

5. An excess of ammonia favors the inclusion of silica in the ammonia precipitate, but this has a slightly solvent action on the aluminum hydroxide.

6. A Sørensen value of from 7 to 8, as shown by a pink color with rosolic acid, is advised in making the ammonia precipitation.

7. A very small quantity of silica, roughly 0.3 mg., escapes precipitation, and an equal quantity is generally found in the wash waters from the ammonia precipitate.

8. In rock analysis a single evaporation with hydrochloric acid is sufficient, provided silica is also determined in the ammonia precipitate.

WASHINGTON, D. C.

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

## A STUDY OF THE VELOCITY OF HYDROLYSIS OF ETHYL ACETATE

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From various considerations regarding the independent character of the ions in dilute solutions, MacInnes<sup>2</sup> has assumed that, in dilute solutions of the same molality of hydrochloric acid and potassium chloride, the chloride ion has the same activity. Further, he assumed that in a solution of potassium chloride of a given strength, the activities of the potassium and chloride ions are the same. Harned<sup>3</sup> found evidence from electromotive-force data for the validity of these assumptions in conc. solutions and calculated the individual activity coefficients of the ions of these electrolytes. If these assumptions are correct, it follows from these calculations that the activity coefficient of the hydrogen ion in solutions of hydrochloric acid decreases with increasing concentration until a concentration of 0.15 *M* is reached, and then increases.

In many recent studies,<sup>4</sup> the contention has been made that the velocities of homogeneous reactions catalyzed by ions are a function of the ion activities and not the ionic concentrations. It has been pointed out by Jones and Lewis that other causes such as "the water displacement effect" may also influence the reaction velocity. From this point of view,

<sup>1</sup> Presented to the Faculty of the Graduate School of the University of Pennsylvania by Robert Pfanstiel in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> MacInnes, *THIS JOURNAL*, **41**, 1086 (1919).

<sup>3</sup> Harned, *ibid.*, **42**, 1808 (1920).

<sup>4</sup> (a) Harned, *ibid.*, **40**, 1461 (1918). (b) Jones and Lewis, *J. Chem. Soc.*, 117, 1120 (1920). (c) Scatchard, *THIS JOURNAL*, **43**, 2387 (1921). (d) Akerlöf, *Z. physik. Chem.*, **98**, 260 (1921). (e) Harned and Seltz, *THIS JOURNAL*, **44**, 1475 (1922); etc.

a study of the hydrogen-ion catalysis of a simple ester in aqueous solution should afford information regarding the individual activity coefficient of the hydrogen ion. Owing to secondary influences such as "the water displacement effect," it is not to be expected that exact relationships are to be found immediately.

Earlier work on this subject is of considerable interest. A compilation of previous data taken from the work of Taylor,<sup>5</sup> Kay,<sup>6</sup> and Lunden<sup>7</sup> on the hydrolysis of ethyl acetate and other esters is contained in a paper by Schreiner.<sup>8</sup> The results in this paper on the velocity of hydrolysis of ethyl acetate by hydrochloric acid of concentration  $c$  are reproduced in Table I.

TABLE I  
SCHREINER'S COMPILATION

$c$ Mols. per liter	$(k'_1F_0)^a \times 10^5$	$\left(\frac{k'_1F_0}{c}\right) \times 10^5$
0.010	2.93	293
0.025	6.99	280
0.050	13.83	278
0.100	28.29	283
0.132	38.1	288
0.150	43.2	288
0.200	57.0	285
0.250	71.6	286
0.479	138.0	288
0.493	145.0	296

<sup>a</sup>  $K'_1F_0$  is the observed monomolecular velocity constant obtained by the formula  $\frac{1}{t} \log \frac{A}{A-X}$ .

Thus, the velocity constant divided by the concentration passes through a minimum at about 0.1  $M$  hydrochloric acid concentration. This is similar to the behavior of the activity coefficient of the hydrogen ion as mentioned above. This evidence is by no means conclusive, but is suggestive owing to the parallelism between these properties. Consequently, further careful work has been undertaken. Apart from the above considerations, the data accumulated in the present research will help to a considerable extent to supplement what has been done, especially, the excellent study of Griffith and Lewis<sup>9</sup> on the velocity of hydrolysis of methyl acetate.

