Conductivity of Sulphuric Acid in the 92—98 % Range

Determinations of Conductivity in Sulphuric Acid with and without Additions of Ferrous Sulphate

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By the erection of an ethylene-sulphuric acid-alcohol plant for *Aktieselskabet De Danske Spritfabrikker (The Danish Alcohol Factories Ltd.)*, Denmark, the problem arose of determining acid strength of sulphuric acid with an accuracy of 0.2 % in the 92—98 % range. After consideration of the possibilities the conductivity was chosen as a measure for acid strength. As the values found in the literature displayed rather large variations a series of measurements were made in pure sulphuric acid having a strength of 92—98 %, and in acid saturated with ferrous sulphate, at 15, 20, and 25° C. Tables have been made for the relation between strength and conductivity at different temperatures. Above 94.5 % ferrous sulphate has a considerable influence on the conductivity. Mixtures of saturated and non-saturated acid have conductivities varying proportional with the contents of ferrous sulphate.

Determination of acid strength in strong sulphuric acid by means of measurement of specific conductivity is a method widely used, and several papers have been published on this subject. Also several instruments for measurement of conductivity with scales divided in per cent sulphuric acid are available.

The classical figures for specific electrical conductivity in sulphuric acid were measured by F. Kohlrausch ¹, who determined the conductivity in the whole range 0—100 % together with the temperature coefficient. This work was shortly afterwards supplied by W. Kohlrausch ² with measurements in 96—100 % and in oleum.

Knietsch ³ in a detailed paper mentions a multiplicity of physical constants for sulphuric acid, and among these also the resistance as determined in a special measuring vat. Dr. Bazlen, who had assisted in the work, has later on recalculated the figures found to yield figures for specific conductivity (*cf.* Abegg ⁴).

Fig. 1. Specific conductivity of sulphuric acid at 25° C.

- × *F. Kohlrausch*
- + *W. Kohlrausch*
- *R. Knietsch*
- ▽ *F. J. Symon*
- ▲ *J. E. Roughton*

Among more recent investigations may be mentioned those of Symon ⁵, who has determined the conductivity for three concentrations in the 93—99 % range and Roughton ⁶ in the 90—95 % range. The two last mentioned works deal substantially with conductivity at elevated temperatures. Finally Ust-Kachkintzev and Zhdanov ⁷ have determined the conductivity at temperatures from 20° C to 60° C in the concentration range from 9.9 to 97.5 % sulphuric acid. (Unfortunately it proved impossible to provide this last mentioned paper, the above has therefore been taken from Chemical Abstracts).

The above mentioned figures (excepting the Russian ones) have been plotted in Fig. 1 as specific conductivity at 25° C, the values given by F. and W. Kohlrausch being thereby corrected by means of the temperature coefficients given by the authors. It appears that there is some variation in the results.

Fig. 2. The Immersion type cell CDC
104 (Courtesy Radiometer, Copenhagen).

APPARATUS AND MATERIALS

Apparatus. The determinations have been performed by means of a commercially available apparatus Radiometer Conductivity Meter, Type CDM 2, supplied with an immersion type cell CDC104 from the firm Radiometer in Copenhagen. The apparatus functions with a constant alternating voltage with a frequency of 3 000 cps.

The measurements have been made with the cell shown in Fig. 2. The electrodes consist of three interspaced platinum rings, the uppermost and nethermost of which are interconnected. In the measurements two individual cells have been used.

As a control a few measurements have been made in a cell consisting of 2 platinum plates with a surface of 1 cm² with an interspacing of 1 cm. The same values for the conductivity were found with both types of cells. The measurements were made in glass containers provided with thermometer, and the contents were kept at constant temperature within 0.1° C in a water thermostat.

Materials used. In preparing the mixtures of acid analytical grade sulphuric acid was used without further purification as a single measurement with redistilled acid did not show any differences due to the distillation.

The ferrous sulphate used was anhydrous, analytical grade, which was dried one night at 100°C before use.

The titrations have been performed with anhydrous, analytical grade sodium carbonate.

EXPERIMENTAL

A series of sulphuric acid mixtures having a concentration of 92 to 98 % were prepared by weighing.

Acid saturated with ferrous sulphate was prepared by addition of excess dried ferrous sulphate to the acid and standing for 2 days with frequent agitation. That the solutions were really saturated was secured by repeated measurements with an interval of 1 day, by which identical results were found.

Determination of acid strength

The accurate acid strength was determined by neutralization with sodium carbonate, at least two determinations being made on each acid sample.

About 2 g of acid were weighed exactly in a weighing bottle with cap. Due to the hygroscopic properties of the acid these weighings were performed as quickly as possible. In preliminary experiments it had been found that no uptake of water could take place under the circumstances used.

The sodium carbonate previously dried at 300° C was weighed in a platinum crucible and was dried for further 30 minutes before final weighing.

