# PARTITION RATIOS OF SOME ORGANIC ACIDS
# BETWEEN
# ETHER AND WATER

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By

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# PREFACE

One of the earliest observations which can be classed as chemical is that some substances dissolve when placed in contact with various liquids. The first quarter of the twentieth century was a time in which one of the chief occupations of chemists was the study of solutions. Nevertheless, present knowledge of solutions is very inadequate, although there are many theories which attempt to explain the nature of solutions. Studies on partition have been valuable in elucidating the state of substances in solvents.

The ratio of the concentrations of a substance which is distributed between two phases at constant temperature is known as the distribution or partition ratio. This partition between solvents is the basis for numerous preparation, separation, and purification processes.

In the literature there exist several discrepancies in regard to the partition ratios of some organic acids in water and ether. There is a dearth of partition data for normal to 0.01 normal solutions between ether and water at 25° C. A possible use for these data is the qualitative identification of individual organic acids in small amounts by their partition ratios. The purpose of this investigation was to find out the partition ratios of several organic acids for the reasons mentioned above.

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# INTRODUCTION

In 1872 Berthelot and Jungfleisch (5) studied the partition of iodine between carbon disulfide and water and concluded that the familiar Henry's law, concerning the equilibrium between a gas and its solution in a liquid, follows the same general principle as the distribution of a solute between two liquid phases. Nernst (35) imposed an important restriction upon this generalization which is now called the distribution or partition law. He showed that for ideal liquid-liquid systems a constancy of the partition ratio exists only when the molecules of the distributed substance are in the same condition in both phases. Furthermore, the two solvents must be absolutely insoluble in each other, even when both contain large amounts of solute. Of course these ideal conditions are seldom more than approximately realized, the disturbing influences becoming greater with increasing concentration. The system carbon tetrachloride-water-iodine approaches this ideal.

In this work ether was chosen for the second solvent phase because it is a relatively "non-polar" solvent (47) and the many organic acids which dissolve in it are <u>believed to be</u> in the simple molecular state. In chloroform, benzene and many other associating solvents the acids are considered to be partly associated (17,24). Frequently there is dissociation in the water. Many attempts have been made to correct for this in order to make the partition ratio constant. Some acids are more highly associated in the water layer than in the organic solvent, e. g., 3,5-dinitrobenzoic acid (50). The solute and solvent may combine to form definite compounds, e.g., hydrates in aqueous solution (1,18). Ethereal solutions separate readily from aqueous solutions which have been shaken; other solvents do not separate nearly so readily. This is an aid in titrating near the end point. Ether is especially useful because there is a tremendous range in the partition of organic acids between it and water. Chandler (7) finds ether to be the best non-aqueous solvent in general for the determination of the state of equilibrium in solutions of dibasic acids and their salts. However, methylal may be more efficient as an extraction solvent for several common organic acids (12). Werkman (54) suggests the use of isoamyl ether for partition work because it is less soluble in water than either ethyl ether or isopropyl ether. For this reason he uses it to determine partition ratios for fatty acids. Later work shows isopropyl ether to be unstable, i. e., it becomes acid upon standing (37a).

There is no obvious relationship between the solubilities of organic acids in pure water or pure ether and their solubilities in ether-saturated water or water-saturated ether (46) as shown on page 36 of this thesis. Pershke (39) shows in theory and by experiment that the partition ratio is the ratio of the concentrations of the dissolved substance in the two solvents for the system succinic acid-ether-water and others. He shows that the partition ratio is markedly different from the ratio of the solubilities of succinic acid in the pure solvents. Furthermore, the limiting value of the partition ratio at high total concentrations of the distributed substance is not determined, in general, by the ratio of the solubilities of the two solvents but by the ratio of the concentrations of the two phases at the triple point: solid-liquid-liquid (44).

The solute may have one of three possible effects upon the partition ratio (32,52) because of its effect upon the mutual solubilities of the solvents. First, the distributed phase may lower the mutual solubilities. At the limit, upon subsequent additions of solute, it is conceivable that the mutual solubilities would be reduced to zero so that the limiting distribution ratio would be that of the solubilities in the pure solvents. Second, the distributed phase may increase the mutual solubilities. At the limit the phases would be soluble in all proportions. This would cause the distribution ratio to approach unity at the consolute concentration. Klobbie (29) points out the case of malonic acid distributed between ether and water as an example of this second type. Third, the solubility of one liquid in the second may increase, and that of the second in the first decrease, upon the addition of solute.

This would cause the partition ratio to vary throughout the concentration range. Any of these three possibilities may be realized experimentally.

Although this work was done at constant temperature, it is well to remember that the solubility of ether in water decreases with rising temperature while the solubility of water in ether increases with a rise in temperature (36). Consideration of the effect of temperature is important if the partition method is to be used for the rapid qualitative characterization of organic acids, because it is more practical to determine these ratios at room temperature. The partition ratio may be expected to vary with temperature because solubilities ordinarily are affected by temperature changes. The solubility of the acid in the water phase probably does not vary to the same extent as does the solubility in the ether phase, and, as has been pointed out previously, the mutual solubilities of the ether and water are affected in opposite ways. Forbes and Coolidge (13) in their thorough work on "The Relations between Distribution Ratio, Temperature, and Concentration in the System: Water, Ether, and Succinic Acid" calculate the temperature coefficient for the partition ratio in this system to be 0.0258 units per degree. This agrees favorably with their experimental figure of 0.0255. Perschke (39a) finds a temperature coefficient of 0.0222 between 17 and 18.4° C. for succinic acid in ether and water where the concentration of acid in the ether layer is 0.06 to 0.07

grams per liter. For the system acetic acid-water-ether, Hantzsch and Sebaldt (21) find the partition ratio to be 2.031 at 0° and only 2.19 at 25° C. It appears that these small changes are true <u>only</u> in systems where the temperature coefficients of the solubilities in the two phases are little different, because this ratio is altered only when the solubility ratios are altered. This is the basis for the general statement that temperature changes have little effect upon partition ratios (4, 10, 56).

Solubility is known to be affected by pressure; theoretically, it may be assumed that there should be a pressure coefficient of the partition ratios between the liquid phases. However, pressure must have an exceedingly small effect upon partition ratios, and as yet no such effects have been noted (52).

Impurities in the solute or solvent naturally affect partition ratios. Water is easily obtained relatively pure, and hence impurities in water will not be discussed here. Impurities in ether are discussed in the section on reagents. Twelve C. P. acids were used in this work, and purification of the other three is discussed in the section on reagents, but since pure acids may not always be available it is appropriate to consider the effect that impurities in the solute would have upon partition ratios. Because the partition ratio is determined by alkali titration ratios, the effect of any foreign acidic or basic substances is obvious and serious. Taylor (52) states that for extraction purposes:

> The distribution ratio may be changed in the desired direction by addition of another compound which depresses the dissociation of the substance being extracted; an organic acid of moderate strength for example can be most advantageously extracted from water after addition of a strong inorganic acid, which by its excess of hydrogen ion will convert the organic acid chiefly into undissociated molecules, which are soluble in the ethereal phase whereas the ions are not. An organic base, by the same reasoning, is most easily extracted in the presence of a strong inorganic base. The addition of neutral bodies such as salts will also in many cases lower the solubility of the organic compound in water (the so-called salting-out effect) and thus favor the extraction by the ether.