### General Theory

For the present purpose, it will suffice if we assume that the velocity of hydrolysis of the ester proceeds according to the equation

$$v_1 = k_1 a_{\text{ea}}' a_{\text{H}^+} a_{\text{w}} \quad (1)$$

<sup>5</sup> Taylor, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 37 (1913).

<sup>6</sup> Kay, *Proc. Roy. Soc. Edinburgh*, **22**, 484 (1897).

<sup>7</sup> Lunden, *Z. physik. Chem.*, **49**, 189 (1904).

<sup>8</sup> Schreiner, *Z. anorg. Chem.*, **116**, 102 (1921).

<sup>9</sup> Griffith and Lewis, *J. Chem. Soc.*, 109, 67 (1916).

where  $a_e$ ,  $a'_H$ , and  $a_w$  are the activities of the ester, the hydrogen ion and water, respectively, in the solution;  $v_1$  is the velocity, and  $k_1$  the velocity constant of hydrolysis. This follows from the activity theory of homogeneous catalysis,<sup>4c</sup> on the assumption that we are dealing with a simple hydrogen-ion catalysis, and that the water enters to the first power.

Since, by definition,  $F_e c$  equals  $a_e$  where  $F_e$  is the activity coefficient of the ester and  $c$  is its concentration, substitution in (1) gives

$$v_1 = k_1 F_e c a'_H a_w \quad (2)$$

At a given temperature  $k_1$  remains constant under changing conditions of all other factors in Equation 2. Let  $k'_1 = k_1 a'_H a_w$  or

$$k_1 = \frac{k'_1}{a'_H a_w} \quad (3)$$

Substituting in (2) gives

$$v_1 = k'_1 F_e c \quad (4)$$

From (3),  $k'_1$  is proportional to  $a'_H$  and  $a_w$ . During the course of reaction in a given experiment,  $a'_H$  and  $a_w$  remain constant,<sup>10</sup> and therefore  $k'_1$  represents the velocity constant in each experiment. But the velocity constant is obtained by measurement of  $c$ , and, consequently, Equation 4 shows that  $k'_1 F_e$  instead of  $k'_1$  is obtained in an actual measurement. Therefore, in all tables,  $k'_1 F_e$  will always denote the observed velocity constant.

$F_e$  probably remains constant in a solution containing hydrochloric acid at a given concentration, because  $k'_1 F_e$  is practically constant when obtained by Equation 4.  $F_e$  may vary with a change in hydrochloric acid concentration, and thus  $k'_1 F_e / a'_H a_w$  will vary, according to Equation 3.  $F_e$  can be determined from measurements of the solubility<sup>11</sup> of the ester in different strengths of hydrochloric acid, as can be seen from the following thermodynamic reasoning. The activity of the ester in a saturated solution in the presence of the liquid ester at the same pressure and temperature will always have the same value. Therefore, if  $F'_e$ ,  $F''_e$ ,  $F'''_e$ , etc., represent the activity coefficients of the ester in solutions containing acid at different concentrations,  $S'$ ,  $S''$ ,  $S'''$ , etc., represent the concentrations of the ester in the saturated solutions, or the solubilities, then

$$F'_e S' = F''_e S'' = F'''_e S''' = F_e S = \text{constant} \quad (5)$$

The simplest convention to adopt in measuring  $F_e$  is to let the constant equal "1". Then

$$k_1 = k_1(F_e S) = \frac{k'_1 F_e}{a'_H a_w} S \quad (6)$$

Thus, if  $F_e$  varies with the concentration of acid, it is necessary to multiply

<sup>10</sup> This assumption is justified because, in an actual experiment,  $k'_1 F_e$  is independent of the time.

<sup>11</sup>  $F_e$  could also be obtained by measurement of the partial vapor pressure of the ester.

$k'_1 F_e$ , the observed velocity constant, by the solubility, or  $1/F_e$ , in order to obtain the true velocity constant  $k'_1$ .

Van't Hoff<sup>12</sup> from thermodynamic considerations regarding reaction velocities in liquid systems, showed that, if the solubility of the reacting substance is taken as the unit of concentration measurement, the reaction velocities in different solvents will be independent of the nature of the medium. These considerations, accordingly, make the reaction velocity a function of the activities of the reactants. Van't Hoff, however, did not apply this reasoning to cases of homogeneous catalysis, in which the activity coefficients of the reacting substances may be influenced by different concentrations of the catalyst. The above deduction is thus an extension of the views of Van't Hoff to cases where the solvent is a solution of the catalyst, and the result will be of particular importance in studies on the neutral salt effect, where there is a considerable "salting out" of the reacting substance by the added salt.