The acid was quantitatively transferred to a high glass beaker by means of a little water, and the sodium carbonate was added in small portions taking care that no losses due to spraying occurred. The carbon dioxide was removed by boiling, and the solution was thereafter electrometrically titrated to pH 7.0. The amounts of acid and carbonate were in each case adjusted to each other, so that less than 1 ml decinormal NaOH was required for the titration. The titration error could hereby be limited to within about 0.5 %.

In order to control the titrations a constant boiling sulphuric acid was prepared according to Kunzler⁸. The acid was prepared at a barometric reading of 762 mm Hg corresponding to 98.48 % by weight of sulphuric acid (all weighings corrected for the buoyancy caused by the air).

Fig. 3. Specific conductivity of sulphuric acid and of acid saturated with ferrous sulphate at 15°, 20°, and 25° C.

Full line: Sulphuric acid.

Dotted line: Sulphuric acid with ferrous sulphate.

Four titrations were made with this acid with the following results:

	98.49 %
	98.52 %
	98.49 %
	98.50 %
Average:	98.50 %

The first three titrations were made with the amounts mentioned above, while in the fourth titration ten times as much acid and carbonate was used. From the titrations of the constant boiling acid it was concluded that the method for checking acid strength was sufficiently accurate.

Measurement of electrical conductivity

The resistance capacity of the cell was determined by measuring the conductivity in a saturated solution of sodium chloride and in 1, 0.1, 0.02, and 0.01 *N* potassium chloride, the glass container with the test solution being thereby placed in the thermostat. The values for the conductivity of these solutions were taken from Handbook of Chemistry and Physics⁹. The scale readings of the apparatus were adjusted to correspond with the known conductivities of these solutions, and the adjustment of the apparatus was identical for all these solutions.

The measurements in sulphuric acid were performed as follows: the cells were rinsed with some of the acid to be measured, whereafter the cell filled with the acid was placed in the thermostat with thermometer directly in the cell. When temperature equilibrium was attained which took about 30 minutes,

Table 1. Specific conductivity of sulphuric acid
 $1 \text{ mS} = 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$
 mS

	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°
92.0	99.2	102.7	106.1	109.6	113.0	116.5	119.4	122.4	125.3	128.3	131.2
2	99.8	103.1	106.4	109.7	113.0	116.3	119.3	122.2	125.2	128.1	131.1
4	100.3	103.5	106.7	109.8	113.0	116.2	119.1	122.1	125.0	128.0	130.9
6	100.8	103.9	106.9	110.0	113.0	116.1	119.0	122.0	124.9	127.9	130.8
8	101.2	104.1	107.1	110.0	113.0	115.9	118.9	121.8	124.8	127.7	130.7
93.0	101.5	104.3	107.2	110.0	112.9	115.7	118.7	121.6	124.6	127.5	130.5
2	101.6	104.4	107.2	109.9	112.7	115.5	118.4	121.4	124.3	127.3	130.2
4	101.4	104.2	107.0	109.7	112.5	115.3	118.2	121.1	124.0	126.9	129.8
6	101.1	103.9	106.7	109.4	112.2	115.0	117.9	120.8	123.6	126.5	129.4
8	100.7	103.5	106.3	109.0	111.8	114.6	117.5	120.4	123.2	126.1	129.0
94.0	100.2	103.0	105.8	108.6	111.4	114.2	117.1	119.9	122.8	125.6	128.5
2	99.6	102.4	105.2	108.0	110.8	113.6	116.5	119.3	122.2	125.0	127.9
4	98.8	101.6	104.4	107.2	110.0	112.8	115.7	118.5	121.4	124.2	127.1
6	98.1	100.9	103.7	106.4	109.2	112.0	114.8	117.7	120.5	123.4	126.2
8	97.2	100.0	102.8	105.6	108.4	111.2	114.0	116.8	119.6	122.4	125.2
95.0	96.2	99.0	101.8	104.6	107.4	110.2	112.9	115.7	118.4	121.2	123.9
2	95.2	98.0	100.8	103.6	106.4	109.2	111.9	114.6	117.3	120.0	122.7
4	94.2	97.0	99.8	102.6	105.4	108.2	110.8	113.5	116.1	118.8	121.4
6	93.2	96.0	98.8	101.5	104.3	107.1	109.7	112.2	114.8	117.3	119.9
8	92.1	94.9	97.6	100.4	103.1	105.9	108.4	110.9	113.4	115.9	118.4
96.0	91.0	93.7	96.5	99.2	102.0	104.7	107.1	109.5	112.0	114.4	116.8
2	89.8	92.5	95.2	97.9	100.6	103.3	105.7	108.1	110.4	112.8	115.2
4	88.5	91.2	93.8	96.5	99.1	101.8	104.1	106.5	108.8	111.2	113.5
6	87.1	89.7	92.3	94.9	97.5	100.1	102.4	104.7	107.1	109.4	111.7
8	85.6	88.1	90.6	93.0	95.5	98.0	100.3	102.7	105.0	107.4	109.7
97.0	83.9	86.3	88.6	91.0	93.3	95.7	98.0	100.4	102.7	105.1	107.4
2	81.8	84.1	86.3	88.6	90.8	93.1	95.4	97.7	100.1	102.4	104.7
4	79.5	81.6	83.7	85.9	88.0	90.1	92.4	94.8	97.1	99.5	101.8
6	77.1	79.1	81.1	83.0	85.0	87.0	89.4	91.7	94.1	96.4	98.8
8	74.2	76.1	78.0	79.9	81.8	83.7	86.1	88.5	90.9	93.3	95.7
98.0	71.2	73.0	74.8	76.6	78.4	80.2	82.7	85.2	87.6	90.1	92.6

the conductivity of the cell was measured, from which the specific conductivity was found.

