[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE CATALYSIS OF ETHYL FORMATE BY MONOCHLORO-ACETIC ACID AND ETHYL ACETATE BY DICHLORO-ACETIC ACID IN NEUTRAL SALT SOLUTIONS

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With the exception of a few results obtained by Taylor[1] on the catalysis of ethyl acetate by dichloro-acetic acid and trichloro-acetic acid in potassium chloride solutions, few experimental data are available on ester hydrolysis by moderately strong acids in neutral salt solutions. To fill in this gap in the experimental material and to suggest a method of calculating the results are the objects of the present study.

Experimental Results

The usual method of titrating portions of the reaction mixtures with sodium hydroxide and barium hydroxide or with sodium hydroxide alone was employed. The unimolecular equation for the velocity was used. In the case of ethyl acetate hydrolysis, the variation of the velocity constants from the mean value during a given experiment was never greater than ±2% and was usually less than this amount. The calculation

TABLE I

MONOMOLECULAR VELOCITY CONSTANTS AT 25°

Part 1

Values of $k \times 10^4$

$CH_3COOC_2H_5$ (0.1 N)					0.202 M $CHCl_2COOH$		
Molal salt concn.	$BaCl_2$	NaCl	KCl	NaBr	KBr	$NaNO_3$	KNO_3
0.00	2.35	2.35	2.35	2.35	2.35	2.35	2.35
.25	2.98	2.74	2.66	2.66	..	2.65	2.37
.49	3.30	..	..	..	..	..	..
.50	..	2.88	2.70	2.80	2.56	2.71	2.36
.74	3.59	..	..	..	..	..	..
.75	..	..	..	..	..	2.74	2.40
.98	3.75	..	..	..	..	..	..
1.00	..	3.05	2.85	2.87	2.70	2.77	2.38
1.23	3.89	..	..	..	..	..	..
1.48	4.03	..	..	..	..	..	..
1.50	..	..	2.86	2.96	2.73	..	2.57
1.77	4.13	3.33	..	..	..	..	..
2.00	..	..	2.87	3.01	2.68	2.71	2.43
2.50	..	..	3.00	..	..	..	..
3.00	..	3.71	3.00	2.97	2.61	2.60	2.13
3.50	..	3.80	2.99	..	..	..	..
4.00	..	3.87	..	2.87	2.55	2.55	..
5.00	..	3.75	..	2.70	..	2.51	..

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[1] Taylor, *Medd. Vetenskapsakad. Nobelinst.*, Vol. 2, No. 37 (1913).

Table I (*Concluded*)

Part 2

Molal salt concn.	$MgSO_4$	Na_2SO_4	K_2SO_4
0.000	2.35	2.35	2.35
.125	1.56	1.66	1.59
.250	1.49	1.37	1.28
.375	..	..	1.07
.500	1.39	1.16	1.02
.750	1.41	1.06	..
.875	..	1.07	..
1.000	1.44	1.04	..
1.250	1.52	1.01	..
1.500	..	1.06	..
2.000	2.00	..	..

Part 3

$HCOOC_2H_5$ (0.1 *N*)

Molal salt concn.	NaCl	KCl
0.00	1.95	1.95
.50	2.52	2.11
1.00	2.62	2.43
1.50	2.77	2.44
2.00	2.82	2.49
2.50	2.89	2.43
3.50	..	2.25
4.00	2.90	..
5.00	2.84	..

0.287 *M* $CH_2ClCOOH$

Molal salt concn.	Na_2SO_4	K_2SO_4
0.00	1.95	1.95
.125	..	1.55
.25	1.67	1.44
.375	..	1.35
.50	1.53	1.28
.75	1.52	..
1.00	1.61	..
1.25	1.70	..
1.50	1.50	..

of the results for the hydrolysis of ethyl formate showed some indication of autocatalysis. However, the results up to half decomposition of the ester showed little variation and their mean value was taken. In Table I the experimental results are given. All measurements were carried out at 25 ± 0.02°.