### Experimental

The experimental method employed throughout in determining the velocity constants was the same as that usually employed, namely, the determination from time to time of the total acid present in the ester-hydrochloric acid mixture by means of sodium and barium hydroxide solutions. Densities of all the solutions were determined so that the calculations could be made on either a weight or a volume normal basis. Further, all solutions were so standardized that it was possible to compute the absolute quantities of all the molecular species present at any time during the course of the reaction. Since calculations were made by both the monomolecular formula and by the general kinetic equation for the reaction, it will be necessary to discuss the procedure in some detail.

**Materials.**—Ethyl acetate was prepared from alcohol and acetic acid and purified in the usual way. After repeated fractional distillation, the portion which passed over between 77° and 78° was collected for the investigation. Analysis of this fraction gave 98.81% of saponifiable ester, free from acetic acid. Tests for free acetic acid were made from time to time during the course of the investigation and in no case was it found present.

Constant-boiling hydrochloric acid was made, diluted to about 3 *M*, and checked by gravimetric analysis. All solutions of the acid were made from this sample by the weight method. The solutions of the acid were correct to within  $\pm 0.1\%$  of the total hydrochloric acid content.

Conductivity water freed from carbon dioxide by boiling was employed. All the necessary precautions were employed in making up and keeping the sodium and barium hydroxide solutions used in the work.

**Method of Procedure.**—Each determination was carried out in a 250cc. flask, and in every determination 200 g. of water was employed. The molal concentration of the hydrochloric acid (mols of acid in 1000

<sup>12</sup> Van't Hoff, "Lectures on Theoretical and Physical Chemistry," Arnold, London, 1898, Part I, p. 221.

g. of water) varied from 0.01 *M* to 1.5 *M*. The same quantity of ethyl acetate was added in each determination in a given series. Thus, in every determination of a given series, the same quantity of water, and the same quantity of ester was employed, the only variable being the hydrochloric acid content. Two series of results were obtained, using 5 cc. and 1 cc. of ester to 100 g. of water, respectively. The reaction was carried out at  $25.00 \pm 0.01^\circ$ .

The addition of as much as 10 cc. of ester to 200 g. of water caused a noticeable rise in temperature, amounting to  $1^\circ$  in cases where the molal concentration of hydrochloric acid was 0.5 or higher. Therefore, before making the initial titration, it was necessary to wait until the temperature was reduced to  $25^\circ$ .

The velocity measurements were made in the usual way by pipetting out 10cc. portions from time to time and titrating. Considerable care was exercised throughout all subsequent work.

**The Kinetics of the Reaction.**—In what follows, a very careful study has been made of the velocity constants calculated by both the simplified and approximate monomolecular reaction equation, and the more general kinetic equation which takes into consideration the reverse reaction.

1. *The Kinetics of the First Order Reaction.*—The general equation for the kinetics of the reaction  $\text{RCOOR}' + \text{H}_2\text{O} \rightleftharpoons \text{RCOOH} + \text{R}'\text{OH}$  in going from left to right, assuming that the activities of the 4 molecular species are proportional to their concentrations during the course of the reaction, and that the hydrogen-ion activity remains constant, will be

$$\frac{dx}{dt} = k''_1{}^{13}(A - X)(B - X) - k_2x^2 \quad (7)$$

where  $dx/dt$  is the velocity, *A* and *B* the initial concentrations of ester and water, *x* the amount of ester changed in a time *t*, and  $k''_1$  and  $k_2$  are the velocity constants of hydrolysis and esterification, respectively. Since the water concentration, *B*, varies only slightly during the reaction and since the reaction goes nearly to completion when a large quantity of water is present, Equation 7 may be reduced to the much simpler and approximate monomolecular equation

$$\frac{dx}{dt} = k''_1(A - X) \quad (8)$$

which upon integration takes the well-known form

$$k''_1 = \frac{1}{t} \ln \frac{A}{A - x} \quad (9)$$

This equation expressed in terms of the number of cubic centimeters of alkali employed becomes

$$k''_1 = \frac{1}{t} \ln \frac{T_\infty - T_0}{T_\infty - T} \quad (10)$$

<sup>13</sup>  $k''_1 = k'_1 F_e$ .

where  $T_\infty$  is a number slightly greater than the final titration,<sup>14</sup>  $T_0$  the initial titration, and  $T$  the titer at a time  $t$ .