In this way 13 mixtures of sulphuric acid were measured at 15, 20, and 25° C.

RESULTS

The results found have been plotted in Fig. 3, and smoothed curves drawn through the plotted points. From the curves the conductivity for each 0.2 % acid strength was read, and the conductivity was interpolated for the intermediate temperatures. The figures found in this manner are listed in Tables 1 and 2. By comparison of the values at 25° C on Fig. 1 with the curve found it will be seen that the values found correspond with those of F. Kohlrausch in the 92—98 % range.

Table 2. *Specific Conductivity of sulphuric acid saturated with ferrous sulphate.*
mS

	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°
94.4	98.8	101.6	104.4	107.2	110.0	112.8	115.7	118.5	121.4	124.2	127.1
6	98.1	100.9	103.7	106.4	109.2	112.0	114.8	117.7	120.5	123.4	126.2
8	97.4	100.2	103.0	105.8	108.6	111.4	114.2	117.1	119.9	122.8	125.6
95.0	96.8	99.6	102.4	105.2	108.0	110.8	113.6	116.4	119.3	122.1	124.9
2	96.1	98.9	101.7	104.6	107.4	110.2	113.0	115.8	118.6	121.4	124.2
4	95.3	98.1	100.9	103.8	106.6	109.4	112.2	115.0	117.8	120.6	123.4
6	94.6	97.4	100.2	103.1	105.9	108.7	111.5	114.2	117.0	119.7	122.5
8	93.8	96.6	99.4	102.2	105.0	107.8	110.5	113.2	115.9	118.6	121.3
96.0	92.8	95.6	98.4	101.2	104.0	106.8	109.4	112.0	114.6	117.2	119.8
2	91.8	94.6	97.4	100.2	103.0	105.8	108.3	110.8	113.3	115.8	118.3
4	90.7	93.5	96.3	99.0	101.8	104.6	107.0	109.4	111.9	114.3	116.7
6	89.5	92.2	95.0	97.7	100.5	103.2	105.5	107.8	110.2	112.5	114.8
8	88.2	90.9	93.5	96.2	98.8	101.5	103.7	105.9	108.2	110.4	112.6
97.0	86.7	89.2	91.7	94.3	96.8	99.3	101.5	103.7	105.8	108.0	110.2
2	84.8	87.2	89.6	92.0	94.4	96.8	99.0	101.1	103.3	105.4	107.6
4	82.7	85.0	87.2	89.5	91.7	94.0	96.2	98.4	100.5	102.7	104.9
6	80.4	82.6	84.7	86.9	89.0	91.2	93.4	95.5	97.7	99.8	102.0
8	77.9	79.9	81.9	83.9	85.9	87.9	90.1	92.3	94.6	96.8	99.0
98.0	75.3	77.2	79.0	80.9	82.7	84.6	86.9	89.2	91.4	93.7	96.0

From the curves on Fig. 3 it will be seen that the conductivity of sulphuric acid saturated with ferrous sulphate is higher than for the pure acid. An error of about 0.25 % in acid strength will be made by neglecting this effect in the 94.5—98 % range.

In order to examine this fact, the conductivity was measured in mixtures of acids of identical strength, one of which was saturated with ferrous sulphate and the other of which did not contain the salt. It was by these determinations found that the variation is practically proportional with the content of ferrous sulphate. Two experiments of this kind have been listed in Table 3.

Accuracy. The determination of the acid strength as above mentioned has been performed with an accuracy within 0.5 %.

Table 3. *Specific conductivity of sulphuric acid with varying concentrations of ferrous sulphate.*

		mS at 20° C
Pure acid, 97.43 % by weight		90.1
» » 97.43 » » » 1/3 saturated		91.0
» » 97.43 » » » 2/3 »		91.8
» » 97.43 » » » , saturated		92.5
Pure acid, 96.21 » by weight		103.2
» » 96.21 » » » , 1/2 saturated		104.2
» » 96.21 » » » , saturated		105.5

The determination of the conductivity has for each acid mixture been performed in two different cells, and three readings have been made for each. The furnisher of the apparatus states an accuracy of 2 % in the range used, but as the results are mean values of six readings the accuracy of the measurements is substantially better.

The temperature has been read before and after each reading of the conductivity with an accuracy of less than 0.05° C.

The measurements all in all are believed to be accurate within 1 %.

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