

mechanism such curve fitting may be useful in other ways. The carboxylate ion in the intermediate product is seen to cause the nitrile grouping in the opposite ring of the naphthalene nucleus to hydrolyze at only 38% of the rate which it would if the first nitrile had not been hydrolyzed. This is a quantitative measure of the ease of electromeric relay of the negative charge of the carboxylate ion across this ring system. The rate constants make possible the calculation of the time when the concentration of monosubstitution product is at a maximum, a useful fact if an isolation of the intermediate product is to be attempted.

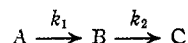
$$t = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} = 2.18 \text{ hr.}$$

The maximum concentration of this cyanonaphthoic acid is calculated from equation (2) to be 67.6% of a .

Acknowledgment.—The author wishes to express his indebtedness to Professor E. B. Wilson, Jr., who suggested to him the possibility of throwing equation (4) into the form of equation (6) on which the generality of the method depends. He also wishes to thank Professor Paul D. Bartlett for many helpful suggestions in writing the manuscript.

Summary

Given a set of rate constants for consecutive irreversible first order reactions, the changes of concentration of starting material and intermediates can be calculated relatively easily by well known methods. The converse problem of obtaining the rate constants from a set of experimental data requires a tedious calculation involving successive approximations. The initial and final slopes on a simple logarithmic plot are not in practice found to be accurate measures of the two rate constants in a two step process. A generalized graphical solution has been developed for the rate constants of two successive first order reactions



which is especially useful in cases where the rate is followed by measuring the formation or consumption of any substance which is produced or consumed in equal amount in each step. This at once gives the rate constants to better than 1% accuracy from the values of the time for two different percentage reactions. The same graphs are used for all cases, and the data for drawing them are presented in tabular form.

CAMBRIDGE, MASS.

RECEIVED JULY 13, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Conductivity of Sulfuric Acid in Methanol at 20, 30 and 35°¹

BY E. W. KANNING,² J. B. BYRNE³ AND E. G. BOBALEK²

Recent measurements⁴ of the conductance of sulfuric acid in methanol at 25° indicate that the primary dissociation of sulfuric acid is very nearly complete at high dilution, and in even the most dilute solutions secondary dissociation can be considered as negligible. Thus, sulfuric acid may be regarded essentially as a univalent electrolyte when dissolved in methanol. From such a consideration, values were reported for the limiting equivalent conductance and thermodynamic dissociation constant of sulfuric acid in methanol at 25°.

In order to confirm the conclusions indicated by the measurements at 25° and to obtain data useful in the interpretation of electromotive force studies being made in this Laboratory, measurements were made of the conductivity of sulfuric acid in methanol at 20, 30 and 35°. It was the original intention of the authors to cover

a wider range of temperature but because of experimental difficulties at higher temperatures the work was discontinued above 35°. Results are reported for the limiting equivalent conductances and thermodynamic dissociation constants of sulfuric acid in methanol at 20, 30 and 35°.

Experimental

The apparatus and technique, including the preparation of reagents, for this investigation were the same as described in the previous publication.⁴ The entire series of measurements was made using two of the three cells described therein. The constants of these cells, determined at 25°, were 0.63741 and 0.30995. The constants at other temperatures were computed from the constant at 25° by the equation,

$$C_t = C_{25}(1 - \alpha \Delta t)$$

C_t represents the cell constant at t° , Δt the difference in temperature, $t^\circ - 25^\circ$ and α the linear coefficient of expansion of Pyrex glass. The value of α ⁵ taken was 0.37×10^{-6} .

Solutions were prepared by direct weighing of solute and solvent for concentrations greater

(1) This paper is constructed from a dissertation presented by Joseph B. Byrne to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Present address: The Dow Chemical Company, Midland, Michigan.

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(4) Kanning, Bobalek and Byrne, *THIS JOURNAL*, **65**, 1111 (1943).

(5) G. W. Morey, "Properties of Glass," Reinhold Pub. Corp., New York, N. Y., 1938, p. 289.

than 0.003 molar and by weight dilution of these for the lower concentrations. Molarities were computed from molalities assuming the density of dilute solutions to be the same as the density of pure solvent. The following values were used for the density of pure methanol: 0.79134 at 20°, 0.78184 at 30° and 0.77710 at 35°.⁶

The same technique was followed in filling the cells and measuring the resistance as previously described. The drift in resistance at 20 and 30° for solutions less concentrated than 0.005 molar was not appreciable within the time necessary for the attainment of temperature equilibrium. However, at 35° the drift became very significant even for solutions as dilute as 0.003 molar.