2. *The General Kinetic Equation.*— $k_2$  may be eliminated from Equation 7 by employing the relation

$$k_2 = k''_1 K \quad (11)$$

where  $K$  is the equilibrium constant. Substituting for  $k_2$  in (7) gives

$$\frac{dx}{dt} = k''_1(A-x)(B-x) - k''_1 K x^2 \quad (12)$$

which on rearrangement and integration becomes

$$\int \frac{dx}{x^2 - \frac{A+B}{1-K}x + \frac{AB}{1-K}} = k''_1(1-K)t + C \quad (13)$$

By letting

$$\alpha + \beta = \frac{1-K}{A+B} \quad (14)$$

and

$$\alpha\beta = \frac{AB}{1-K} \quad (15)$$

the expression on the left side of (13) may be integrated, and the constant of integration may be evaluated from the fact that when  $t = 0$ ,  $x = 0$ . Substituting the values for  $\alpha$  and  $\beta$  obtained from (14) and (15) in this equation, the general kinetic equation is obtained, which upon simplification becomes

$$k''_1 = \frac{l}{t} \log \left( \frac{(n-mx)}{n-2(1-K)x} \right) \quad (16)$$

in which

$$l = \frac{2.303}{\sqrt{(A+B)^2 - 4AB(1-K)}};$$

$$m = \frac{(A+B) - \sqrt{(A+B)^2 - 4AB(1-K)}}{(A+B) + \sqrt{(A+B)^2 - 4AB(1-K)}} \cdot 2(1-K);$$

$$n = (A+B) - \sqrt{(A+B)^2 - 4AB(1-K)}$$

Griffith and Lewis<sup>9</sup> indicate how Equation 7 may be integrated by a different substitution. Knoblauch<sup>15</sup> integrated a similar equation by a different substitution.

**Calculations and Tables of Velocity Constants Computed by Monomolecular Equation.**—In computing  $k''_1$ , according to the monomolecular Equation 10,  $T_\infty$  represents the quantity of alkaline hydroxide solutions which would be required for titration after complete hydrolysis. Since the reaction does not go to completion,  $T_\infty$  cannot be determined experimentally. Therefore,  $T_\infty$  was calculated in each experiment as follows. The weight of 10 cc. of the solution, delivered from the pipet used in each titration was determined. Let this be called "a". In the preparation

<sup>14</sup> Explained in a later section.

<sup>15</sup> Knoblauch, *Z. physik. Chem.*, **22**, 268 (1897).

of the solutions, the weight of each component was known. Let "b" equal the weight of the water, "d" the weight of the hydrochloric acid, and "e" the weight of the ester in the reaction flask. Then  $\frac{a}{b+d+e} \times d$  is the number of grams of hydrochloric acid, and  $\frac{a}{b+d+e} \times e$  is the number of grams of ethyl acetate (assuming no hydrolysis) in each pipet. Therefore, the alkali equivalent of both the hydrochloric acid and ethyl acetate in cubic centimeters, or  $T_\infty$  is readily obtained. It is important to note that, employing this value for  $T_\infty$  gives values for the velocity constant which are lower than those obtained by taking for  $T_\infty$  the titration when equilibrium is reached. Although the velocity constants show a greater variation in value (due to the influence of the reverse reaction) as the reaction approaches equilibrium than is apparent when the final titration value for  $T_\infty$  is employed in the calculations, the values for the velocity constants at the beginning of the reaction are somewhat more consistent. The results for  $k''_1$  will be lower than the other results in the literature for this reason.

The values of the velocity constants for the different concentrations are given in Table II. They are the mean of the constants for the first

TABLE II  
MONOMOLECULAR VELOCITY CONSTANTS

(1) 0.470 N Ester				
$c_1$	$c_2$	$(k'_1 F_0)^a \times 10^5$	$(k'_1 F_0) \times 10^5$	$(k'_1 F_0) \times 10^5$
			$c_1$	$c_2$
0.010	0.00952	6.11	611	642
0.030	0.02857	18.30	610	641
0.050	0.04759	30.00	600	630
0.070	0.06666	41.79	597	627
0.100	0.0951	60.15	601	632
0.150	0.1425	91.1	607	639
0.200	0.1900	122.2	611	643
0.300	0.2840	185.5	618	653
0.500	0.4726	312.4	625	661
0.700	0.6604	450	643	681
1.000	0.9354	640	640	684
1.500	1.391	1006	671	723
(2) 0.100 N Ester				
0.010	0.00987	6.37	637	645
0.030	0.02961	18.96	632	640
0.050	0.0493	31.74	634	644
0.070	0.0690	44.44	635	644
0.100	0.0985	63.56	636	645
0.150	0.1477	95.54	637	647
0.200	0.1966	129.0	645	656
0.300	0.2944	197.2	657	670

