quantities are expressed in cubic centimeters at a pressure of one millimeter of mercury.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF WYOMING]

THE DECOMPOSITION OF FORMIC ACID BY SULFURIC ACID. II[1]

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Introduction

In a previous paper by one of the authors[2] it was found that the velocity of decomposition of formic acid in sulfuric acid showed some irregularities when the concentration of sulfuric acid was 91.8%. Knietsch[3] found that specific conductance, melting point and viscosity do not increase continuously on progressive dilution of sulfuric acid. Abnormal values for these properties occur in the range of concentration 92–93.5%.

The present investigation was undertaken to determine the velocity constants for the rate of decomposition of formic acid for various concentrations of sulfuric acid from 85–97% at temperatures of 15, 25, 35 and 45° and to observe whether the irregularity referred to above existed at other concentrations.

Experimental Part

Preparation and Purification of Materials.—The formic acid and the sulfuric acid were prepared by the same methods as those previously used. The formic acid distilled at 25.0–25.5° at 37–38 mm.; $d^{20} = 1.220$; refractive index (Abbé) $n_D^{20} = 1.3708$ and melted at 8°.

Apparatus.—The apparatus used was modified to a slight extent only. The measuring burets were of 100-cc. capacity so that it would not be necessary to use a smaller amount of formic acid. The volume of carbon monoxide evolved from 0.07 cc. of formic acid was about 63 cc. at 45° and the prevailing average pressure 585 mm.

The Effect of Water on the Decomposition of Formic Acid by Sulfuric Acid.—The effect of water on the velocity of the reaction was determined by proceeding in the same manner as in the previous investigation, using like amounts of reagents. The results are summarized in Table I. In

[1] The work included in this paper is from the thesis presented by Henry T. Ward in partial fulfilment of the requirements for the degree of Master of Science at the University of Wyoming.

[2] Schierz, THIS JOURNAL, **45**, 447 (1923).

[3] Knietsch, *Ber.*, **34**, 4089 (1901).

order to conserve space, the values of 0.4343 K, the velocity constants calculated from the equation for unimolecular reaction, were each multiplied by 10^3 and entered in the table as K_s. The table contains some values which have been obtained by graphical extrapolation. According to Rice[4] the graphical representation of the logarithm of velocity constants plotted against reciprocal of absolute temperature, for each concentration of sulfuric acid, should be a straight line or nearly so. In cases where the reaction was too slow to measure, extrapolated values, indicated by an asterisk, are inserted in the table; where the velocity was very great (more than half of the total volume of carbon monoxide, 51 cc., being evolved in the first fifteen seconds), both determined and extrapolated values are given.

Table I

Decomposition of Formic Acid by Sulfuric Acid with Various Concentrations of Sulfuric Acid at Several Temperatures

H_2SO_4, %	K_s 15°	25°	35°	45°
96.69	28.5	91.5	312 (300)*	810 (975)*
94.40	10.4	33.5	106	280 (330)*
92.78	5.1	16.6	53.5	159
91.49	2.7	8.9	28.7	86.2
89.53	1.2*	4.0	13.1	41.4
85.52	0.24*	0.78*	2.5	7.8

The values from Table I are shown graphically in Fig. 1. It will be seen that for like concentrations of sulfuric acid the effect of small amounts of water becomes more marked as the temperature at which decomposition occurs increases. For the addition of 1% of water to the sulfuric acid (diluting from 93 to 92%) in the decomposition of formic acid, the constant changes from 19 to 12 (obtained from interpolation on Fig. 1) at 25° and from 175 to 113 at 45°.

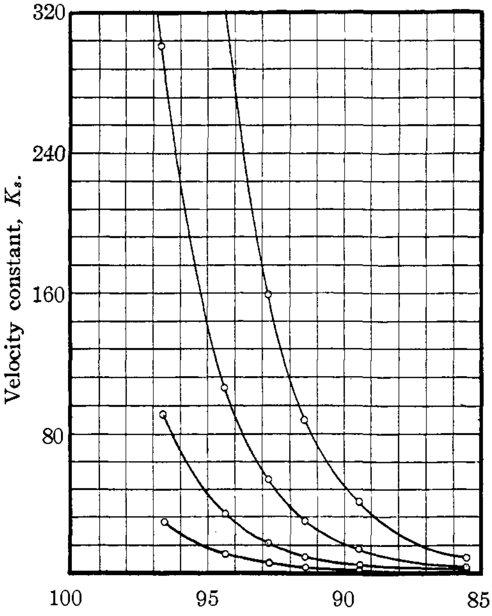

Fig. 1.

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[4] Rice in Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1924, p. 885.