Data and Results

The experimental data are listed in the first two columns of Tables I, II and III. Since sulfuric acid is to be considered as a univalent electrolyte, Λ , the equivalent conductance, and C , the normality, are identical, respectively, with the molar conductance and the molarity of the solutions. Figure 1 represents the Kohlrausch plot of the molar conductance against the square root of the concentration for each of the temperatures studied, including the curve previously obtained at 25°.⁵

TABLE I

CONDUCTIVITY DATA AT 20°

$C \times 10^4$	Λ	α	f_{\pm}	$CAf_{\pm}^2/F(z)$	$(F(z)/\Lambda) \times 10^3$
0.43123	174.0	1.003	0.9707	0.007150	5.683
.71059	173.6	1.004	.9626	.01163	5.698
.86114	172.6	1.000	.9590	.01356	5.703
2.0540	170.0	0.9936	.9389	.03155	5.739
4.3476	167.0	.9870	.9107	.06242	5.777
8.2295	163.1	.9766	.8785	.1089	5.836
1.0802	160.5	.9681	.8641	.1370	5.888
1.6841	157.1	.9615	.8339	.1975	5.930
2.6914	151.5	.9445	.7964	.2828	6.035
4.6062	144.2	.9244	.7448	.4144	6.166

TABLE II

CONDUCTIVITY DATA AT 30°

$C \times 10^4$	Λ	α	f_{\pm}	$CAf_{\pm}^2/F(z)$	$(F(z)/\Lambda) \times 10^3$
0.84680	194.0	1.003	0.9580	0.01463	5.072
2.0330	190.2	0.9923	.9360	.03475	5.126
3.9026	187.1	.9857	.9128	.06301	5.160
7.4777	182.4	.9740	.8820	.1114	5.222
11.086	178.5	.9633	.8589	.1549	5.280
13.396	177.1	.9615	.8462	.1813	5.290
22.886	170.2	.9427	.8056	.2753	5.396
25.905	168.6	.9390	.7939	.3022	5.417
36.673	163.0	.9237	.7627	.3874	5.507
37.261	162.8	.9233	.7611	.3918	5.509
41.688	160.8	.9177	.7482	.4210	5.542

The straight lines representing the data intersect the conductance axis at 177.2, 198.8 and 210.9, respectively, for the temperatures 20, 30 and 35°.

(6) "International Critical Tables," Vol. III, p. 27.

TABLE III
CONDUCTIVITY DATA AT 35°

$C \times 10^4$	Λ	α	f_{\pm}	$CAf_{\pm}^2/F(z)$	$(F(z)/\Lambda) \times 10^3$
0.41878	207.0	1.002	0.9697	0.008248	4.775
.43686	207.1	1.003	.9690	.008598	4.771
.82387	204.8	0.9964	.9579	.01573	4.804
.84166	204.4	.9947	.9575	.01603	4.812
1.2300	202.8	.9902	.9490	.02291	4.833
1.7691	201.0	.9853	.9392	.03212	4.857
5.1817	195.7	.9759	.8986	.08524	4.904
8.6298	191.4	.9659	.8718	.1323	4.955
10.496	189.0	.9589	.8600	.1554	4.990
10.915	189.0	.9601	.8574	.1608	4.984
11.406	187.8	.9551	.8548	.1682	5.010
12.103	187.4	.9549	.8508	.1747	5.011
22.388	178.6	.9304	.8050	.2817	5.141

The equations for these curves, calculated from the experimental data by the method of least squares, are

$$\begin{aligned} \Lambda_{20} &= 177.2 - 491.9C^{1/2} \\ \Lambda_{30} &= 198.8 - 592.9C^{1/2} \\ \Lambda_{35} &= 210.9 - 677.2C^{1/2} \end{aligned}$$

These equations represent the experimental data within the range of concentrations studied with an average deviation of approximately 0.2% at 20 and 30° and of approximately 0.3% at 35°.