<sup>a</sup> Obtained by Equation 9 and equals 2.303 times the values in Table I.

half of the reaction which in all cases gave concordant values. The constants for the two series differing in concentration of ester employed, are given. Two determinations of the velocity constants were made at each concentration of acid and the mean value recorded.  $k''_1$  or  $k'_1F_e$  is the mean monomolecular velocity constant,  $c_1$  is the molal concentration of hydrochloric acid, and  $c_2$  is its normal concentration.

**Calculation of the Equilibrium Constant.**—In the calculation by means of the general equation, it is necessary to employ a value for the equilibrium constant. The classic work of Berthelot and St. Gilles leads to the value of 4. Knoblauch,<sup>15</sup> using an equimolecular mixture of alcohol and water, a high concentration of ester, and hydrochloric acid as catalyst, obtained 2.67. Jones and Lapworth<sup>16</sup> found that, in the presence of large quantities of hydrochloric acid (over 1 *M*), the equilibrium constant was considerably greater than 4. Since no definite information regarding the value of *K* for the ethyl acetate reaction in the presence of hydrochloric acid at the concentrations here employed was available, the equilibrium constant was determined at each acid concentration. Since, under the experimental conditions, the ethyl acetate is 97% hydrolyzed, great accuracy could not be obtained. The observed values for *K* were 3.39, 3.87, 3.50, 3.89, 3.87, 3.61, 4.01, 4.00, 3.93, 3.68, and 3.35 at the molal concentrations 0.01, 0.03, 0.05, 0.07, 0.10, 0.15, 0.20, 0.30, 0.50, 0.70, 1.00, respectively. Since there was no apparent increase or decrease of the equilibrium constant within the limits of the hydrochloric acid concentrations, and since the mean value (3.74) checks within the experimental error the value of Berthelot and St. Gilles, 4, has been employed in all subsequent calculations.

**Method of Calculation by the General Equation and Tables of Velocity Constants Computed by the General Equation.**—In order to employ Equation 16, it is necessary to obtain the values of *A*, the initial concentration of ester, *B* the initial concentration of water, and *x*, the concentration of ester changed in a time *t*. *A* and *B* were readily obtained since the weights of the ester and water, and the densities of the solutions were known. Their calculation needs no explanation. Therefore, it is necessary only to show how *x* is calculated and how a slight change is made in  $T_0$  and in the first reading of *t*. From Equation 16, when *t* equals 0, *x* must equal 0. Under the experimental conditions, it is impossible to start the experiment at the beginning of the hydrolysis. When the first titration is made, some ester has hydrolyzed and *x*, therefore, has an appreciable value when *t* equals 0. Therefore,  $T_0$ , the initial titration, is corrected to a value which will make *x* equal to 0, and *t* is corrected so as to make the starting time of the reaction the moment when *x* equals 0. The following explanation will show how this correction is made. Let

<sup>16</sup> Jones and Lapworth, *J. Chem. Soc.*, 99, 1427 (1911).



the initial titration be  $T_0$ . Calculate  $T_\infty$ . Then the ester equivalent,  $T_E$ , of the contents of one pipet of the solution in terms of cubic centimeters of alkali is calculated. Let  $T_\infty - T_E = T'_0$ .  $T'_0$  is less than  $T_0$  by a quantity of alkali equivalent to the acetic acid formed from the beginning of the hydrolysis up to the time of the first titration. From this, the lapse of time from the beginning of hydrolysis up to the time of the first titration may be computed from the equation

$$t = \frac{2.303}{k''_1} \log \frac{(T_\infty - T'_0)}{(T_\infty - T_0)}$$

This time is added to the time period of each subsequent titration. The value of  $x$  for each titration will be  $\frac{T'_0 - T}{T_E} = x$ . Table III contains a comparison of the velocity constant obtained from the first order equation and from Equation 16.  $k''_1$  equals  $k'_1 F_e$ .