Salts are usually insoluble in organic liquids, and conversely the amount of substance distributed in the water layer is decreased upon the addition of salt. The "salting-out effect" is larger the smaller the size of the ion and the greater the ionic charge. According to Herz and Stanner (25), $Cl^-$ is more effective than $Br^-$ which is more effective than $I^-$. Sugar content does not influence the partition of succinic acid between ether and water, according to Pinnow (40).

Polymorphic forms of crystalline substances are common, and since they differ among themselves in crystalline form, free energy and other physical and chemical properties, a mixture of two forms might conceivably be present, one as an impurity. There is a difference in solubility of polymorphic forms (6). In solutions, however, there should be no effect on the partition ratio if there were mixtures of polymorphic forms dissolved because the crystal lattice no longer exists.

The application of the partition law to liquid-liquid systems has furnished many interesting as well as useful results. Numerous experimenters have determined degree of dissociation or association or both. The ordinary procedure is to use the equations known to apply to association, the degree of dissociation being determined from independent conductivity experiments. If the chemical potential or activity of the solute is known in one solvent it may be determined for the other solvent (11, 33). This furnishes a means of calculating free energies. A host of chemical equilibria may be studied to advantage by partition methods (17, 52). Studies of distribution may also furnish the means of proving the existence of compounds (9), or determining heats of dissociation, hydration, or ammoniation. Ordinarily the partition principle is most used in the process of extraction. It has been possible, in some instances, to establish the identity of a single acid by partition methods (49a), or a single acid in a mixture of acids by partition methods (37). In summarizing the applications of partition studies, it may be said that it is obvious that the principle of distribution is intimately related to the state of aggregation of matter in solution. When sufficient partition data are known it will be possible to determine the identity of an organic acid by a comparison of known partition ratios with ratios of the acid to be identified. Additional chemical equilibrium studies need to be made. Our meager knowledge in this field justifies the determination of more partition data in the hope that order may be wrought from the present chaos.

# EXPERIMENTAL PART

REAGENTS. The following reagents were used: amino- (glycine), monobromo-, monochloro-, dichloro-, and trichloroacetic, adipic, barbituric, benzenesulfonic, crotonic, formic, 2-furoic, glycolic, alpha-hydroxyisobutyric, succinic, and d-tartaric acids, ethyl ether, ethyl alcohol (denatured), phenolphthalein, thymolphthalein, sodium hydroxide, and water.

WATER. Ordinary distilled water was used. It is important that this water be neutral, alcohol-free, and carbon-dioxide-free for this work. Carbon dioxide may be removed by boiling the water.

ETHYL ETHER. Although Merck reagent grade absolute ethyl ether was used, it was washed by shaking with distilled water and kept in this water-saturated condition over water until desired for use. The solubility of water in ethyl ether is 1.34 percent by weight at 25° C., whereas the solubility of ether in water is 6.04 percent by weight at 25° C. (27). Alcohol affects the distribution of succinic acid between water and ether more than any other impurity likely to be present. Forbes and Coolidge (13) find that the presence of one percent of alcohol increases the solubility of ether in water by about two percent of itself, and that the solubility of the acid in ether is increased by as much as twenty percent of itself, while the increase of the solubility of the acid in water was much less. After washing the absolute ether four times with water the author found the distribution of succinic acid to be the same as without washing. This was done to see whether the impurities, a maximum of 0.005 percent of acids (as acetic) and not more than 0.1 percent of alcohol, would affect the distribution. Any impurities which may have been present evidently had no effect upon the distribution in this particular case.

INDICATORS. Although Hall (20) recommends the use of dibromothymolsulfonphthalein, commonly called bromothymol blue, as an indicator for titrations in ether solutions because it is not extracted from the water layer by the ether, it was found by the author to be impractical to use because the color change at the end point was not as sharp as with phenolphthalein. Also, the pH at the end point is too low for the best titration of a weak acid with a strong base by means of this indicator. Furthermore, almost without exception, other investigators in partition work with organic acids have preferred to use phenolphthalein.

The thymolphthalein used in the glycine titration was 0.5 percent by weight in alcohol.

SODIUM HYDROXIDE. This reagent was standardized with potassium acid phthalate, and stored in a glass carboy connected to a soda-lime tower. Air pressure from a rubber pressure bulb was used to force the sodium hydroxide from the carboy through a tube to a burette also connected to a soda-lime tower. In this manner all air in contact with the sodium hydroxide was carbon-dioxide-free. A one normal solution of barium chloride, equal in volume to one percent of the sodium hydroxide solution, was added to the solution to precipitate any carbonates which might have been present. Kay and Sheehan (28) give excellent directions for preparing and using very dilute standard solutions of sodium hydroxide. It was found advantageous to make one alkali solution about four times the strength of the other, i.e., 0.03219 and 0.1237 normal. The hydrochloric acid used for back titration was 0.01525 normal.

ETHYL ALCOHOL. The 95 percent alcohol was denatured with five percent methyl alcohol.

2-FUROIC ACID. Following the suggestion of Milas and Walsh (34), furoic acid was purified by recrystallization from a hot mixture of two parts of carbon tetrachloride and one part chloroform. These crystals melted at 132-133°.

Gilman (16) states:

> Furoic acids, in general, undergo relatively ready decarboxylation and the smoothness of this reaction with 2-furoic acid commends it as the best present method for the preparation of furan.

and reports that this decarboxylation takes place at 158°. Furoic acid melts at 132° and boils at 230°. Although furan, b. 32°, is easily obtained by decarboxylating furoic acid, it is not certain that the long white needles of furoic acid which sublime readily from the tarry melt are pure enough for partition studies. The yield of furoic acid by distillation even under reduced pressure is not over fifty percent. Furthermore, purification was apparently unnecessary because the purified crystals when dissolved gave a partition ratio which was almost identical (within experimental error) with the commercial practical crystals before purification.

DICHLOROACETIC ACID. This acid was purified by distillation, after some difficulty with decomposition products, by Dr. O. C. Dermer. The hydrochloric acid which was found to be present was removed by boiling until the dichloroacetic acid was practically chloride-free. Titration of the acid with standard base indicated more than 99 percent dichloroacetic acid to be present.

BENZENESULFONIC ACID.* This acid was prepared by Dr. O. C. Dermer from benzenesulfonyl chloride by the method of Davies and Davies (8a).

