

7. The last two observations indicate that the apparent energy of activation is higher for dehydration than for dehydrogenation.

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI]

## QUANTITATIVE DETERMINATIONS WITH THE CENTRIFUGE AND FACTORS AFFECTING THEM<sup>1</sup>

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### Introduction

The first recorded use of the centrifuge in quantitative analysis was by George W. Goetz, who used it for a rapid method of determining phosphorus in iron and steel. The method consisted in oxidizing the phosphorus to phosphate, precipitating as the phosphomolybdate, packing the resulting precipitate into a graduated capillary tube by centrifugal force, and reading the volume of the packed precipitate. By comparing this volume with the volume produced under similar conditions with the use of a standard sample, the phosphorus content of the unknown sample could be estimated. Goetz communicated his findings to Dr. Wedding of Berlin, Germany, who published the first results obtained by this method.<sup>2</sup>

The method was extended to various steels,<sup>3</sup> to rapid filtration,<sup>4</sup> to separation of colloids and of crystalloids,<sup>5</sup> and to barium sulfate, calcium oxalate, magnesium ammonium phosphate and nitron nitrate.<sup>6</sup>

Heretofore all the work that has been done on the centrifuge method for quantitative determinations has not taken into account the quantitative relations between the conditions of precipitating and centrifuging and the volume of the packed precipitate. The investigations presented in this paper were therefore undertaken for the following reasons: (1) to determine the degree of accuracy one can expect from centrifuge determinations; (2) to determine what factors enter into these determinations, *i. e.*, to determine how and to what extent the conditions of centrifuging and of preparation of sample affect the volume of the centrifuged precipi-

<sup>1</sup> An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Cincinnati, 1930.

<sup>2</sup> Wedding, *Stahl und Eisen*, **7**, 118 (1887).

<sup>3</sup> M. Ukena, *ibid.*, **7**, 407 (1887); Bormann, *Z. angew. Chem.*, **2**, 638 (1887); M. A. von Reis, *Stahl und Eisen*, **9**, 1025 (1889); *ibid.*, **10**, 1059 (1890); Reinhart, *Chem.-Ztg.*, **15**, 410 (1891).

<sup>4</sup> Parker, *THIS JOURNAL*, **31**, 549 (1909).

<sup>5</sup> Friedenthal, *Ber.*, **44**, 904 (1911).

<sup>6</sup> Arrhenius, *THIS JOURNAL*, **44**, 132 (1922).

tate; (3) to discover to what type, or types, of precipitate this method is applicable; and (4) to apply, if possible, the centrifuge method to rapid technical analysis.

**Theoretical.**—The use of the centrifuge is advantageous in any process where an acceleration greater than that due to gravity is desirable. Such is desired when packing precipitates into capillary tubes for volume determinations.

The velocity with which particles of precipitate will settle is proportional to the first power of the acceleration causing that velocity (Stokes' law). The acceleration due to the centrifuge is directly proportional to the square of the r. p. m. and to the radius of rotation. It would therefore be expected that the final volume of the centrifuged precipitate would depend upon the rate and duration of centrifuging.

Also, the volume of a centrifuged precipitate will depend to a certain extent upon the physical properties of the particles composing the precipitate. It is therefore important that the conditions of precipitation be taken into account, since the physical properties of a precipitate will depend upon these conditions. The most important of these conditions are: (1) temperature of precipitation; (2) concentration of reagents; (3) rate of addition of precipitant; (4) nature of reagents; and (5) time of settling of particles before centrifuging.

**Experimental Apparatus and Reagents.**—The centrifuge machine used was the Type C, manufactured by the International Equipment Company, operating on 110 volts a. c., and capable of a r. p. m. of about 2500. The r. p. m. was varied by a multiple point rheostat in series with the machine. The machine was calibrated as follows: an accurate voltmeter was connected across the terminals of the rheostat and the machine loaded with the usual number of tubes. By means of an extension tachometer, the r. p. m. was determined for different rheostat contacts. At the same time the terminal voltages were also noted. These voltages were plotted against the r. p. m., giving a graph from which the r. p. m. could be obtained for any contact provided the voltage drop across the rheostat was known. This necessitated only that a voltmeter be kept permanently connected across the terminals of the rheostat.

The centrifuge used carried two tubes which were fitted into rubber cushions that rode in small slots on the centrifuge head. The distance from the slots to the center of rotation was 8.5 cm.