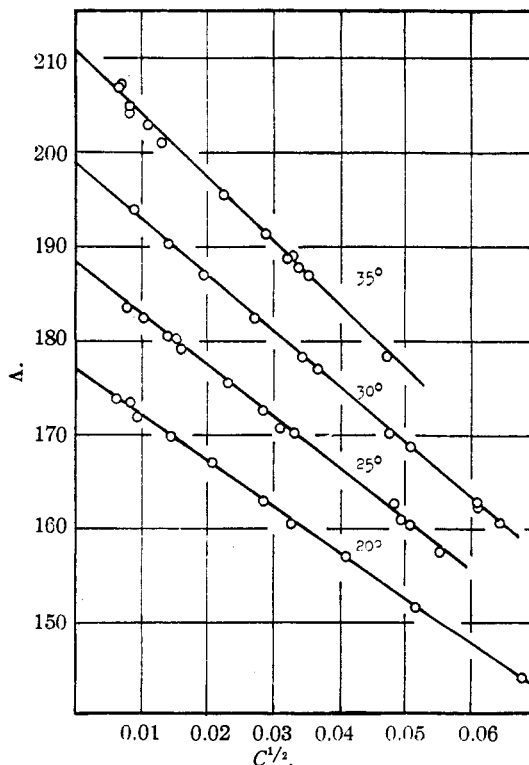


Fig. 1.—Kohlrausch plot for sulfuric acid in methanol.

In general, the data at 20, 30 and 35° appear to confirm the univalent properties of sulfuric

acid indicated by the measurements at 25°. Within the limits of experimental error inherent in the technique employed, there is no substantiating evidence that secondary dissociation effects become significant enough at any of the temperatures to obscure the univalent characteristics of the Kohlrausch plots for sulfuric acid in methanol solutions.

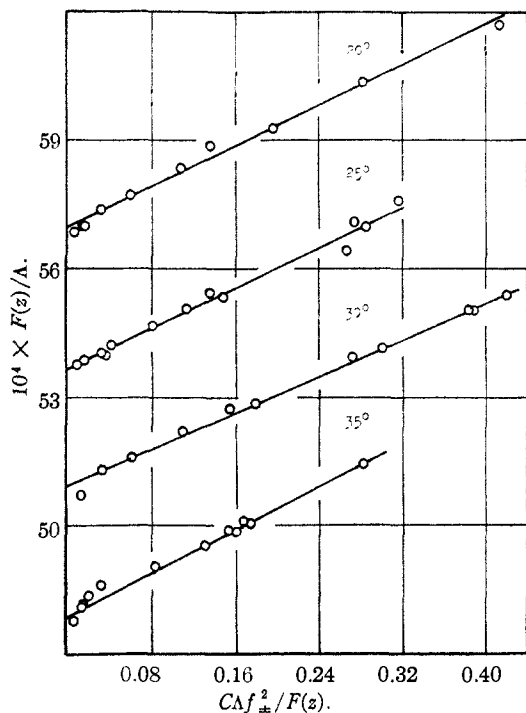


Fig. 2.—Fuoss-Kraus plot for sulfuric acid in methanol.

In order to check the consistency of the data at the various temperatures, the values of the limiting equivalent conductance and the dissociation constant can be calculated by the method of Fuoss and Kraus.^{7,8} It has been demonstrated⁴ that this type of calculation yields the same results as more laborious methods of extrapolation that can be used for determining these quantities.⁴

The Fuoss and Kraus method involves the computation of the degree of dissociation, α , and the molar activity coefficient, f_{\pm} , the values of which, at each concentration, are included in the third and fourth columns of Tables I, II and III. In the last two columns of the same tables are listed the values of $F(z)/\Lambda$ and $CAf_{\pm}^2/F(z)$. The arbitrary variable, z , is defined by the equation

$$z = (\theta\Lambda_0 + \sigma)\Lambda_0^{-3/2} (CA)^{1/2}$$

where θ and σ are the constants of the Onsager equation. The function $F(z)$ is given by the expression

$$F(z) = 1 - z(1 - z(1 - z(1 - \dots)^{-1/2})^{-1/2})^{-1/2}$$

(7) Fuoss, *THIS JOURNAL*, **57**, 488 (1935).

(8) MacInnes, "Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 384.