The source and purity of the other acids used follow.

| | |
|---|---|
| MONOBROMOACETIC ACID* | EASTMAN C. P. |
| MONOCHLOROACETIC ACID* | CENCO C. P. |

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*Some water was present in this acid, but since this acid was studied in a water solution this impurity was unimportant.

| | |
|---|---|
| TRICHLOROACETIC ACID* | MERCK C. P. |
| ADIPIC ACID | EASTMAN C. P. |
| BARBITURIC ACID | EASTMAN C. P. |
| CROTONIC ACID | EASTMAN C. P. |
| FORMIC ACID* | MERCK C. P. |
| AMINOACETIC ACID (GLYCINE) | EASTMAN C. P. |
| GLYCOLIC ACID* | EASTMAN C. P. |
| SUCCINIC ACID | MERCK C. P. |
| d-TARTARIC ACID | MERCK C. P. |
| ALPHA-HYDROXYISOBUTYRIC ACID | EASTMAN C. P. |

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*Some water was present in this acid, but since this acid was studied in a water solution this impurity was unimportant.

## PROCEDURE

A 300 ml stock solution of each organic acid was adjusted to a concentration of about one normal. From the stock solution were pipetted three 50, three 25, three 10, and three 5 ml samples into twelve 125 ml ground glass stoppered bottles. The stoppers did not fit well enough as they came from the manufacturer so they were ground with water and emery to fit their respective bottles. When a water-saturated ether solution could be vigorously shaken in a bottle with no ether leaking thru the joint the stopper was deemed properly fitted. Water was measured by means of a burette into the sample bottles containing the acid, no water in the first three, 25 ml in each of the second three, 40 ml in each of the next three, and 45 ml in the last three. This made 50 ml of acid solution in each of the twelve sample bottles. The acid concentration in the sets of bottles was then approximately normal, N/2, N/5, and N/10 respectively. Next, 50 ml of water-saturated ether was pipetted into each bottle, so that the total volume of solution in each of the twelve bottles was approximately 100 ml.

It was not necessary to be accurate in preparing these solutions. The unpleasant task of sucking ether into a 50 ml pipette was avoided by placing the pipette in one hole of a two-hole cork stopper, and a short right-angled piece of 2-mm glass tubing in the other hole. Rubber tubing, connected at one end to a rubber pressure bulb, was then slipped over the end of the small right-angled tubing. When the stopper was placed in the ether bottle and the tube of the pipette extended into the ether a few squeezes on the bulb would furnish enough pressure to send the ether shooting up into the pipette.

The glass stoppers were tightly fitted in their respective bottles and a rubber band, which was fastened to a wire hook around the neck of each bottle, was snapped over each stopper to keep it tight while the solutions reached equilibrium in the bath, and while shaking. All twelve bottles were laid side by side and shaken manually in a wooden box built for that purpose. The box and its contents were allowed to remain submerged in the water thermostat for at least thirty minutes at 25 ± 0.2° C. After that time the box was removed from the water bath and again shaken by pulling it to and fro on a table top for five minutes to insure complete equilibrium. The box containing the bottles was then returned to the bath for at least ten minutes to allow the liquid phases time to separate completely.

Each sample bottle was allowed to remain in the water bath until the 25 ml samples were to be taken from the ether layer and the water layer. Water around the top of the stopper was removed and a 25 ml pipette in a small rubber two-hole stopper with the rubber pressure bulb attachment, like the one used to remove the water-saturated ether from its container, was placed in the neck of the bottle so that the tip of the pipette was about 5 mm above the aqueous layer. About 15 ml of the ether layer was forced into a clean, but not necessarily dry, pipette. The inside of the pipette was rinsed with the 15 ml of ether solution after removing the pipette, stopper and all. When the pipette was placed in the bottle again, exactly 25 ml of the ether layer was removed, placed in a 250 ml Erlenmeyer flask, and the flask stoppered until the solution could be titrated. The method of removing ether by means of pressure reduces evaporation. One pipette was used for removing all samples from the ether layer and another for all from the water layer. Samples from the ether layer were placed in the larger flask to permit the addition of about 100 ml of water before titration, and also to help one to remember which layer the sample had come from. As an added precaution a finger was held over the protruding end of the pipette while it was going through the ether layer. Before removing the 25 ml portion from the water layer, a few bubbles of air were blown into the water layer to expel any ether which might have entered the pipette.

Samples of both layers of all acids used in this investigation, except glycine, were titrated with 0.03219 or 0.1237 normal sodium hydroxide using phenolphthalein as an indicator. Since ether extracted some of the indicator from the rest of the solution, about one and one-half times as much phenolphthalein was added to each sample from the ether layer as to the water layer samples. It was found expedient to titrate all of the samples from one layer in succession, beginning with the most dilute.

Special technique is required for the titration of ethereal solutions. Chandler (7) added water and distilled off the ether. Dr. M. T. Kelley, of Monsanto Chemical Company in Saint Louis, suggested adding about 100 ml of water, an excess of sodium hydroxide, and back titrating with hydrochloric acid. The latter was found to be the best method.

Glycine is an amino acid which forms a zwitterion and cannot be titrated with phenolphthalein as the indicator. From the several methods of titrating amino acids (13a, 23, 34a) we chose the following for the titration of our glycine samples. All ether was evaporated from ether layer samples, and water layer samples were evaporated to about 2ml. This was done to insure an excess of about 85 percent alcohol for the titration after adding 50 ml of alcohol to each sample. The 85 percent excess of alcohol must be present for the accurate determination of glycine by this method. One ml of 0.5 percent thymolphthalein was added, the mixture heated to boiling, and titration with standard base was performed in the boiling solution to a greenish-blue end point for the samples from the ether layer, and a faint sky-blue end point for the water layer samples. This titration is considered to be a measure of the carboxyl groups present in the amino acid.

## TABLE 1

### ADIPIC ACID

$HOOC.CH_2.CH_2.CH_2.CH_2.COOH$

M. W. = 146.14

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 40.10 | ---- | 20.58 | ---- | 1.95 |
| 40.31 | ---- | 20.76 | ---- | 1.94 |
| 40.40 | ---- | 20.80 | ---- | 1.94 |
| 99.15 | ---- | 52.25 | ---- | 1.90 |
| 96.72 | ---- | 50.85 | ---- | 1.90 |
| 100.40 | ---- | 52.83 | ---- | 1.90 |
| 159.02* | 41.38 | 84.58 | ---- | 1.88 |
| 158.72* | 41.30 | 84.38 | ---- | 1.88 |
| 155.26* | 40.40 | 32.41 | ---- | 1.86 |
| 196.15* | 51.04 | 106.18 | ---- | 1.85 |
| 198.49* | 51.65 | 107.60 | ---- | 1.84 |
| 197.07* | 51.28 | 107.43 | ---- | 1.83 |

### CALCULATED MEAN VALUES

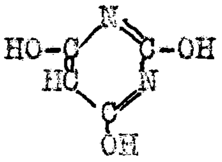
| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0129 | 1.88 | 0.0065 | 0.95 | 1.98 |
| 0.1069 | 15.62 | 0.0557 | 8.14 | 1.92 |
| 0.1700 | 24.84 | 0.0904 | 13.21 | 1.88 |
| 0.2357 | 34.45 | 0.1281 | 18.72 | 1.84 |
| 0.2705 | 39.53 | 0.1486 | 21.72 | 1.82 |

---

*Calculated.