TABLE III  
COMPARISON OF VELOCITY CONSTANTS BY MONOMOLECULAR AND GENERAL EQUATION

$c_1 = 0.20$ Equation 10			$c_2 = 0.1897$ Equation 16			
1	2	3	4	5	6	7
Time Min.	$T - T_0$	$k'_1 F_e \times 10^3$	Time	$T - T'_0$	$x$ g.	$k'_1 F_e \times 10^3$
..	....	...	48	6.03	0.02675	2.340
71	8.47	1.240	119	14.50	0.06433	2.345
158	17.82	1.236	206	23.85	0.1058	2.345
259	27.48	1.234	307	33.51	0.1486	2.337
371	36.71	1.226	419	42.74	0.1895	2.347
491	45.42	1.226	539	51.45	0.2283	2.335
638	54.30	1.218	686	60.33	0.2676	2.335
837	63.90	1.208	885	69.93	0.3102	2.338
1010	70.75	1.206	1058	76.78	0.3406	2.353
..	97.00 <sup>a</sup>	...	..	103.03 <sup>d</sup>	0.4570 <sup>e</sup>	...
..	100.45 <sup>b</sup>	...	..	106.46 <sup>e</sup>	0.4724 <sup>a</sup>	...

<sup>a</sup> End-point.

<sup>b</sup>  $T_e$ .

<sup>c</sup>  $T_\infty - T_0$ .

<sup>d</sup> End-point.

<sup>e</sup>  $x'$  = equilibrium value of  $x$ .  $A$  = initial ester quantity.

From this table, it is seen that the time of hydrolysis began 48 minutes before the first titration was made and, in that time, enough acetic acid was formed to neutralize 6.03 cc. of alkali. The time in Col. 4 was obtained by adding 48 to the values in Col. 1, and the values in Col. 5 were obtained by adding 6.03 to the values in Col. 2. Equation 16 was proved to give constant values for  $k'_1 F_e$  when calculated from the titrations near the equilibrium point of the reaction. In Table IV are compiled the mean values of  $k'_1 F_e$ , obtained by Equation 16;  $c_1$  is the molal concentration, and  $c_2$  is the normal concentration of the hydrochloric acid. In Cols. 3 and 4 have been included the observed velocity constants, and in Col. 5 their mean values.

Table IV shows that in the first series, corresponding to an initial concentration of ester of 0.47 *N*, the values obtained for the ratios of the velocity constants to the hydrochloric acid normalities are greater than they are in the second series, which corresponds to an initial ester concentration of 0.100 *N*. If the activity of the hydrogen ion is not changed by increas-

TABLE IV  
VELOCITY CONSTANTS BY THE GENERAL KINETIC EQUATION

0.47 <i>N</i> Ester						
1	2	3	4	5	6	7
$c_1$	$c_2$	$k'_1 F_0 \times 10^6$			$k'_1 F_0 \times 10^6$	$k'_1 F_0 \times 10^6$
		(Obs.)	(Obs.)	(Mean)	$c_1$	$c_2$
0.010	0.00952	1.168	1.165	1.167	116.7	122.6
0.030	0.02857	3.462	3.422	3.442	114.7	120.5
0.050	0.0476	5.729	5.728	5.729	114.5	120.4
0.070	0.0667	7.95	7.98	7.97	113.9	119.6
0.100	0.0951	11.49	11.44	11.46	114.6	120.5
0.150	0.1425	17.41	17.31	17.36	115.8	121.8
0.200	0.1900	23.42	23.12	23.27	116.3	122.5
0.300	0.2840	35.68	35.00	35.34	117.8	124.5
0.500	0.473	59.90	60.20	60.05	120.1	127.1
0.700	0.660	86.23	85.83	86.03	122.9	130.2
1.000	0.935	124.7	125.5	125.2	125.2	133.8
1.500	1.391	196.1	.....	196.1	130.8	141.0
0.100 <i>N</i> Ester						
0.010	0.00987	1.166	1.166	1.166	116.6	118.2
0.030	0.02961	3.460	3.440	3.450	115.0	116.5
0.050	0.0493	5.77	5.79	5.78	115.6	117.3
0.070	0.0690	8.06	8.13	8.09	115.6	117.3
0.100	0.0984	11.55	11.56	11.55	115.6	117.4
0.150	0.1477	17.50	17.64	17.57	117.1	119.0
0.200	0.1966	23.61	23.69	23.65	118.3	120.3
0.300	0.2944	36.00	35.90	35.95	119.8	122.1

ing the ester concentration and there is no other catalytic influence, then, according to the general kinetic equation, a change in ester concentration at constant hydrochloric acid normality should not affect the velocity constant. This difference is, however, in agreement with the results of Griffith and Lewis<sup>9</sup> who, working at constant volume and constant hydrochloric acid concentration, found that the velocity increased with increasing ester concentration. They ascribed the cause to a negative catalytic effect of the water.