$F(z)$ may be evaluated from values of z by means of an interpolation table computed by Fuoss.⁷ These values of $F(z)$ are used in the computation of the degree of dissociation, α , which Fuoss has shown to be equal to the ratio of the equivalent conductance to the product of Λ_0 and $F(z)$. The molar activity coefficient, f_{\pm} , is computed from the limiting Debye-Hückel equation

$$-\log f_{\pm} = A(C\alpha)^{1/2}$$

The values of the constants associated with the Onsager and Debye-Hückel equations used in these various calculations are

$t, ^\circ\text{C.}$	D^3	η^{10}	θ	σ	A
20	32.35	0.005858	0.8815	143.4	1.961
30	30.68	.005080	.9086	167.1	2.021
35	29.8	.00478	.926	178.7	2.064

D represents the dielectric constant of methanol, η the viscosity in poise, θ and σ constants of the Onsager equation and A the constant of the Debye-Hückel limiting equation.

Figure 2 represents a plot of $F(z)/\Lambda$ against $CAf_{\pm}^2/F(z)$ for each of the temperatures studied, including also the data previously determined at 25°. The values plotted represent the variables of the linear equation

$$\frac{F(z)}{\Lambda} = \frac{1}{K\Lambda_0^2} \left(\frac{CAf_{\pm}^2}{F(z)} \right) + \frac{1}{\Lambda_0}$$

Approximate values of Λ_0 taken from the intercepts of the Kohlrausch plot were used in the preliminary calculation of the variables of the above equation. Three successive computations and subsequent extrapolations of a plot of the variables were sufficient to yield a constant value of Λ_0 . The equations for the curves shown in Figure 2, determined by the method of least squares, for the temperatures 20, 25, 30 and 35° are, respectively, as follows

$$\frac{F(z)}{\Lambda} = 0.001189 \left(\frac{CAf_{\pm}^2}{F(z)} \right) + 0.005695$$

$$\frac{F(z)}{\Lambda} = 0.001191 \left(\frac{CAf_{\pm}^2}{F(z)} \right) + 0.005364$$

$$\frac{F(z)}{\Lambda} = 0.001070 \left(\frac{CAf_{\pm}^2}{F(z)} \right) + 0.005093$$

$$\frac{F(z)}{\Lambda} = 0.001281 \left(\frac{CAf_{\pm}^2}{F(z)} \right) + 0.004787$$

From the value of the intercept and slope of each of these equations, values were calculated of the limiting equivalent conductances, Λ_0 , and thermodynamic dissociation constants, K , listed in Table IV.

The experimental error in the determination of the equivalent conductances has been estimated at 0.2 and 0.3%. The uncertainty of the value of the limiting equivalent conductance, Λ_0 , is of the same order of magnitude. For a nearly completely dissociated electrolyte this degree of experimental error causes an error as great as 25% in the computation of the dissociation con-

(9) Åkerlöf, *THIS JOURNAL*, **54**, 4125 (1932).

(10) Amis, Choppin and Padgett, *ibid.*, **54**, 1207 (1942).

TABLE IV
LIMITING EQUIVALENT CONDUCTANCES AND THERMODYNAMIC DISSOCIATION CONSTANTS OF SULFURIC ACID IN METHANOL

t , °C.	Λ_0	K
20	175.6	0.027
25	186.4	.024 ^a
30	196.4	.024
35	208.9	.018

^a Due to typographical error this value was reported as 0.029 in the first publication.⁵

stant, K . Consequently, the present techniques of conductivity measurements can be used only to determine the order of magnitude of the disso-

ciation constant. A general consistency of the values of K in Table IV is indicated. Electromotive force measurements conducted in this Laboratory may yield more precise values of the dissociation constants of sulfuric acid in methanol.

Summary

Conductance data for dilute solutions of sulfuric acid in methanol are given at 20, 30 and 35°. In general, the data permit the same conclusions that were deduced from earlier measurements at 25°⁴; namely, that sulfuric acid in methanol exhibits properties of a strong univalent electrolyte.