## TABLE 2

## BARBITURIC ACID



M. W. = 128.09

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 23.41 | --- | 0.72 | --- | 32.6 |
| 23.27 | --- | 0.57 | --- | 40.8 |
| 23.36 | --- | 0.57 | --- | 41.0 |
| 46.55 | --- | 1.09 | --- | 42.7 |
| 45.62 | --- | 1.02 | --- | 44.7 |
| 45.71 | --- | 1.00 | --- | 45.7 |
| 60.70* | --- | 1.44* | --- | 42.2 |
| 61.17 | --- | 1.43 | --- | 42.8 |
| 60.42 | --- | 1.39 | --- | 43.5 |

---

*Both layers are saturated at this concentration.

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0258 | 3.30 | 0.0006 | 0.08 | 43.0 |
| 0.0386 | 4.94 | 0.0009 | 0.12 | 43.0 |
| 0.0515 | 6.60 | 0.0012 | 0.15 | 43.0 |
| 0.0644 | 8.25 | 0.0015 | 0.19 | 43.0 |
| 0.0773 | 9.90 | 0.0018 | 0.23 | 43.0 |

## TABLE 3

## CROTONIC ACID
$CH_3.CH:CH.COOH$

M. W. = 86.09

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 14.48 | ---- | 57.13 | ---- | 0.253 |
| 14.55 | ---- | 57.61 | ---- | 0.253 |
| 14.55 | ---- | 57.74 | ---- | 0.251 |
| 27.89 | ---- | 116.74 | ---- | 0.239 |
| 27.80 | ---- | 116.86 | ---- | 0.238 |
| 27.61 | ---- | 116.50 | ---- | 0.237 |
| 62.68 | ---- | 294.40* | 76.61 | 0.213 |
| 62.95 | ---- | 294.92* | 76.74 | 0.213 |
| 63.10 | ---- | 296.00* | 77.02 | 0.213 |
| 110.49* | 28.75 | 588.17* | 153.05 | 0.188 |
| 110.91* | 28.86 | 588.21* | 153.06 | 0.187 |
| 111.22* | 28.94 | 588.98* | 153.26 | 0.187 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0078 | 0.67 | 0.0296 | 2.55 | 0.263 |
| 0.0542 | 4.67 | 0.2280 | 19.63 | 0.238 |
| 0.0885 | 7.62 | 0.4212 | 36.26 | 0.210 |
| 0.1194 | 10.28 | 0.6041 | 52.01 | 0.198 |
| 0.1506 | 12.97 | 0.8127 | 69.97 | 0.185 |

---

*Calculated.

## TABLE 4

## FORMIC ACID
## HCOOH

M. W. = 46.03

### EXPERIMENTAL RESULTS AT $25^{\circ}$ C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 57.00 | ---- | 19.83 | ---- | 2.87 |
| 57.06 | ---- | 20.75 | ---- | 2.74 |
| 57.00 | ---- | 20.88 | ---- | 2.73 |
| 115.14* | 29.96 | 40.67 | ---- | 2.83 |
| 115.21* | 29.98 | 40.81 | ---- | 2.82 |
| 114.33* | 29.75 | 41.87 | ---- | 2.73 |
| 296.30* | 77.10 | 106.85 | ---- | 2.77 |
| 295.91* | 77.00 | 108.14 | ---- | 2.74 |
| 296.41* | 76.13 | 108.29 | ---- | 2.74 |
| 578.42* | 150.52 | 220.46* | 57.37 | 2.62 |
| 583.06* | 151.72 | 222.08* | 57.79 | 2.62 |
| 582.52* | 151.58 | 222.31* | 57.85 | 2.62 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0515 | 2.37 | 0.0182 | 0.84 | 2.83 |
| 0.2357 | 10.85 | 0.0848 | 3.90 | 2.78 |
| 0.3800 | 17.49 | 0.1387 | 6.38 | 2.74 |
| 0.5796 | 26.68 | 0.2163 | 9.96 | 2.68 |
| 0.7470 | 34.38 | 0.2852 | 13.13 | 2.62 |

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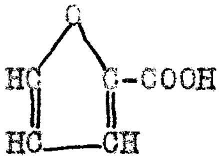
*Calculated.

## TABLE 5

## FUROIC ACID



M. W. = 112.08

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 8.70 | --- | 30.40 | --- | 0.287 |
| 8.69 | --- | 30.40 | --- | 0.286 |
| 8.71 | --- | 30.44 | --- | 0.287 |
| 16.40 | --- | 61.52 | --- | 0.267 |
| 16.39 | --- | 61.51 | --- | 0.267 |
| 15.90 | --- | 60.88 | --- | 0.262 |
| 37.49 | --- | 156.60* | 40.75 | 0.239 |
| 37.50 | --- | 158.25* | 41.18 | 0.237 |
| 36.50 | --- | 156.66* | 40.76 | 0.233 |
| 59.40 | --- | 271.55* | 70.66 | 0.219 |
| 57.28 | --- | 261.32* | 68.00 | 0.219 |
| 57.99 | --- | 260.56* | 67.80 | 0.223 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0087 | 0.98 | 0.0296 | 3.18 | 0.294 |
| 0.0324 | 3.63 | 0.1288 | 14.44 | 0.251 |
| 0.0564 | 6.32 | 0.2447 | 27.43 | 0.230 |
| 0.0782 | 8.76 | 0.3168 | 35.51 | 0.222 |
| 0.0811 | 9.09 | 0.3697 | 41.44 | 0.217 |

---

*Calculated.