The centrifuge tubes were of the Goetz type. They were pear-shaped bulbs ending in capillaries, as shown in Fig. 1. The total capacity of a tube was approximately 125 cc., with calibrations for each 25 cc. Tubes with terminal capillaries of different bores and capacities are obtainable. In this investigation all sizes were used, depending upon the precipitate to be determined. For dense crystalline precipitates, such as barium

sulfate, a capillary 25 mm. long, 1.1 mm. inside diameter and calibrated in 20 equal divisions was employed. The total capacity of the capillary was approximately 20 cu. mm., or 0.02 cc. Each division, therefore, represented approximately 1 cu. mm. For less dense but crystalline precipitates, such as calcium oxalate, a tube with a capillary of approximately 200 cu. mm. was used. This capillary was approximately 2.6 mm. inside diameter and was divided in 20 equal calibrations extending over a range of 35 mm. Each division, therefore, represented 10 cu. mm. For gelatinous or voluminous precipitates, such as hydrous aluminum oxide and nickel dimethylglyoxime, a tube with a terminal tube 5.8 cm. long, 1.04 cm. inside diameter and calibrations for each 0.1 cc. was employed.

The bore, and therefore the capacities, of capillaries varied from tube to tube, and also within the same tube near the bottom. It was therefore necessary to calibrate each capillary. This was accomplished by filling the capillary to the desired mark with mercury, withdrawing the mercury and weighing.

Packed precipitates may be removed from the capillaries by the use of a smaller capillary tubing made by drawing out ordinary glass tubing. This small capillary is filled with water by suction, and the water then forced out into the capillary to the centrifuge vessel, thus rinsing out the precipitate. Each vessel should be cleaned between determinations with a sulfuric-chromic acid mixture in order to prevent particles of precipitate from clinging to the sides.

**Determination of Barium as Barium Sulfate.**—A solution of barium chloride was made up and standardized by the ordinary gravimetric method. One cc. of this solution was equivalent to 0.00612 g. of barium sulfate. This solution was used in all subsequent work with barium sulfate determinations.

Different amounts of the barium chloride solution were measured into beakers and diluted until 60 cc. of the solution contained approximately 18 mg. of barium. The solution was heated to 90° and the barium sulfate was precipitated by the addition of an excess of *N*/20 sulfuric acid at the rate of 30 drops per minute and with constant stirring. The source of heat was then removed from the precipitating vessel. After standing for one hour, the precipitate with the mother liquor was transferred to the centrifuge tube and centrifuged for four minutes at 2000 r. p. m. The volume of the precipitate was then read.

It is always necessary to exclude air bubbles from the capillary or else there will be uneven packing and gaps will show up in the packed pre-

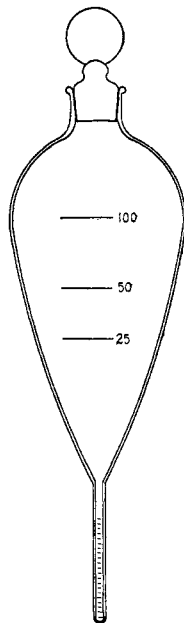


Fig. 1.

cipitate. This exclusion of air bubbles may be accomplished by filling the capillaries with water before transferring the precipitate to the flask.

It was found that barium sulfate tended to form a scum on top of the solution which was not broken by centrifuging, and thus the volume of the packed precipitate did not represent all the available barium sulfate. The addition of 1 cc. of ethyl acetate before centrifuging aids in the prevention of the scum.

Table I gives the results obtained with the use of two different tubes and various quantities of the standard barium chloride solution. The procedure as outlined above was used for all these determinations. Column 1 shows the theoretical weight of barium sulfate produced, which values were obtained from the amounts of standard barium chloride used. The second and third columns give the average volume of barium sulfate after it had been corrected for volume deviations of the tube used. Each of these values represents the average of five individual determinations whose average variations from the average are also given. For instance, the volume of 6.12 mg. of barium sulfate, as determined by this procedure, is 2.15 cu. mm. with an average variation of  $\pm 0.08$  cu. mm. from the mean. From these values, it will be seen that the average deviation is not more than 5% for smaller volumes or than 1% for larger volumes. The fourth and fifth columns give the apparent density for flasks I and II. These values were obtained by dividing the theoretical weight of barium sulfate by the observed volume.