MIDLAND, MICHIGAN

RECEIVED JULY 18, 1944

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Silicon Methoxyisocyanates. Molar Refractions in Carbon, Silicon and Germanium Compounds Containing Isocyanate

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

The better to evaluate the properties and functions of cyanate and thiocyanate radicals as pseudohalogens, efforts have been made in this Laboratory to prepare complete series of compounds containing both halogen and pseudohalogen. The only series previously completed has been that of the silicon chloroisocyanates,¹ although compounds formulated as PCl_2NCO ,² POCl_2SCN ,² SiCl_3SCN ² and presumably GeCl_3Br ³ have recently been obtained. The chief difficulty encountered has been the redistribution reaction,³ which has often proved so rapid that fractional distillations produced mixtures only. Of course the higher boiling intermediates have proved the hardest to isolate. The gaps in the series already blocked out have hampered our efforts to follow trends in physical and chemical properties due to successive substitutions.

The stability of the silicon-oxygen bond suggested an additional approach to the problem. Through the new compounds $\text{Si}(\text{OCH}_3)_3\text{NCO}$, $\text{Si}(\text{OCH}_3)_2(\text{NCO})_2$ and $\text{Si}(\text{OCH}_3)(\text{NCO})_3$ a second complete series has now become available. The data already in hand have made possible certain calculations of refraction equivalents as described below. In addition, we have investigated the reactions of silver isocyanate with silicochloroform and hexachlorodisilane, and identified the products.

Preparation of Silicon Methoxyisocyanates.—In view of the success of the hot tube method for obtaining the intermediate members of the silicon chloroisocyanate series,¹ we first passed the mixed vapors of methyl silicate and silicon isocyanate through a tube at 450° (approximately). At a higher temperature methyl silicate becomes unstable. The reaction, if any, at this temperature proved too slow

for detection, due perhaps to the stability of the silicon-oxygen bond mentioned above. Therefore a method analogous to one devised by Friedel and Crafts⁴ was next employed. A small-scale reaction between silicon isocyanate and methyl alcohol proved vigorous, and gave no immediate precipitate suggestive of silicic acid. Thereupon 40 g. of silicon isocyanate containing 0.82 mole of (NCO) was placed in a 100-cc. flask, and 26 ml. of absolute methyl alcohol (0.65 mole) was added very slowly, with agitation. A solid which gradually settled out was shown to be a polymer of cyanic acid-cyanuric acid or cyamelide. In a second experiment 1.31 mole of isocyanate and 0.49 of the alcohol were combined. After an hour on the steam-bath the volatile products were repeatedly fractionated in a 50-cm. Podbielniak-type column of 6 mm. o. d. with a close-fitting copper spiral. If spaced evenly between the boiling point of methyl silicate, 121°, and that of silicon isocyanate, 186°, the boiling points of the mixed compounds would be 138, 154 and 170°, respectively. We collected them in the (uncorrected) temperature intervals 135.9–136.2°, 150.3–150.6°, and 166.5 to 166.8°. The corrected boiling points are found in Table III.

Analyses.—A preliminary attempt was made to check the composition of the above fractions by direct determination of cyanate. Weighed samples, in 50-ml. conical flasks, were hydrolyzed in dilute sodium hydroxide, and carefully neutralized. Excess of standard silver nitrate was added, and the precipitated silver cyanate filtered off. As the solubility of silver cyanate in pure water is 0.072 g./l. at 19° the washing of the precipitate and paper introduced a serious uncertainty. The results, though mediocre, supported the postulated formulas. For $\text{Si}(\text{OCH}_3)_3\text{NCO}$, (NCO) found was 27.1% and 27.7%, calculated 25.8%; for $\text{Si}(\text{OCH}_3)_2(\text{NCO})_2$, found 48.2% and 47.0%, calculated 48.3%; for $\text{Si}(\text{OCH}_3)(\text{NCO})_3$ found 67.1% and 65.3%, calculated 68.1%.

Preliminary microanalyses, by combustion, for carbon, hydrogen and nitrogen in the Converse Laboratory yielded results fairly consistent with theory, in spite of the difficulty of burning the mixed compounds completely in oxygen. The final analyses, performed in a microchemical laboratory elsewhere, appear in Table II. Unfortunately, methoxyl determinations could not be undertaken.

The above report stressed the difficulties encountered

(1) Anderson, *THIS JOURNAL*, **66**, 934 (1944).

(2) Anderson, unpublished data.

(3) Forbes and Anderson, *THIS JOURNAL*, **66**, 931 (1944).

(4) Friedel and Crafts, *Ann. chim.*, [4] **9**, 35 (1866).

(5) Birckenbach and Huttner, *Z. anorg. Chem.*, **190**, 26 (1930).