## TABLE 6

## GLYCOLIC ACID
## $HOCH_2.COOH$

M. W. = 76.05

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 66.78 | ---- | 2.00 | ---- | 33.4 |
| 66.47 | ---- | 1.90 | ---- | 35.0 |
| 66.50 | ---- | 1.86 | ---- | 35.8 |
| 131.58* | 34.24 | 3.82 | ---- | 34.4 |
| 134.12* | 34.90 | 3.88 | ---- | 34.6 |
| 133.74* | 34.80 | 3.63 | ---- | 36.8 |
| 336.15* | 87.47 | 9.51 | ---- | 35.3 |
| 335.92* | 87.41 | 9.45 | ---- | 35.5 |
| 335.80* | 87.38 | 9.27 | ---- | 36.2 |
| 669.63* | 174.26 | 18.94 | ---- | 35.4 |
| 671.18* | 174.65 | 18.90 | ---- | 35.5 |
| 671.44* | 174.71 | 18.88 | ---- | 35.5 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0644 | 4.90 | 0.0018 | 0.14 | 35.5 |
| 0.2254 | 17.14 | 0.0064 | 0.48 | 35.5 |
| 0.3864 | 29.39 | 0.0109 | 0.83 | 35.5 |
| 0.6440 | 49.00 | 0.0181 | 1.38 | 35.5 |
| 0.9016 | 68.57 | 0.0254 | 1.93 | 35.5 |

---

*Calculated

## TABLE 7

## ALPHA-HYDROXYISOBUTYRIC ACID
$(CH_3)_2C(OH).COOH$

M. W. = 104.10

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 53.28 | ---- | 11.77 | ---- | 4.52 |
| 53.41 | ---- | 11.89 | ---- | 4.49 |
| 53.63 | ---- | 12.02 | ---- | 4.46 |
| 107.50 | ---- | 24.42 | ---- | 4.40 |
| 107.48 | ---- | 24.50 | ---- | 4.39 |
| 105.11 | ---- | 23.97 | ---- | 4.39 |
| 255.41* | 66.46 | 60.62 | ---- | 4.21 |
| 270.16* | 70.30 | 64.49 | ---- | 4.19 |
| 261.94* | 68.16 | 62.63 | ---- | 4.18 |
| 534.29* | 139.03 | 138.50 | ---- | 3.86 |
| 535.02* | 139.22 | 138.68 | ---- | 3.86 |
| 536.91* | 139.71 | 139.31 | ---- | 3.85 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0708 | 7.37 | 0.0158 | 1.64 | 4.46 |
| 0.2293 | 23.87 | 0.0533 | 5.55 | 4.30 |
| 0.3967 | 41.30 | 0.0958 | 9.97 | 4.14 |
| 0.5410 | 56.32 | 0.1352 | 14.07 | 4.00 |
| 0.6994 | 72.81 | 0.1821 | 18.96 | 3.84 |

---

*Calculated

## TABLE 8

## MONOBROMOACETIC ACID
$BrCH_2.COOH$

M. W. = 138.96

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 19.20 | ---- | 62.37 | ---- | 0.308 |
| 18.93 | ---- | 61.98 | ---- | 0.306 |
| 18.91 | ---- | 62.23 | ---- | 0.304 |
| 36.13 | ---- | 126.23 | ---- | 0.286 |
| 35.92 | ---- | 125.81 | ---- | 0.286 |
| 35.68 | ---- | 125.13 | ---- | 0.285 |
| 84.87 | ---- | 318.26* | 82.82 | 0.267 |
| 84.14 | ---- | 317.03* | 82.50 | 0.265 |
| 84.05 | ---- | 318.06* | 82.76 | 0.265 |
| 159.79* | 41.78 | 636.90* | 165.73 | 0.251 |
| 159.06* | 41.39 | 635.94* | 165.48 | 0.250 |
| 158.06* | 41.13 | 633.63* | 164.88 | 0.249 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0204 | 2.83 | 0.0644 | 8.95 | 0.317 |
| 0.0735 | 10.21 | 0.2705 | 37.59 | 0.272 |
| 0.1247 | 17.33 | 0.4740 | 65.87 | 0.263 |
| 0.1645 | 22.86 | 0.6414 | 89.13 | 0.256 |
| 0.2200 | 30.57 | 0.8887 | 123.49 | 0.248 |

---

*Calculated

## TABLE 9

## MONOCHLOROACETIC ACID
$ClCH_2.COOH$

M. W. = 94.50

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 23.54 | ---- | 51.65 | ---- | 0.457 |
| 24.05 | ---- | 52.63 | ---- | 0.457 |
| 23.67 | ---- | 51.85 | ---- | 0.457 |
| 46.02 | ---- | 106.80 | ---- | 0.431 |
| 45.89 | ---- | 106.95 | ---- | 0.429 |
| 45.94 | ---- | 107.30 | ---- | 0.429 |
| 107.11 | ---- | 271.51* | 70.65 | 0.395 |
| 108.00 | ---- | 273.24* | 71.10 | 0.395 |
| 106.60 | ---- | 270.82* | 70.47 | 0.394 |
| 204.45* | 53.20 | 545.51* | 141.95 | 0.375 |
| 205.33* | 53.43 | 549.55* | 143.00 | 0.373 |
| 204.56* | 53.23 | 550.39* | 143.22 | 0.372 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0247 | 2.33 | 0.0515 | 4.87 | 0.481 |
| 0.0908 | 8.58 | 0.2190 | 20.70 | 0.415 |
| 0.1471 | 13.90 | 0.3735 | 35.30 | 0.394 |
| 0.2114 | 19.98 | 0.5538 | 52.33 | 0.382 |
| 0.2767 | 26.15 | 0.7470 | 70.59 | 0.370 |

---

*Calculated.

# TABLE 10

## SUCCINIC ACID
$HOOC.CH_2.CH_2.COOH$

M. W. = 118.09

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 60.38 | ---- | 7.71 | ---- | 7.83 |
| 60.32 | ---- | 7.72 | ---- | 7.81 |
| 59.79 | ---- | 7.86 | ---- | 7.61 |
| 122.02* | 31.75 | 15.62 | ---- | 7.81 |
| 121.78* | 31.69 | 15.59 | ---- | 7.81 |
| 119.90* | 31.20 | 15.43 | ---- | 7.77 |
| 303.87* | 79.07 | 39.55 | ---- | 7.68 |
| 304.98* | 79.36 | 39.76 | ---- | 7.67 |
| 304.17* | 79.15 | 39.69 | ---- | 7.66 |
| 606.48* | 157.91 | 80.55 | ---- | 7.53 |
| 608.65* | 158.38 | 80.87 | ---- | 7.53 |
| 607.85* | 158.17 | 80.83 | ---- | 7.52 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0515 | 6.08 | 0.0066 | 0.78 | 7.83 |
| 0.2705 | 31.94 | 0.0349 | 4.12 | 7.74 |
| 0.5152 | 60.84 | 0.0674 | 7.96 | 7.64 |
| 0.7020 | 83.51 | 0.0929 | 10.97 | 7.56 |
| 0.9016 | 106.47 | 0.1207 | 14.25 | 7.47 |

---

*Calculated.