TABLE I  
PRECIPITATION AT 90° WITH N/20 SULFURIC ACID AT THE RATE OF 30 DROPS  
PER MINUTE

BaSO <sub>4</sub> , mg.	Volume of BaSO <sub>4</sub> , cu. mm.		Apparent density	
	Tube I	Tube II	Tube I	Tube II
6.12	2.5 $\pm$ 0.08	2.4 $\pm$ 0.12	2.45	2.55
12.25	4.9 $\pm$ 0.10	4.8 $\pm$ 0.20	2.50	2.55
18.37	7.3 $\pm$ 0.10	7.3 $\pm$ 0.14	2.52	2.52
24.50	9.6 $\pm$ 0.12	9.6 $\pm$ 0.10	2.55	2.55
30.62	11.9 $\pm$ 0.10	11.7 $\pm$ 0.12	2.57	2.62
36.74	14.0 $\pm$ 0.16	13.7 $\pm$ 0.10	2.62	2.68
42.87	16.2 $\pm$ 0.10	15.7 $\pm$ 0.20	2.65	2.73
49.00	18.2 $\pm$ 0.13	17.6 $\pm$ 0.08	2.69	2.78
55.10	.. ..	19.6 $\pm$ 0.13	..	2.81

It will be noticed that the apparent density rises as the amount of barium sulfate increases. Therefore, in order to determine an unknown sample, the relation between the volume of barium sulfate, precipitated and centrifuged under definite conditions, and its weight must be known. This relationship may be obtained by plotting the volume of barium sulfate against its weight. This relationship must be obtained for each tube,

since it varies from tube to tube according as the shape, cross section, etc., of the capillaries vary. The variation, in general, is only slight for a slight variation in the capillary, but in some cases it is great enough to cause a considerable difference. For accurate work, therefore, each capillary should be calibrated under definite conditions with the use of known amounts of barium sulfate and used under those conditions for all subsequent determinations.

**Effect of Conditions of Precipitation and Centrifuging.**—Various experiments were carried out to determine the effects of conditions of precipitation and of centrifuging on the volume of precipitate produced. The conditions investigated were: (1) temperature of precipitation; (2) rate of precipitation; (3) concentration of reagents; (4) nature of precipitant; (5) effect of time of standing after precipitation; (6) rate of centrifuging; and (7) duration of centrifuging. The results of such investigations are given in Tables II to IX, respectively. These results were obtained by varying one condition at a time, the other conditions being the same as those under which the results in Table I were obtained. The results may therefore be compared with those in Table I for corresponding weights of barium sulfate in order to determine the effect of each condition when varied independently.

TABLE II  
EFFECT OF TEMPERATURE OF PRECIPITATION

Theoretical weight of barium sulfate, 30.62 mg. Precipitated at temperature indicated by addition of *N*/20 sulfuric acid at the rate of 20 drops per min. Allowed to stand for one hour. Centrifuged at 2000 r. p. m. for four minutes.

Precipitation temp., °C.	Volume of BaSO <sub>4</sub> , cu. mm.		Apparent density	
	Tube I	Tube II	Tube I	Tube II
26	20.0 ± 0.10	19.8 ± 0.18	1.53	1.55
40	17.2 ± 0.08	17.0 ± 0.13	1.78	1.80
60	14.3 ± 0.08	14.0 ± 0.18	2.14	2.19
80	13.0 ± 0.14	12.9 ± 0.13	2.36	2.37
90	11.9 ± 0.12	11.8 ± 0.13	2.57	2.60
100	11.8 ± 0.14	11.6 ± 0.10	2.60	2.64

TABLE III  
EFFECT OF RATE OF PRECIPITATION

Theoretical weight of BaSO<sub>4</sub>, 30.62 mg. Precipitated at 90° by addition of *N*/20 H<sub>2</sub>SO<sub>4</sub> at rate indicated. Allowed to stand for one hour and centrifuged for four minutes at 2000 r. p. m.

Drops H <sub>2</sub> SO <sub>4</sub> per minute	Volume of BaSO <sub>4</sub> , cu. mm.		Apparent density	
	Tube I	Tube II	Tube I	Tube II
10	11.7 ± 0.08	11.6 ± 0.13	2.62	2.64
20	11.9 ± 0.08	11.7 ± 0.13	2.57	2.62
30	11.9 ± 0.13	11.8 ± 0.18	2.57	2.60
50	12.5 ± 0.23	12.5 ± 0.18	2.45	2.45
70	13.6 ± 0.23	13.3 ± 0.15	2.25	2.30
∞	14.3 ± 0.15	14.3 ± 0.15	2.09	2.09

TABLE IV  
EFFECT OF CONCENTRATION OF REAGENTS

Theoretical weight of BaSO<sub>4</sub>, 30.62 mg. Precipitated at 90° with *N*/20 H<sub>2</sub>SO<sub>4</sub> at rate of 20 drops per minute. Allowed to stand for one hour. Centrifuged at 2000 r. p. m. for four hours.