In Fig. 1 the velocity constants of the hydrolysis of ethyl acetate in the dichloro-acetic acid-salt solutions are plotted against the concentration of the added salt. Upon the first addition of the halides or sodium nitrate a very rapid increase in velocity constant occurs and as the salt concentration increases the velocity constant reaches a maximum and then decreases. No increase is observed in the case of potassium nitrate. With barium chloride the saturated solution is reached before a maximum occurs. Upon the addition of sulfates a rapid decrease in velocity constant is to be observed. As will be shown this is due to the removal of hydrogen ions to form HSO_4^-. In general this behavior parallels the neutral salt action on the velocity of hydrolysis of ethyl formate either in pure aqueous salt solutions or in salt solutions containing monochloro-acetic acid.[2,3]

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[2] Manning, *J. Chem. Soc.*, **119**, 2079 (1921).

[3] Harned, This Journal, **49**, 1 (1927).

Calculation of Results

(1) Halide Solutions

We may express the velocity of hydrolysis by the equation

$$v = kmm_{e\mathrm{H}}\,F \tag{1}$$

where m_e and m_{H} are the concentrations of the ester and hydrogen ion, respectively, and F is a kinetic factor which differs from unity because

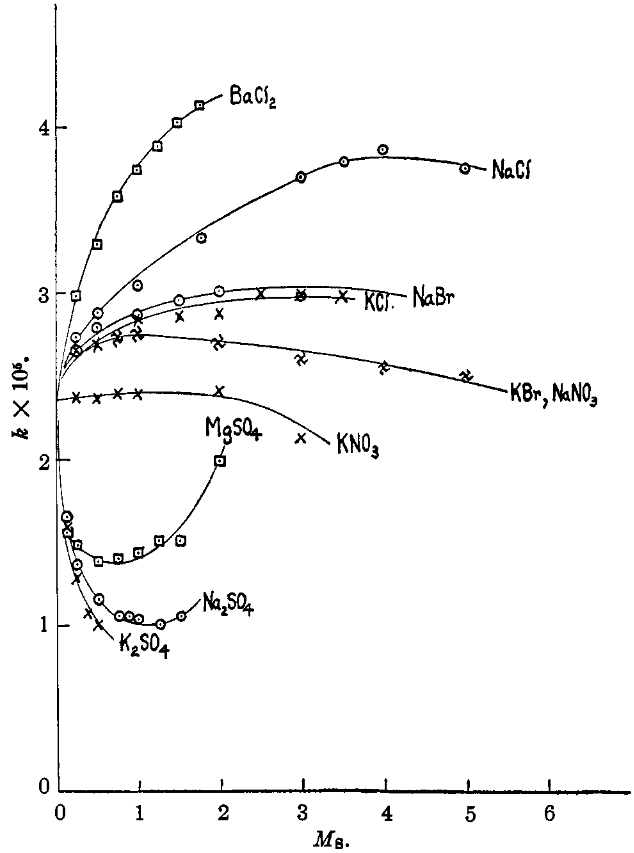

Fig. 1.—Velocity constants of hydrolysis of ethyl acetate by dichloro-acetic acid in salt solutions.

of the electrical field effects caused by the presence of the ions. If F equals $\gamma_e\gamma_{\mathrm{H}}$, the activity rate theory results, and if F equals $\gamma_e\gamma_{\mathrm{H}}/\gamma_i$, we obtain the equation of Brönsted.[4] γ_e, γ_{H} and γ_i are the activity coefficients of the ester, the hydrogen ion and the collision complex, respectively. In concentrated solutions and when dealing with reactions between ions and electrically neutral substances, recent experimental

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[4] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

work seems to indicate that F is a more complicated factor than that given by either of the above theories. In any case thermodynamics demands that F be expressed, in part at least, in terms of the activity coefficients of the species present. In a recent investigation[3] of the autocatalysis of ethyl formate in aqueous neutral salt solutions, approximate results were obtained by making F unity. This, in these cases of ester hydrolysis, is not an exact procedure. Consequently, we have resorted to a method of computation by which the salt effect, F, is eliminated from the calculation.

Two assumptions are necessary:

(1) That hydrochloric acid at 0.1 M is completely dissociated.