## TABLE 11

## TARTARIC ACID
HOOC.CHOH.CHOH.COOH

M. W. = 168.10

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 73.92 | ---- | 0.20 | ---- | 369 |
| 73.66 | ---- | 0.22 | ---- | 335 |
| 73.80 | ---- | 0.37 | ---- | 200 |
| 148.80* | 38.72 | 0.54 | ---- | 276 |
| 148.72* | 38.70 | 0.59 | ---- | 252 |
| 148.65* | 38.68 | 0.61 | ---- | 244 |
| 374.15* | 97.36 | 1.30 | ---- | 288 |
| 374.42* | 97.43 | 1.34 | ---- | 280 |
| 375.00* | 97.58 | 1.36 | ---- | 276 |
| 750.38* | 195.26 | 2.48 | ---- | 303 |
| 750.92* | 195.40 | 2.58 | ---- | 291 |
| 750.81* | 195.37 | 2.59 | ---- | 290 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0644 | 10.83 | 0.0002 | 0.04 | 244 |
| 0.2898 | 48.72 | 0.0011 | 0.18 | 268 |
| 0.5152 | 86.61 | 0.0018 | 0.31 | 281 |
| 0.7406 | 124.49 | 0.0026 | 0.43 | 289 |
| 0.9660 | 162.38 | 0.0032 | 0.54 | 295 |

---

*Calculated.

## TABLE 12

## TRICHLOROACETIC ACID
$Cl_3C.COOH$

M. W. = 163.40

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1238 N. | Ratio w/e |
| 16.38 | ---- | 68.00 | ---- | 0.241 |
| 16.43 | ---- | 68.35 | ---- | 0.240 |
| 17.39 | ---- | 76.11 | ---- | 0.228 |
| 25.16 | ---- | 144.34* | 37.56 | 0.174 |
| 25.35 | ---- | 145.53* | 37.87 | 0.174 |
| 25.10 | ---- | 144.15* | 37.51 | 0.174 |
| 44.75 | ---- | 368.77* | 95.96 | 0.122 |
| 44.90 | ---- | 366.93* | 95.48 | 0.122 |
| 44.70 | ---- | 367.39* | 95.60 | 0.122 |
| 71.96 | ---- | 712.91* | 185.51 | 0.101 |
| 72.17 | ---- | 713.03* | 185.54 | 0.101 |
| 72.36 | ---- | 712.65* | 185.44 | 0.102 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0209 | 3.41 | 0.0876 | 14.31 | 0.238 |
| 0.0314 | 5.13 | 0.1758 | 28.72 | 0.179 |
| 0.0437 | 7.14 | 0.3053 | 49.88 | 0.143 |
| 0.0603 | 9.87 | 0.5068 | 82.81 | 0.119 |
| 0.0934 | 15.26 | 0.9248 | 151.11 | 0.101 |

---

*Calculated.

# TABLE 13

## BENZENESULFONIC ACID

$C_6H_5SO_3H$

M. W. = 158.14

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 72.74 | ---- | 0.18 | ---- | 404 |
| 66.74 | ---- | 0.27 | ---- | 247 |
| 67.93 | ---- | 0.22 | ---- | 308 |
| 136.43* | 35.50 | 0.26 | ---- | 525 |
| 135.89* | 35.36 | 0.22 | ---- | 618 |
| 135.41* | 35.24 | 0.26 | ---- | 521 |
| 340.14* | 88.51 | 0.52 | ---- | 654 |
| 339.76* | 88.41 | 0.46 | ---- | 739 |
| 339.18* | 88.26 | 0.48 | ---- | 708 |
| 661.91* | 172.24 | 0.91 | ---- | 727 |
| 662.54* | 172.40 | 0.91 | ---- | 728 |
| 668.49* | 173.95 | 0.86 | ---- | 777 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0837 | 13.24 | 0.00030 | 0.05 | 280 |
| 0.2769 | 43.79 | 0.00043 | 0.07 | 656 |
| 0.4701 | 74.34 | 0.00067 | 0.11 | 706 |
| 0.6633 | 104.89 | 0.00091 | 0.14 | 727 |
| 0.8630 | 136.47 | 0.00116 | 0.18 | 752 |

---

*Calculated.

# TABLE 14

## DICHLOROACETIC ACID
## $ClCH_2.COOH$

M. W. = 128.93

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 12.60 | ---- | 71.83 | ---- | 0.175 |
| 11.77 | ---- | 67.26 | ---- | 0.175 |
| 12.76 | ---- | 72.11 | ---- | 0.177 |
| 20.87 | ---- | 148.58* | 38.66 | 0.140 |
| 20.60 | ---- | 149.02* | 38.78 | 0.138 |
| 20.04 | ---- | 144.17* | 37.52 | 0.139 |
| 42.00 | ---- | 377.46* | 98.22 | 0.111 |
| 42.20 | ---- | 377.59* | 98.25 | 0.112 |
| 42.23 | ---- | 377.81* | 98.31 | 0.112 |
| 74.55 | ---- | 732.62* | 190.64 | 0.102 |
| 74.60 | ---- | 731.54* | 190.32 | 0.102 |
| 74.01 | ---- | 725.59* | 188.81 | 0.102 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0139 | 1.79 | 0.0773 | 9.97 | 0.182 |
| 0.0325 | 4.19 | 0.2576 | 33.22 | 0.126 |
| 0.0545 | 7.03 | 0.4869 | 62.79 | 0.112 |
| 0.0765 | 9.86 | 0.7213 | 93.01 | 0.106 |
| 0.0979 | 12.62 | 0.9789 | 126.23 | 0.100 |

---

*Calculated

# TABLE 15

## GLYCINE
$H_2NCH_2.COOH$

M. W. = 76.05

### EXPERIMENTAL RESULTS AT 25° C.

| Titration of 25 ml. of water layer | | Titration of 25 ml. of ether layer | | |
|---|---|---|---|---|
| ml. NaOH 0.03219 N. w | ml. NaOH 0.1237 N. | ml. NaOH 0.03219 N. e | ml. NaOH 0.1237 N. | Ratio w/e |
| 71.60* | 18.63 | 0.70 | ---- | 102 |
| 59.34* | 15.44 | 0.65 | ---- | 91 |
| 70.90* | 18.45 | 0.66 | ---- | 107 |
| 135.39* | 35.23 | 0.83 | ---- | 163 |
| 135.27* | 35.20 | 0.84 | ---- | 161 |
| 138.58* | 36.06 | 0.86 | ---- | 161 |
| 318.97* | 83.00 | 1.02 | ---- | 313 |
| 311.36* | 81.02 | 1.00 | ---- | 311 |
| 307.32* | 79.97 | 0.99 | ---- | 310 |
| 559.12* | 145.49 | 1.16 | ---- | 482 |
| 554.39* | 144.26 | 1.13 | ---- | 491 |
| 558.50* | 145.33 | 1.17 | ---- | 477 |

### CALCULATED MEAN VALUES

| Acid in water layer (W) | | Acid in ether layer (E) | | |
|---|---|---|---|---|
| Normality | g./l. | Normality | g./l. | W/E |
| 0.0644 | 4.90 | 0.0007 | 0.06 | 86 |
| 0.2254 | 17.14 | 0.0012 | 0.09 | 195 |
| 0.3864 | 29.39 | 0.0013 | 0.10 | 302 |
| 0.5410 | 41.14 | 0.0014 | 0.10 | 392 |
| 0.7213 | 54.85 | 0.0015 | 0.11 | 483 |