Normality of BaCl <sub>2</sub> solution on precipitation	Volume of BaSO <sub>4</sub> , cu. mm.		Apparent density	
	Tube I	Tube II	Tube I	Tube II
0.025	13.1 ± 0.25	13.0 ± 0.15	2.34	2.36
0.0125	12.7 ± 0.18	12.5 ± 0.15	2.41	2.45
0.01	12.5 ± 0.18	12.3 ± 0.18	2.45	2.49
0.005	12.0 ± 0.18	12.0 ± 0.20	2.55	2.55
0.002	11.8 ± 0.15	11.9 ± 0.13	2.60	2.62

TABLE V  
EFFECT OF NATURE OF PRECIPITANT

Precipitated at 90° by addition of *N*/20 reagent at rate of 20 drops/min. Centrifuged after one hour at 2000 r. p. m. for four min. Theoretical weight of BaSO<sub>4</sub>, 30.62 mg.

Precipitant <i>N</i> /20	Volume of BaSO <sub>4</sub> , cu. mm.		Apparent density	
	Tube I	Tube II	Tube I	Tube II
H <sub>2</sub> SO <sub>4</sub>	11.9 ± 0.12	11.7 ± 0.13	2.57	2.62
Na <sub>2</sub> SO <sub>4</sub>	13.0 ± 0.16	12.7 ± 0.15	2.36	2.41
K <sub>2</sub> SO <sub>4</sub>	13.4 ± 0.18	13.2 ± 0.18	2.29	2.32
MgSO <sub>4</sub>	13.7 ± 0.18	13.5 ± 0.20	2.24	2.27

TABLE VI  
EFFECT OF DURATION OF STANDING BEFORE CENTRIFUGING

Precipitated at 90° with *N*/20 H<sub>2</sub>SO<sub>4</sub> at rate of 30 drops per min. Allowed to stand length of time indicated. Centrifuged at 2000 r. p. m. for four minutes.

Duration of standing, hrs.	Volume of BaSO <sub>4</sub> , cu. mm.		Apparent density	
	Tube I	Tube II	Tube I	Tube II
0	11.9 ± 0.10	11.7 ± 0.15	2.57	2.62
1	11.9 ± 0.13	11.7 ± 0.20	2.57	2.62
2	11.8 ± 0.20	11.7 ± 0.18	2.60	2.62
6	11.6 ± 0.28	11.5 ± 0.15	2.64	2.66
24	11.2 ± 0.18	11.1 ± 0.13	2.73	2.76

TABLE VII  
EFFECT OF RATE OF CENTRIFUGING

Theoretical weight of BaSO<sub>4</sub>, 30.62 mg. Precipitated at 90° by addition of *N*/20 H<sub>2</sub>SO<sub>4</sub> at 30 drops per min. Allowed to stand one hour. Centrifuged for four minutes at rate indicated.

R. p. m.	Volume of BaSO <sub>4</sub> , cu. mm.		Apparent density	
	Tube I	Tube II	Tube I	Tube II
800	16.3 ± 0.08	16.1 ± 0.14	1.84	1.90
1250	14.1 ± 0.14	13.8 ± 0.14	2.17	2.22
1600	12.3 ± 0.18	12.2 ± 0.20	2.49	2.51
2000	12.0 ± 0.12	11.9 ± 0.14	2.55	2.57
2200	.. ..	11.9 ± 0.10	..	2.57

TABLE VIII  
EFFECT OF DURATION OF CENTRIFUGING

Theoretical weight of BaSO<sub>4</sub> produced, 30.62 mg. Precipitated at 90° by *N*/20 H<sub>2</sub>SO<sub>4</sub> at 30 drops per min. Centrifuged at 2000 r. p. m. for time indicated.

Duration of centrifuging, min.	Volume of BaSO <sub>4</sub> , cu. mm.		Apparent density	
	Tube I	Tube II	Tube I	Tube II
1	14.2 ± 0.16	14.0 ± 0.12	2.16	2.19
2	12.4 ± 0.10	12.8 ± 0.12	2.47	2.39
3	12.2 ± 0.10	12.1 ± 0.12	2.51	2.53
4	11.9 ± 0.12	12.1 ± 0.10	2.57	2.53
5	11.9 ± 0.16	12.1 ± 0.13	2.57	2.53
6	12.0 ± 0.10	.. ..	2.55	..
7	11.8 ± 0.24	.. ..	2.60	..