### Discussion

The point of view adopted in this investigation is based on thermodynamic reasoning.<sup>4e</sup> Further, the assumption is made that all the catalytic effect of the hydrochloric acid is caused by the hydrogen ion. An inspection of Tables I, II and IV shows that, in each case, the ratio of the

velocity constant to the concentration of the hydrochloric acid has a minimum value somewhere between 0.06 *M* and 0.100 *M* hydrochloric acid concentration. This fact is supported by the work of others, and in every instance is verified in the present investigation.<sup>17</sup>

The individual hydrogen-ion activity coefficient in pure solutions of hydrochloric acid, according to the assumptions mentioned in the introduction, will be given by the equation<sup>18</sup>

$$\log F_H = 0.330 c_1 - 0.284 c_1^{0.471} \quad (17)$$

where  $F_H$  is the activity coefficient of the hydrogen ion, and  $c_1$  the molal concentration of the hydrochloric acid.

In Fig. 1 are given the plots of  $k'_1 F_e / c_1$  against  $\log c_1$ , and also  $F_H$  against  $\log c_1$ . It is clear that with increasing acid concentration, the value of

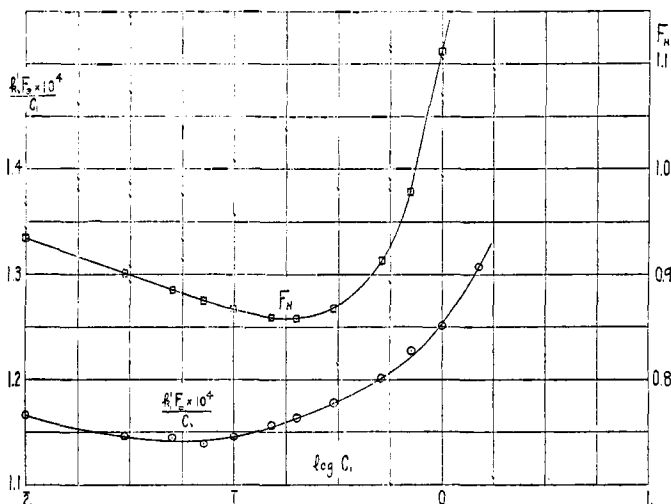


Fig. 1.

the ordinate first passes through a minimum and then rises rapidly in both cases. The minimum of each curve occurs between 0.07 *M* and 0.200 *M* concentration of hydrochloric acid. In dilute solutions  $F_H$  decreases more rapidly than  $k'_1 F_e / c_1$  with increasing acid concentration, while in concentrated solutions it increases more rapidly. Therefore, if the values of  $k'_1 F_e$  are divided by the activity of the hydrogen ion of pure hydrochloric acid solution, a constant will not be obtained. This

<sup>17</sup> It was thought that possibly the rise in the ratio of the velocity constant,  $k'_1 F_e$ , to the concentration at the low concentrations, could be caused by the catalytic effect of the increase in number of hydrogen ions formed during the course of the reaction. This is not the case because  $k'_1 F_e$ , calculated by either the monomolecular or the general equation, had as high values at the beginning of the reaction as at any time during the course of the reaction. In other words, the present experimental method failed to detect such an autocatalysis.