---

*Calculated

## Comparison of Our Results with Literature Values

### CROTONIC ACID

Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 69.97 | 0.185 |
| 52.01 | 0.198 |
| 36.26 | 0.210 |
| 19.63 | 0.238 |
| 2.55 | 0.263 |

at 25°, H. W. Smith (48)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 0.961 | 0.303 |
| 0.472 | 0.307 |
| 0.337 | 0.316 |
| 0.235 | 0.312 |
| 0.146 | 0.317 |

### FORMIC ACID

Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 13.13 | 2.62 |
| 9.96 | 2.68 |
| 6.38 | 2.74 |
| 3.90 | 2.78 |
| 0.84 | 2.83 |

at 18°, Auerbach and Zeglin (2)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 13.13* | 2.34 |
| 9.96 | 2.38 |
| 6.38 | 2.44 |
| 3.90 | 2.48 |
| 0.84 | 2.53 |

at 25°, Auerbach and Zeglin (2)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 0.599 | 2.27 |
| 0.414 | 2.44 |
| o.230 | 2.63 |
| 0.092 | 2.86 |

at 25°, H. W. Smith (48)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 0.610 | 2.26 |
| 0.219 | 2.82 |
| 0.150 | 2.72 |
| 0.106 | 2.85 |
| 0.075 | 2.94 |

---

*Calculated from the linear equation $W = 22E - 8.655$

## MONOBROMOACETIC ACID

### Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 123.49 | 0.248 |
| 89.13 | 0.256 |
| 65.87 | 0.263 |
| 37.59 | 0.272 |
| 8.95 | 0.317 |

at 18°, Knaus (30)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 106.99 | 0.24 |
| 82.48 | 0.23 |
| 62.25 | 0.26 |
| 41.41 | 0.26 |
| 25.84 | 0.27 |
| 1.75 | 0.29 |

at 25°, H. W. Smith (48)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 1.327 | 0.445 |
| 0.875 | 0.485 |
| 0.483 | 0.568 |
| 0.262 | 0.694 |
| 0.186 | 0.719 |

## MONOCHLOROACETIC ACID

### Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 70.59 | 0.370 |
| 52.33 | 0.382 |
| 35.30 | 0.394 |
| 20.70 | 0.415 |
| 4.87 | 0.481 |

at 18°, Knaus (30)

| | |
|---|---|
| 89.92 | 0.34 |
| 78.96 | 0.36 |
| 62.90 | 0.36 |
| 46.85 | 0.36 |
| 31.43 | 0.38 |

at 25°, Hantzsch and Vogt (22)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 1.89 | 0.555 |
| 1.42 | 0.588 |
| 0.95 | 0.625 |
| 0.47 | 0.714 |
| 0.19 | 0.862 |

at 25°, H. W. Smith (48)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 1.44 | 0.565 |
| 1.27 | 0.581 |
| 0.80 | 0.602 |
| 0.63 | 0.690 |
| 0.35 | 0.769 |
| 0.22 | 0.826 |
| 0.15 | 0.926 |

## DICHLOROACETIC ACID

### Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 126.23 | 0.100 |
| 93.01 | 0.106 |
| 62.79 | 0.112 |
| 33.22 | 0.126 |
| 9.97 | 0.182 |

at 18°, Knaus (30)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 142.82 | 0.19 |
| 133.28 | 0.16 |
| 70.51 | 0.18 |
| 40.60 | 0.20 |
| 27.58 | 0.21 |

at 25°, H. W. Smith (48)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 3.22 | 0.373 |
| 1.93 | 0.431 |
| 1.29 | 0.503 |
| 0.65 | 0.503 |
| 0.26 | 0.962 |

## TRICHLOROACETIC ACID

### Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 151.11 | 0.101 |
| 82.81 | 0.119 |
| 49.88 | 0.143 |
| 28.72 | 0.179 |
| 14.31 | 0.238 |

at 18°, Knaus (30)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 288.24 | 0.10 |
| 172.88 | 0.10 |
| 170.07 | 0.10 |
| 110.20 | 0.10 |
| 71.89 | 0.12 |
| 43.73 | 0.14 |
| 40.52 | 0.15 |

at 25°, H. W. Smith (48)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 2.78 | 0.518 |
| 1.74 | 0.625 |
| 1.70 | 0.680 |
| 0.88 | 0.943 |
| 0.41 | 1.280 |
| 0.14 | 2.294 |

## SUCCINIC ACID

Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 14.25 | 7.47 |
| 10.97 | 7.56 |
| 7.96 | 7.64 |
| 4.12 | 7.74 |
| 0.78 | 7.83 |

at 25°, Forbes and Coolidge (13)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 11.95 | 7.40 |
| 8.69 | 7.43 |
| 5.76 | 7.58 |
| 2.93 | 7.69 |

at 25°, Chandler (7)

| | |
|---|---|
| 2.63 | 7.73 |
| 0.88 | 7.79 |
| 0.32 | 7.81 |
| 0.18 | 7.95 |
| 0.08 | 8.39 |
| 0.05 | 8.42 |
| 0.03 | 8.79 |

Forbes and Coolidge give a temperature coefficient for the succinic acid-ether-water system of 0.0255 units per degree C. for the partition ratio.

at 25°, H. W. Smith (48)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 0.32 | 5.03 |
| 0.18 | 5.13 |
| 0.10 | 5.05 |
| 0.06 | 5.38 |
| 0.03 | 5.55 |

at 15°, Bertholet and Jungfleisch (5)

| | |
|---|---|
| 7.3 | 6.6 |
| 6.7 | 6.3 |
| 6.1 | 6.0 |
| 4.1 | 5.7 |
| 2.2 | 5.4 |
| 1.3 | 5.2 |
| 0.46 | 5.2 |

(cf. trend of W/E with other data)

at 14°, Getman and Daniels (15)

| | |
|---|---|
| 7.9 | 6.0 |
| 7.4 | 5.9 |
| 7.1 | 6.1 |

## SUCCINIC ACID

The solubility in g./l. for ISOLATED pure water (Sw) and ISOLATED pure ether (Se) compared with g./l. in water layer (Cw) and ether layer (Ce) in contact with each other at equilibrium.

at 23°, Silov, Lepin, Janiak (46)

| Sw | Se | Solubility Ratio | Cw | Ce | Partition Ratio |
|---|---|---|---|---|---|
| 72 | 3.8 | 19.0 | 82 | 11.5 | 7.1 |

at 17.5°, Perschke (39)

| | | | | | |
|---|---|---|---|---|---|
| 56.52 | 3.19 | 17.72 | 59.98 | 8.48 | 7.07 |

## d-TARTARIC ACID

Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 0.54 | 295 |
| 0.43 | 289 |
| 0.31 | 281 |
| 0.18 | 268 |
| 0.04 | 244 |

at 25°, H. W. Smith (48)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 1.02 | 16.3 |
| 0.43 | 14.6 |
| 0.25 | 14.4 |
| 0.11 | 13.4 |

at 27°, Pinnow (42)

| Ether layer g./l. | Ratio W/E |
|---|---|
| 11.77 | 234 |
| 6.72 | 253 |
| 3.36 | 266 |

temp. not given, Espil (12)
N/2 to N/20 260
(The concentration is for the aqueous solution before shaking with ether.)