(2) That the activity coefficients of the ester and ionic species are the same in the hydrochloric acid-salt solution containing the ester as in the dichloro-acetic acid-salt solution containing the ester at the same ionic strength.

Upon these assumptions, we find that

$$\frac{k_{\mathrm{HCl}}}{k_{\mathrm{di}}} = \frac{0.1}{m_{\mathrm{H}}} \tag{2}$$

where k_{HCl} is the velocity constant in the hydrochloric solutions and k_{di} is the velocity constant in the presence of the dichloro-acetic acid solutions.[5] In this way, the concentration of the hydrogen ion, m_{H}, in the dichloro-acetic acid solutions may be evaluated. The results of this calculation for potassium and sodium chloride and sodium bromide are given in Table II. Col. 1 contains the salt concentrations, m_{S}, Col. 2 the velocity constants of hydrolysis of ethyl acetate in 0.1 N hydrochloric acid solutions containing potassium chloride and sodium chloride taken from the results of Harned,[6] and sodium bromide from the results of Bowe.[7] Col. 3 contains the velocity constants read off from the curves of the data in Table I. Col. 4 contains the values of the hydrogen-ion concentration computed by Equation 2. The dissociation constant of dichloro-acetic acid is given by

$$K = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Ac}}}{\gamma_{\mathrm{HAc}}}\,\frac{m_{\mathrm{H}}^2}{m_{\mathrm{HAc}}} = \gamma_{\mathrm{A}}\,\frac{m_{\mathrm{H}}^2}{m - m_{\mathrm{H}}} \tag{3}$$

By substituting 0.0816 for m_{H} and 0.202 for m, we obtain 5.53×10^{-2} for $\frac{m_{\mathrm{H}}^2}{m - m_{\mathrm{H}}}$, which agrees with the value 5.1×10^{-2} obtained from conductance data.[8] To evaluate K, we take γ_{A} to equal $\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}}$ or 0.60 at an ionic

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[5] This method of computing kinetic results has been employed by Brönsted and King, This Journal, **47**, 2523 (1925).

[6] Harned, *ibid.*, **40**, 1461 (1918).

[7] Bowe, *J. Phys. Chem.*, **31**, 290 (1927).

[8] Drucker, *Z. physik. Chem.*, **49**, 563 (1904).

strength of 0.0816.[9] Hence K equals 3.32×10^{-2}. From this value of K, and from the values of m_H in Col. 4, γ_A for the salt solutions of different strengths was calculated by Equation 3. The results are given in Col. 5.

TABLE II

ACTIVITY COEFFICIENTS OF DICHLORO-ACETIC ACID IN SOME HALIDE SOLUTIONS

(1) Potassium Chloride

0.202 $M CHCl_2COOH$ $K = 3.32 \times 10^{-2}$

(1) m_s	(2) $k_{HCl} \times 10^5$	(3) $k_{di} \times 10^5$	(4) m_H	(5) γ_A
0.0	28.8	23.5	0.0816	0.600
.2	29.8	26.2	.0879	.490
.5	31.4	27.5	.0876	.495
1	34.1	28.6	.0839	.557
2	39.4	29.6	.0751	.747
3	44.6	29.2	.0655	1.056
		(2) Sodium Chloride		
0.2	30.1	27.0	0.0897	0.463
.5	32.1	28.8	.0897	.463
1	35.7	30.7	.0860	.521
2	43.1	34.3	.0796	.647
3	52.3	37.1	.0709	.868
		(3) Sodium Bromide		
0.2	29.7	26.2	0.0882	0.486
.5	30.9	27.7	.0896	.465
1	33.1	28.9	.0873	.500
2	37.4	30.0	.0802	.629
3	41.7	29.7	.0712	.857

The results for the monochloro-acetic acid hydrolysis of ethyl formate had to be calculated by a somewhat different method. Since no data are available on the hydrolysis of ethyl formate in hydrochloric acid-salt solutions, a direct determination of m_H by Equation 2 cannot be made. If we assume that the relative salt effect in this case is the same as in the case of ethyl acetate, then m_H may be evaluated by

$$\frac{k_{HCl}}{k_{mono}} = \frac{0.1\,R}{m_H} \tag{4}$$

where R is a constant factor which relates the acetate with the formate hydrolysis. This was determined by calculating m_H in the 0.287 M monochloro-acetic acid solution. K was taken to be 4.2×10^{-3}, whence m_H equals 0.04 if γ_A is assigned the value 0.65 which is the ionic activity coefficient product of water at an ionic strength of 0.04.[10] Substituting

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[9] Harned, THIS JOURNAL, **47**, 930 (1925).