The Effect of Temperature on the Reaction.—The temperature coefficients for 10° intervals have been calculated from the velocity constants at the various temperatures for all of the concentrations of sulfuric acid used. The effect of temperature is summarized in Table II. It will be seen that in general these values decrease as the velocity of reaction increases and that the irregularity found by Schierz[2] has not been found at these concentrations.

The values for E (critical increment) calculated from the integrated form of the simple Arrhenius[5] equation for various temperature intervals are shown in Table II.

TABLE II

TEMPERATURE COEFFICIENTS AND VALUES OF E FOR THE DECOMPOSITION OF FORMIC ACID BY VARIOUS CONCENTRATIONS OF SULFURIC ACID

H_2SO_4, %	K_{25}/K_{15}	E (calcd.)	K_{35}/K_{25}	E (calcd.)	K_{45}/K_{35}	E (calcd.)
96.69	3.22	19,920	3.27	21,600	3.25	22,900
94.40	3.22	19,920	3.17	21,420	3.12	22,200
92.78	3.25	20,080	3.22	21,350	2.98	21,300
91.49	3.29	20,310	3.23	21,400	3.10	22,080
89.53	3.33	20,500	3.28	21,650	3.16	22,410
85.52	3.3	20,900	3.2	21,210	3.12	22,200

An examination of these values shows that they are all very nearly the same for any one temperature interval and that there is a general tendency to increase but slightly with increase in temperature. This constancy is in agreement with the work of Essex and Gelormini[6] and Daniels and Johnston,[7] who conclude that for isolated reactions the critical increment is independent of the temperature.

Conclusions

The results of this investigation, in which the reaction was allowed to proceed at higher temperatures for the more concentrated sulfuric acid, indicate that under these conditions also the role of sulfuric acid is primarily that of a dehydrating agent.

The curves (Fig. 1) show that the change in velocity constant as a function of the percentage composition of sulfuric acid is continuous.

Lichty[8] found the same relation to obtain in his study of the decomposition of oxalic acid by sulfuric acid.

The value of the velocity constant obtained by Schierz for concentration 91.8% (at which the irregularity was noticed) falls on the curve for 25°.

Summary

1. The velocity of decomposition of formic acid by sulfuric acid has

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[5] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[6] Essex and Gelormini, THIS JOURNAL, **48**, 882 (1926).

[7] Daniels and Johnston, *ibid.*, **43**, 53 (1921).

[8] Lichty, *J. Phys. Chem.*, **11**, 225 (1914).

been measured using the following concentrations of sulfuric acid: 85.52, 89.53, 91.49, 92.78, 94.40 and 96.69% at 15, 25, 35 and 45°.

2. The temperature coefficients have been given. They decrease in magnitude as the velocity constant increases.

3. The values for E (critical increment) have been calculated and found to be nearly equal for all concentrations at the temperature intervals 25°/15°, 35°/25° and 45°/35°.

4. For equal concentrations of sulfuric acid, the effect of small quantities of water becomes more marked with increase in temperature.

5. No irregularities in velocity constants or temperature coefficients were observed in the temperatures and concentrations studied.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE USE OF POTASSIUM IODATE IN BACK TITRATION FOR THE DETERMINATION OF THE HYPOCHLORITE CONTENT OF SOLUTIONS

BY JOHN R. LEWIS AND R. F. KLOCKOW

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Volumetric iodate methods for the analysis of a variety of substances have been collected and published by Jamieson.[1] While searching the literature for methods of analyzing sodium hypochlorite solutions, it occurred to the authors that potassium iodate may also be used here. When a standard arsenite, thiosulfate or iodide solution was used in excess to reduce the hypochlorite, it was found that the excess could be determined by titration with potassium iodate according to the method described by Jamieson for the determination of hydrogen peroxide.

Method I (Sodium Arsenite Method).—To a known excess of standard arsenite is added a measured volume of hypochlorite. The unoxidized excess is then titrated with 0.1 N iodate in the presence of at least 12% hydrochloric acid. The results are accurate in the presence of small amounts of nitrate or chlorate.

Method II (Sodium Thiosulfate Method).—This method is based upon the fact that sodium hypochlorite oxidizes sodium thiosulfate to sulfate in an acid solution.[2] The titration mixture should be cooled in an ice-bath before adding the iodate. It makes no difference whether the hypochlorite is added to the acid or neutral solution of the thiosulfate. Results are not concordant in the presence of chlorate.

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[1] George S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., Inc., New York, **1926**.

[2] Dienert and Wandenbulcke, *Ann. chim. anal. chim. appl.*, **2**, 106 (1920).