0.001954	371.5	0.000483	372.2
0.000977	371.6	0.007813 and 0.003906	365.2
0.000483	372.6	0.001954	331.3
		0.000977	353.1
0.0312 and 0.015624	233.5	0.000483	330.8
0.007813	293.1	0.003906 and 0.001954	307.5
0.003906	323.5	0.000977	439.1
0.001954	312.3	0.000483	408.3
0.000977	339.3	0.001954 and 0.000977	338.5
0.000483	363.1	0.000483	472.1
		0.000977 and 0.000483	591.3



A comparison of the data of Vorlander and Schilling with that of the writer brings out several interesting facts. The mean error of the constants of the two determinations is slightly different being 0.0012 for Vorlander's values and 0.0009 for those of the writer. The most significant difference however lies in the values for calculated  $\lambda_0$ . Those of Vorlander frequently vary a hundred or more the many of them do not vary more than 40 from the average. This is considerably more variation than the corresponding values obtained in the writer's work show.

Another important difference is apparent when the value used for  $\lambda_0$  is considered. The formula for calculating  $K$  is

$$K = \frac{c \lambda^2}{\lambda_0 (\lambda_0 - \lambda)}$$

As Vorlander used 378 his values should be slightly higher than those of the writer who used 377. This is however not the case but instead the reverse is true. These facts follow because  $\lambda_0$  appears in the denominator.

It was shown earlier in this paper that the conductance of the various solutions was probably too low owing to the presence of a nonionic impurity. This would make the values for  $\lambda$  too small and therefore give a lower constant since  $\lambda$  appears in the numerator.

It seems probable then that not only are the values given by Vorlander and Schilling too low but that the same is also true of the values obtained by the writer.



CALCULATION OF THE  $\Delta$  OXYGEN PLACE FACTOR.



The place factor is calculated by means of the following formula  $\text{Place Influence} = \frac{\text{Ln } K \text{ unsubstituted acid}}{\text{Ln } K \text{ substituted acid}} - 1.$

Before it is possible to calculate the factor it is necessary to know the ionization constant of the unsubstituted acid corresponding to  $\gamma$ acetyl butyric acid. This acid in caproic acid and its ionization constant has been measured by Franke, Ostwall, Billitzer, and Drucker. As it is necessary to know how accurate these determinations are, and which is the most accurate, the data for each is listed below and the results of calculating the  $\lambda_0$  values for all possible combinations of concentrations is given for each.

Calculation of the  $\lambda_0$  Values for Franke's Data on Caproic Acid.

Dilution.	Concentration.	Log C.	$\gamma$	$\lambda$	Log $\lambda$
64	0.015624	3.193792	10.391	11.044	1.043143
128	0.007313	7.892796	14.52	15.435	1.183499
256	0.003906	7.591732	20.25	21.525	1.332953
512	0.001954	7.290325	23.10	29.27	1.475239
1024	0.000977	6.989717	39.00	41.457	1.617598

Concentrations.	$\lambda_0$
0.015624 and 0.0073126	193.7
0.003906	219.4
0.001954	233.4
0.000977	265.1
0.007313 and 0.003906	236.4
0.001954	243.5
0.000977	279.0
0.003906 and 0.001954	243.6
0.000977	369.2
0.001954 and 0.000977	406.9

The water used was of unknown conductivity and the correction was not applied. The irregularity of the values in the above table shows that the data is too inaccurate to use.



Calculation of the  $\kappa_0$  Values for Ostwald's Data on Caproic Acid.

(Zeit. fur. Phys. Chem. 3, 176.)

Dilution.	Concentration.	Log. Conc.	$\gamma$	$\kappa$	Log. $\kappa$
32	0.031250	3.494350	7.45	7.919	0.393639
64	0.015624	3.193792	10.60	11.268	1.051839
128	0.007812	7.892796	14.89	15.828	1.199423
256	0.003906	7.591731	20.94	22.259	1.347510
512	0.001954	7.290325	29.00	30.327	1.488932
1024	0.000976	6.989717	40.31	42.350	1.631946

Concentrations.

	$\kappa_0$
0.03125 and 0.015624	-251.4
0.007812	6203.0
0.003906	1155.0
0.001954	442.1
0.000976	413.6
0.015624 and 0.007812	331.6
0.003906	433.0
0.001954	327.2
0.000976	350.3
0.007812 and 0.003906	533.1
0.001954	303.1
0.000976	333.9
0.003906 and 0.001954	232.2
0.000976	302.4
0.001954 and 0.000976	233.3

The above values are not corrected for the conductivity of the water and this value is not given in the article.

The extreme irregularity of the calculated  $\kappa_0$  values shows that the data is too inaccurate to be reliable.



Calculation of the  $\lambda_0$  Values for Billitzer's Data on Caproic Acid.

(Monat fur Chemie 20, 676.)

Dilution.	Concentration.	Log. Conc.	$\gamma$	$\lambda$	Log. $\lambda$
64	0.015624	3.193792	10.65	11.321	1.053833
128	0.0078126	7.392796	14.93	15.371	1.200593
256	0.0039060	7.591732	21.05	22.380	1.349785
512	0.0019540	7.290925	29.33	31.178	1.493345
1024	0.0009766	6.989717	40.23	42.764	1.631033

Concentrations.	$\lambda^c$	$\lambda^u$
0.015624 and 0.007812	304.7	274.6
0.003906	219.3	435.37
0.001954	196.4	406.6
0.000976	169.4	302.2
0.007812 and 0.003906	238.3	107.5
0.001954	203.1	456.3
0.000976	170.2	306.3
0.003906 and 0.001954	175.6	335.3
0.000976	153.9	257.8
0.001954 and 0.000976	135.0	230.3

The water used had a conductivity of  $2.4 \times 10^{-6}$ . This value was not subtracted in his calculations. The first column of  $\lambda_0$  values given above was calculated from his data after subtracting this value. The second value was determined direct from his data.

The great irregularity of the calculated  $\lambda_0$  values shows that the data is unreliable.



Calculation of the  $\kappa_0$  Values for Druckers Data on Caproic Acid.

(Zeit. for Phys. Chem. 52, 643.)

C.	Log C.	$\kappa^c$	Log $\kappa^c$	$\kappa^u$	Log $\kappa^u$
0.03432	3.541829	7.425	0.370697	7.473	0.373473
0.01741	3.240799	10.53	1.022423	10.633	1.026607
0.00370	7.939519	14.83	1.171141	15.023	1.176757
0.002177	7.337353	29.32	1.467164	30.037	1.473333

Concentrations	$\kappa^c$	$\kappa^u$
0.03432 and 0.01741	-544.5	-255.0
0.00370	2300.0	-761.1
0.002177	1052.0	-166.4
0.01741 and 0.00370	487.3	-1551.0
0.002177	626.4	-136300.0
0.00370 and 0.002177	6254.0	-109300.0

Drucker applied the full water correction to his data. This gives the values marked  $\kappa^c$ . The water had a conductivity of  $1.7 \times 10^{-6}$ .

The extreme irregularity of the calculated  $\kappa_0$  values shows that the data is unreliable.

The above data on Caproic acid is all shown to be too inaccurate to use in calculating the place factor and it is therefore impossible to do this.

I wish to thank Dr. Derick for the kindness and untiring enthusiasm with which he has directed this work.

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