## d-TARTARIC ACID

Solubility in g./l. for ISOLATED pure water (Sw) and ISOLATED pure ether (Se) compared with g./l. in water layer (Cw) and ether layer (Ce) in contact with each other at equilibrium.

at 23.5°, Silov, Lepin, Janiak (46)

| Sw | Se | Solubility Ratio | Cw | Ce | Partition Ratio |
|---|---|---|---|---|---|
| 1470 | 5.7 | 256 | 1370 | 16 | 86 |

It is believed that a mistake was made in transposing to the <u>Tables Annuelles</u> from the original data. Probably the data should read:

| | | | | | |
|---|---|---|---|---|---|
| 1370 | 16 | 86 | 1470 | 5.7 | 256 |

## GLYCOLIC ACID

Our results at 25°

| Ether layer g./l. | Ratio W/E |
|---|---|
| 1.93 | 35.5 |
| 1.38 | 35.5 |
| 0.83 | 35.5 |
| 0.48 | 35.5 |
| 0.14 | 35.5 |

at 26°, Pinnow (42)

| | |
|---|---|
| ---- | 38 ± 1 |

# DISCUSSION OF RESULTS

Each aqueous solution of organic acid was adjusted to four approximate concentrations, i.e., normal (or saturated), N/2, N/5, and N/10, before shaking with ether. Three samples were run at each concentration to determine the partition ratio w/e, the ratio of the acid concentration in the water layer to the ether layer concentration. These partition ratios were plotted against the concentration in the aqueous layer for one set of graphs, and plotted against the acid concentration in the ethereal layer for another set. A smooth curve drawn thru these points was used to get the mean ratios W/E and the concentration (W) in the water layer or (E) in the ether layer. The graphs were too unwieldy to be included in this thesis.

The largest source of error, perhaps, was in pipetting samples after the systems had reached equilibrium. In both the pipette which was used to remove water layer samples and the ether layer pipette there was always the "wine drop effect." In other words the ether, being more volatile, would evaporate first and always leave droplets of water inside the pipette. No way to prevent this error could be found although it is reduced to a certain extent by using 25 ml pipettes instead of the 10 ml ones first tried. Forbes and Coolidge's gravimetric method is probably more accurate than ours, but the apparatus required is far more elaborate, and the work more time-consuming.

Error due to the presence of carbon dioxide is within the experimental error at the concentrations studied in this investigation.

The titration of samples which required less than 5 ml of 0.03219 normal base was subject to an error which could have been decreased if we had used larger volumes of acid solution, microburettes, or a more dilute base; however, the phenolphthalein end point of most of the weak organic acids would be very difficult to see if the solutions were much more dilute.

Titration of glycine with thymolphthalein was somewhat difficult when a large quantity of acid was present; however, by using the first sample as a color standard for all other titrations, any error from titrating to the wrong end point will cancel when calculating the w/e ratios.

Comparison of this work with that of others was difficult in most instances because other investigators worked either with more dilute solutions or at a different temperature. Temperature corrections were not applied because they would be likely to vary with each acid, and they are not known for any acid used in this work except succinic. For comparison, however, all available data were included regardless of concentration as long as the work was done between 14 and 27$^{\circ}$ C. There is some disagreement on partition data in the literature, and our results compare favorably in most instances with literature values IF extrapolation of our curves is permissible in order to compare the partition ratios at the same concentrations. We disagree with Smith on the partition ratios of formic, succinic, and tartaric acids. Knaus worked in approximately the same concentration range as we did. And although his work was done at 18°, IF WE ASSUME the temperature coefficient of the partition ratio to be small, our results compare favorably with those of Knaus' work except on dichloroacetic acid. The outstanding disagreement still seems to be upon succinic acid, no two workers agreeing although discrepancies are less serious. Our work is more nearly in agreement with that of Chandler than of any other worker. The classical data of Berthelot and Jungfleisch are obviously erroneous for succinic acid.

The reader will see that the following conclusions may be drawn from our data in the preceding tables:

1. The partition ratios for glycolic and barbituric acids remain practically <u>constant</u>.

2. The partition ratios of all halogen-substituted acetic acids decrease with an increase in acid concentration, this partition ratio decrease being greatest for trichloroacetic and less for each acid in the order named, dichloroacetic, monobromoacetic, and monochloroacetic.

3. Changes of the partition ratio with concentration for crotonic and furoic acids are similar to those for the halogen-substituted acetic acids.

4. The partition ratios for succinic, adipic, formic, and alpha-hydroxyisobutyric acids decrease with an increase in acid concentration. These ratios, as well as the ones for barbituric, glycolic, and tartaric acids, are directly proportional to the concentration over the concentration range studied.

5. The very large partition ratios for glycine, tartaric acid, and benzenesulfonic acid increase with an increase in acid concentration. These acids are virtually insoluble in ether.

# SUMMARY AND CONCLUSIONS

A simple method was described for determining partition coefficients of organic acids between ether and water at a constant temperature.

The partition coefficients of fifteen organic acids were determined for concentrations ranging from normal, or saturated (before mixing with ether), to one-tenth normal solutions at 25° C.

Available partition ratios from the literature are presented for the systems studied. In most instances our results compare favorably with literature values.

The partition ratios of furoic, alpha-hydroxyisobutyric, aminoacetic (glycine), adipic, barbituric, and benzenesulfonic acids have never been determined previously.

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# AUTOBIOGRAPHY

I, Wendell Glenn Markham, was born in Boulder, Colorado, October 6, 1914. In 1916 I moved to Denver, Colorado, where I attended the public schools, and was graduated from South Denver High School in June 1933.

I entered Colorado State College of Agriculture and Mechanic Arts, Fort Collins, Colorado, September 1933. I was graduated in June 1939, receiving a Bachelor of Science degree.

I was employed by the American Smelting and Refining Co., of Denver, from December 1934 until May 1935; by the Gates Rubber Company, of Denver, during the summers of 1935, 1936, and 1938; by the Dow Chemical Company, of Midland, Michigan, from September 1936 to September 1937; and by the Shattuck Chemical Company, of Denver, during the summer of 1939.

I matriculated in the Graduate School of the Oklahoma Agricultural and Mechanical College in September 1939, where I have been employed half-time as a graduate assistant in the Chemistry Department during the regular school terms of 1939 and 1940.

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