From the above results, it will be noted that the temperature of precipitation has a great effect on the volume of the precipitate produced. This effect is probably due to a change in the size of particles formed, the smaller particles being produced at the lower temperature and occupying a greater volume when packed. To test this assumption, precipitations were made at 90 and 100° and the size of particles measured by the use of a microscope carrying a micrometer. The results are given in Table IX and show that the average ratio of the mass of particles precipitated at 90 and 100° is approximately 1 to 8.

TABLE IX  
PRECIPITATED BY ADDITION OF *N*/20 SULFURIC ACID AT RATE OF THIRTY DROPS PER MINUTE. EXAMINED AFTER ONE HOUR

Temp. of precipitation, °C.	Av. length, mm. × 10 <sup>-3</sup>	No. of readings	Av. width, mm. × 10 <sup>-3</sup>	No. of readings
90	7.0 ± 0.2	5	5.1 ± 0.5	10
90	6.3 ± 0.1	6	5.2 ± 0.5	7
90	7.5 ± 0.4	6	4.8 ± 0.5	9
100	13 ± 1	4	11 ± 1	4

All the conditions investigated affect, to some extent, the volume of the centrifuged precipitate per unit weight of barium sulfate. The magnitude of these relations can be obtained from the tables. The conclusions to be drawn are: (1) that any condition of precipitation which affects the physical properties of the precipitated particles will affect the volume of such particles when packed into capillary tubes by centrifuged force; (2) that for accurate work with the centrifuge, it is only necessary to calibrate a tube under definite conditions by the use of standard samples and to use this tube under those conditions for all subsequent determinations; (3) that the conditions may be selected at will, so long as these conditions are followed in all determinations; and (4) that for volumes above the mid-point of the capillary, results with identical samples under identical conditions may be checked with an error of less than 1%.

**Determination of Sulfur in Steel.**—The applicability of the centrifuge

as a rapid method for determining sulfur in steel was studied. Standard samples of steel were obtained from the Bureau of Standards. In determining the sulfur content of these steels, the procedure for the ordinary gravimetric method was followed up to the point where the sulfur is precipitated as barium sulfate. The precipitate and solution were then transferred to the Goetz tube, centrifuged at 2000 r. p. m. for four minutes and the volume of the precipitate noted.

Surprisingly consistent results were obtained by this method. The volume of the precipitate was approximately 20% higher than that obtained for the same amount of sulfur when the sulfate was precipitated from water solutions as given in Table I. This greater volume is evidently due to the presence of the large amount of iron salts present, some of which were probably adsorbed. It is also probable that the presence of these salts prevented the proper growth of the barium sulfate crystals. Both of these factors would tend to increase the volume of the precipitate per unit weight of barium sulfate present. Therefore, increasing the volumes given in Table I by 20%, we arrive at the approximate volumes produced by the corresponding amounts of sulfur when precipitated from the iron solutions as described above.

This method is recommended for the determination of sulfur in steel. It requires only that the tubes used be calibrated with standard samples of steel under definite conditions, and that all subsequent determinations be carried out under the conditions used for standardization. The distinct advantage is the rapidity with which a determination may be carried out. Troublesome filtrations and ignitions are thus avoided.

**Other Determinations with the Centrifuge.**—The centrifuge method was applied to the determination of (1) calcium as calcium oxalate; (2) aluminum as hydrous aluminum oxide; (3) nickel as the dimethylglyoxime; and (4)  $\text{NO}_3$  as nitron nitrate. The procedures were the same as that given for barium sulfate except for a change of reagents and the type of centrifuge tubes employed.

For calcium oxalate, it was found advantageous to use a tube similar to that employed for barium sulfate but with a larger capillary. The tube adopted was one with a capacity of 0.2 cc., extending over a range of 35 mm. and calibrated in 20 equal divisions. A standard solution of calcium nitrate was employed with ammonium oxalate as the precipitant. The accuracy obtained by this method was comparable to that obtained with barium sulfate, *i. e.*, volumes could be duplicated with an error of less than 1%.

The determination of aluminum as hydrous aluminum oxide seemed very promising and is highly recommended for rapid determinations. For this reason the method will be described somewhat in detail and the results given.