[10] The value used for the dissociation constant is higher than the value, 1.6×10^{-3}, obtained by Ostwald, *Z. physik. Chem.*, **3**, 170 (1889). Our justification for using 4.2×10^{-3} is the agreement obtained between γ_A for monochloro- and dichloro-acetic acids in a given salt solution at the lower concentrations.

the values of k_{HCl} and k_{di} in Equation (4), we obtain 0.591 for R. The values for γ_A in the salt solutions were then calculated by Equation (4). These are compiled in Table III.

TABLE III

THE ACTIVITY COEFFICIENTS OF MONOCHLORO-ACETIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

$CH_2ClCOOH$(0.287 M) $K = 4.2 \times 10^{-3}$ $R = 0.59$

Molal salt concn.	$k \times 10^5$	m_H	γ_A
		(1) KCl	
0.0	19.5	0.0400	0.65
.2	22.6	.0449	.50
.5	23.7	.0445	.51
1	24.2	.0420	.57
2	24.6	.0368	.76
3	24.2	.0321	1.05
		(2) NaCl	
0.2	23.3	0.0459	0.49
.5	25.1	.0463	.49
1	26.6	.0441	.52
2	28.4	.0390	.69
3	29.0	.0333	.96

The results of this calculation are given in Fig. 2. In the lower part, γ_A is plotted against $\mu^{1/2}$ where μ is the ionic strength. The solid lines and points are the values of the dichloro-acetic acid in the designated salt solutions, and the dotted lines represent the activity coefficients product of monochloro-acetic acid in potassium and sodium chloride solutions. In the upper part of the figure are the values of the activity coefficient product of water as determined by Harned[9] and Harned and James.[11] The inked-in circles in the lower part are the values of $\gamma_H\gamma_{OH}/a_{H_2O}$ in sodium chloride solutions. These are seen to agree very well with the values of γ_A of mono- and dichloro-acetic acid in the same salt solutions. It is also interesting to note that the order of the curves for $\gamma_H\gamma_{OH}/a_{H_2O}$ and γ_A in the three salt solutions are the same and their distribution similar. A better agreement is hardly to be expected and is a considerable improvement over the earlier calculations of Harned[8] on the neutral salt catalysis of ethyl formate in aqueous solutions.

(2) Sulfate Solutions

We attribute the decrease in velocity caused by the addition of sulfates to the formation of HSO_4^-. Since in these solutions the predominating influence is that of the removal of hydrogen ions, we may obtain an approximate solution by neglecting the salt effect, or by assuming that F in

[11] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

Equation (1) equals unity. Upon this assumption, the velocity constants will be proportional to the concentration of the hydrogen ion.