<sup>18</sup> Harned, *THIS JOURNAL*, **44**, 252 (1922).

is shown by the results in Table V. In Col. 1 are the molal concentrations of hydrochloric acid, and in Col. 2 are the corresponding activity coefficients of the hydrogen ion of pure hydrochloric acid solution. Col. 3 contains the activity of the water molecule at various acid concentrations, computed from the vapor pressure of water over the hydrochloric acid solutions.<sup>18</sup> Col. 4 gives the ratios of the velocity constants to the corresponding hydrogen-ion activities, and Col. 5 contains the ratios of the velocity constants to the products of the hydrogen-ion and water activities.<sup>19</sup>

TABLE V  
VELOCITY CONSTANT ACTIVITY RATIOS

1	2	3	4	5
$c_1$	$F_H$	$a_w = \frac{p^a}{p_0}$	$\frac{(k'_1 F_e) \times 10^4}{a_H}$	$\frac{k'_1 F_e \times 10^4}{a_H a_w}$
0.010	0.935	...	1.248	1.248
0.030	0.903	...	1.270	1.270
0.050	0.886	...	1.292	1.293
0.070	0.875	...	1.302	1.303
0.100	0.868	0.997	1.320	1.324
0.150	0.858	0.995	1.350	1.357
0.200	0.857	0.993	1.257	1.367
0.300	0.867	0.990	1.359	1.373
0.500	0.914	0.983	1.314	1.337
0.700	0.979	0.975	1.255	1.287
1.000	1.112	0.964	1.126	1.168
1.500	1.416	0.942	0.924	0.980

<sup>a</sup>  $p$  is the partial vapor pressure of water, and  $p_0$  is the vapor pressure of pure water.

It is clear from the above table that the values of  $\left(\frac{k'_1 F_e}{a_H}\right)$  and  $\left(\frac{k'_1 F_e}{a_H a_w}\right)$  are not constant, but have a maximum at 0.3  $M$  acid concentration;  $a_H$  is the activity of the hydrogen ion in pure hydrochloric acid solution; but, as already pointed out,  $\left(\frac{k'_1 F_e}{a_H a_w}\right)$  should not be constant if  $F_e$  varies with the acid concentration, or  $F_H$  with ester concentration. The value of  $F_e$  in solutions of hydrochloric acid can be obtained theoretically from either the measurement of the partial vapor pressure of the ester over the solution, or from its solubility. According to our assumptions, it has been shown that  $\frac{k'_1 F_e}{a'_H a_w} \cdot S$  should be constant if  $a_w$  enters to the first power, and if  $a'_H$  is the true activity of the hydrogen ion in the solution. Consequently, if the solubility decreases with increasing acid concentration at the higher dilutions of the acid, the correction for  $F_e$  will be in the right direction. Determinations of the solubility are difficult on account of hydrolysis. A number of determinations showed that the solubility

<sup>19</sup> It is possible that  $a_w$  should enter to a higher power.

does decrease as the acid concentration increases up to a concentration of 0.3  $M$  and this decrease is of the same order of magnitude as the increase of  $\left(\frac{k'_1 F_e}{a_H a_w}\right)$ . An attempt to determine  $a'_H$  by electromotive-force measurements was made but the results have not been included on account of uncertainties caused by liquid-junction potentials and the high partial vapor pressure of the ethyl acetate. The results obtained up to the present, however, do not vitiate any of the conclusions but substantiate them to a limited extent.

The present study can only be regarded as a preliminary treatment of this complicated problem, the solution of which would require an accurate knowledge of the activity coefficients and concentrations of all the ionic and molecular species present. In conclusion, it is thought that the minimum in the velocity constant- $\log c_1$  plot is contributory evidence of the theory of the independent activity coefficients as developed by MacInnes and Harned. On the other hand, it is thought that further evidence has been obtained for the activity theory of homogeneous catalysis.

### Summary

1. The monomolecular velocity constants of hydrolysis of ethyl acetate at many different hydrochloric acid concentrations have been accurately determined at 25°.
2. A solution of the general equation for the velocity of hydrolysis has been obtained.
3. The velocity constants have been computed by the general equation.
4. In four series of measurements, it has been found that the plot of the velocity constants divided by the molal concentration of hydrochloric acid against  $\log c_1$  ( $c_1$  equals the molal concentration of the hydrochloric acid) shows a minimum at 0.07 to 0.08  $M$  concentration of the acid. This is similar to the plot of the individual hydrogen-ion activity coefficient against  $\log c_1$  which has a minimum at 0.15  $M$  to 0.18  $M$  acid concentration.
5. It has been shown that the velocity constant divided by the product of the activities of the hydrogen ion and the water molecule is not a constant at different acid concentrations but has a maximum at 0.3  $M$  hydrochloric acid concentration.
6. Some factors which may cause this deviation from constancy have been suggested.
7. The kinetics of hydrolysis of ethyl acetate is very complex, but it is thought that enough evidence has been obtained to show that the method of attacking the problem employed in this investigation is in a general way correct.