For this determination a standard solution of aluminum nitrate was employed. The desired amount of this solution was measured out and diluted to a volume such that 50 cc. of the solution contained approximately 20 mg. of aluminum. A few drops of a 1% solution of sodium alizarin sulfonate were then added, the solution heated to 90° and the aluminum precipitated by the addition with constant stirring of *N*/40 ammonium hydroxide at the rate of 30 drops per minute. After standing for one hour (without heating), the solution and precipitate were transferred to the centrifuge tube and centrifuged for five minutes at 2000 r. p. m. A type of tube similar to the Hart casein tube was used. The terminal tube was 5.8 cm. long with an inside diameter of 1.01 cm., a capacity of 5 cc. and with calibration for every 0.1 cc. The sodium alizarin sulfonate was added to produce a red precipitate which facilitated the reading of its volume. The meniscus was surprisingly even in most cases and could be read without any difficulty. The results are given in Table X.

TABLE X

PRECIPITATED AT 90° AND CENTRIFUGED AT 2000 R. P. M. FOR FIVE MINUTES

Weight of Al, mg.	Volume of precipitate, cc.	Al per cc., g.
4.5	1.01 ± 0.04	0.00446
9.0	1.81 ± 0.05	.00497
13.4	2.64 ± 0.02	.00508
18.0	3.40 ± 0.05	.00529
22.5	4.14 ± 0.02	.00544
27.0	4.83	.00559

These results show that volume can be duplicated with an error of about 1% for volume above 2 cc. Further experiments showed that just as consistent results could be obtained with precipitations at room temperature and with centrifuging following immediately. In fact, precipitations may be carried out in the centrifuge flask itself, thus avoiding transference of the precipitate. With this change in procedure, a very rapid determination of aluminum can be made.

The determination of nickel with dimethylglyoxime and  $\text{NO}_3$  with nitron also showed much promise as rapid and efficient methods. Due to the bulky nature of the precipitates, it was necessary to use the same type of tube as that employed for aluminum. The precipitation may be made at room temperature or at 90°. To obtain consistent results, it is necessary that determinations be made under definite conditions. With both methods, results may be easily duplicated with an error of not more than 2 to 4%.

### Summary

1. The relationship between the weight of barium sulfate and its volume after centrifuging under specified conditions is reproducible within 5% for small volumes and within 1% for larger volumes.

2. A comprehensive study has been made of the effects on this relationship of the following factors: (1) rate of centrifuging; (2) duration of centrifuging; (3) temperature of precipitation; (4) rate of precipitation; (5) concentration of solutions; (6) time of standing of precipitates before centrifuging; and (7) nature of the precipitant.

3. The centrifuge method has been applied to the following determinations: (1) sulfur in steel; (2) calcium as oxalate; (3) aluminum as hydrous oxide; (4) nickel as dimethylglyoxime salt; (5) nitrate as nitron salt.

4. The bore of the capillary should vary from 1.1 mm. with dense crystalline precipitates to 10 mm. with those of a gelatinous character.

CINCINNATI, OHIO

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[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

## THE SOLUBILITY OF OXALIC ACID IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID<sup>1</sup>

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The solubility of oxalic acid in aqueous solutions of hydrochloric acid has been studied by Masson<sup>2</sup> at 30° and by Herz and Neukirch<sup>3</sup> at 25°. In both of these researches a minimum solubility was found at a concentration of hydrochloric acid of about 6 *N*, this minimum solubility being about one-third that in pure water. At increasing concentrations above 6 *N* the solubility of oxalic acid increases rapidly. Additional data are here presented at three other temperatures: 0, 50 and 80°. At each of these temperatures similar results are encountered, the solubility curve rising more rapidly from the minimum point than its approach to the minimum point. The position of this minimum shifts with the temperature, being at 10% hydrochloric acid at 80°, at 18% hydrochloric acid at 50° and at 20% hydrochloric acid at 0 and at 30°.

To various solutions of hydrochloric acid in water, oxalic acid was added in excess, and the mixture was heated above the temperature of the determination. Then the bottles were placed in a thermostat regulated within 0.05° of the desired temperature. For the equilibria at 0°, a bucket of cracked ice was used as the thermostat. In all cases equilibrium was reached from above, and was reached within a few hours. Samples of the saturated solutions were drawn off, weighed and analyzed for oxalic

<sup>1</sup> Part of the material presented here was used by Ethel M. Chapin in a thesis presented to the University of North Carolina in June, 1930, in partial fulfillment of the requirements for the degree of Master of Science.

<sup>2</sup> Masson, *J. Chem. Soc.*, **101**, 103 (1912).

<sup>3</sup> Herz and Neukirch, *Z. anorg. allgem. Chem.*, **131**, 303 (1923).