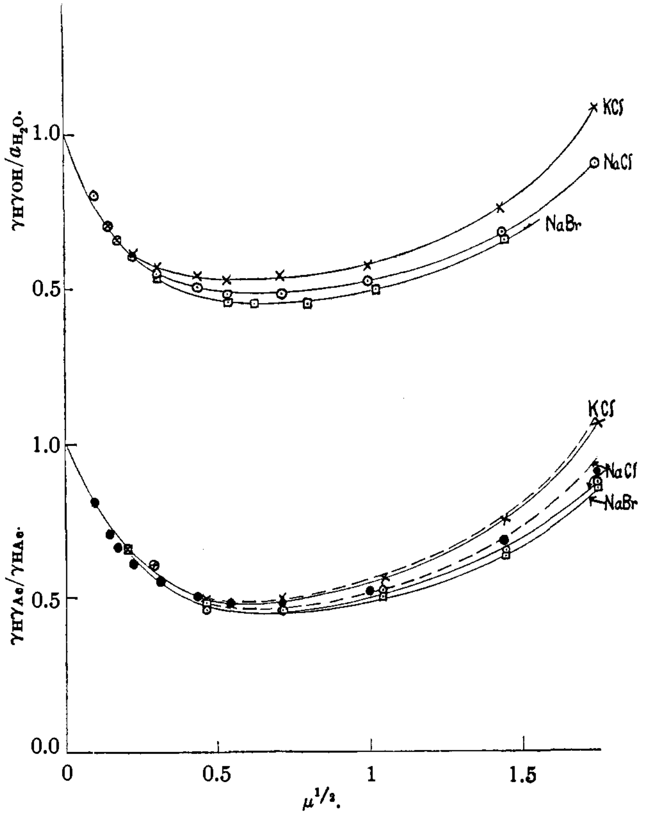

Fig. 2.—The activity coefficient products of mono- and dichloro-acetic acids in some halide solutions.

Let

$$\gamma_S = \frac{\gamma_H\gamma_{SO_4}}{\gamma_{HSO_4}};\quad \gamma_A = \frac{\gamma_H\gamma_{Ac}}{\gamma_{HAc}}$$

where the "γ's" are the activity coefficients of the species denoted by subscripts.

Let

M_{SO_4} = molal concentration of sulfate
M_{Ac} = molal concentration of dichloro-acetic acid
m_H = molal concentration of hydrogen ion
m_{Ac} = molal concentration of dichloro-acetate ion
m_{HSO_4} = molal concentration of HSO_4^-
m_{SO_4} = molal concentration of SO_4^{--}
m_{HAc} = molal concentration of undissociated dichloro-acetic acid molecules.

Then

$$\left\{\begin{aligned} M_{\mathrm{Ac}} &= m_{\mathrm{Ac}} + m_{\mathrm{HAc}} \\ M_{\mathrm{Ac}} &= m_{\mathrm{H}} + m_{\mathrm{HSO_4}} + m_{\mathrm{HAc}} \\ M_{\mathrm{SO_4}} &= m_{\mathrm{SO_4}} + m_{\mathrm{HSO_4}} \end{aligned}\right. \quad \text{or} \quad \left\{\begin{aligned} m_{\mathrm{Ac}} &= M_{\mathrm{Ac}} - m_{\mathrm{HAc}} \\ m_{\mathrm{HSO_4}} &= M_{\mathrm{Ac}} - m_{\mathrm{H}} - m_{\mathrm{HAc}} \\ m_{\mathrm{SO_4}} &= M_{\mathrm{SO_4}} - m_{\mathrm{HSO_4}} \end{aligned}\right. \qquad (5)$$

In dilute solution, according to the theory of Debye and Hückel

$$\log \gamma_{\mathrm{S}} = -2\sqrt{\mu};\ \log \gamma_{\mathrm{A}} = -\sqrt{\mu}$$

and, therefore

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{A}}^2$$

Hence

$$K_1 = \gamma_{\mathrm{A}}^2 \frac{m_{\mathrm{H}}\, m_{\mathrm{SO_4}}}{m_{\mathrm{HSO_4}}} \qquad (6)$$

$$K_2 = \gamma_{\mathrm{A}} \frac{m_{\mathrm{H}}\, m_{\mathrm{Ac}}}{m_{\mathrm{HAc}}} \qquad (7)$$

Divide Equation (6) by the square of Equation (7) and obtain

$$\frac{K_1}{K_2^2} = \frac{m_{\mathrm{SO_4}}\, m_{\mathrm{HAc}}^2}{m_{\mathrm{H}}\, m_{\mathrm{HSO_4}}\, m_{\mathrm{Ac}}^2} \qquad (8)$$

By substituting in the latter the values of the concentrations given in (5)

$$\frac{K_1}{K_2^2} = \frac{(M_{\mathrm{SO_4}} - M_{\mathrm{Ac}} + m_{\mathrm{H}} + m_{\mathrm{HAc}})\, m_{\mathrm{HAc}}^2}{m_{\mathrm{H}}\, (M_{\mathrm{Ac}} - m_{\mathrm{H}} - m_{\mathrm{HAc}})\, (M_{\mathrm{Ac}} - m_{\mathrm{HAc}})^2} \qquad (9)$$

is obtained. By means of this equation m_{HAc} may be evaluated by arithmetical approximation since all other quantities are known. γ_{A} may then be determined by Equation (7) in the form

$$K_2 = \gamma_{\mathrm{A}} \frac{m_{\mathrm{H}}\, (M_{\mathrm{Ac}} - m_{\mathrm{HAc}})}{m_{\mathrm{HAc}}} \qquad (10)$$

For K_2 we have taken the value previously employed, namely, 3.32×10^{-2} and for k, the value 1.15×10^{-2}.[12] The values for γ_{A} calculated by this method are given in Table IV.

TABLE IV

THE ACTIVITY COEFFICIENTS OF DICHLORO-ACETIC ACID IN SULFATE SOLUTIONS

$M_{\mathrm{SO_4}}$	m_{H}	m_{HAc}	γ_{A}
	(1) K_2SO_4		
0.0	0.0816	0.1204	0.600
.125	.0552	.0859	.445
.25	.0444	.0681	.380
.375	.0371	.0573	.354
.5	.0354	.0504	.311
	(2) Na_2SO_4		
0.125	0.0576	0.0855	0.422
.25	.0476	.0683	.356
.5	.0403	.0518	.284
.75	.0368	.0433	.246
.875	.0371	.0406	.223
1	.0361	.0384	.216
1.25	.0351	.0347	.196
1.5	.0368	.0327	.174

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[12] Noyes and Sherrill, THIS JOURNAL, **48,** 1861 (1926).

In Fig. 3 the values of γ_A in Table IV are plotted against the square root of the ionic strength. The values represented by triangles are the squares of the theoretical activity coefficients of a uni-univalent electrolyte computed by the Debye and Hückel equation

$$\log \gamma = -\frac{0.357\sqrt{2\mu}}{1 + A\sqrt{2\mu}}$$

where A represents the term containing the mean ionic diameters. A probable value of 0.8 was assigned to A. It is obvious that as μ decreases, the values of γ_A in these sulfate solutions approach the theoretical values.

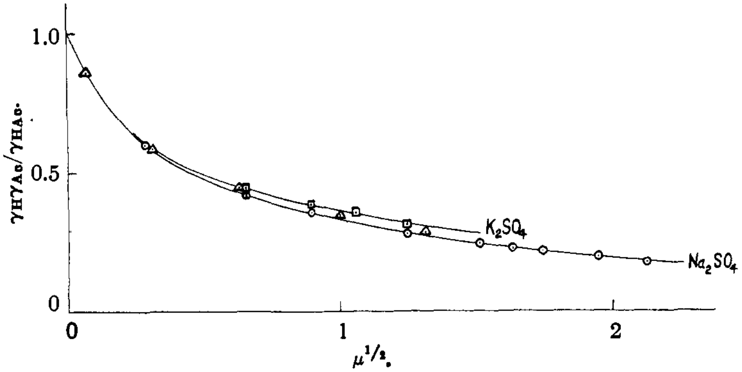

Fig. 3.—The activity coefficient product of dichloro-acetic acid in sulfate solutions.

Further, γ_A is greater in a potassium than a sodium sulfate solution of a given strength, a fact which agrees with the distribution of the ionic activity coefficient product of water as determined by Åkerlöf.[13]

Summary

(1) The velocity of hydrolysis of ethyl acetate at 25°, catalyzed by dichloro-acetic acid, has been determined in a number of salt solutions.

(2) Similar results have been obtained for the velocity of hydrolysis of ethyl formate, catalyzed by monochloro-acetic acid.

(3) A method of computing the activity coefficients of the acids from the kinetic data has been worked out and shown to yield reasonable results.

(4) An approximate method has been employed with success in computing the activity coefficients of the catalyzing acid in sulfate solutions. Although approximate, the method shows that the catalytic behavior in the sulfate solutions is largely determined by the formation of acid sulfate ions.

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[13] Åkerlöf, THIS JOURNAL, **48**, 1160 (1926).