EQUILIBRIUM AND KINETICS OF ESTERIFICATION AND HYDROLYSIS

IN THE PRESENCE OF PERCHLORIC ACID AS CATALYST

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By

EARL L. RICHARDSON

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Drury College

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APPROVED:

H. M. Trimble
_____
Director of Research

D. M. Smith
_____
Head of the Department of Chemistry

O. E. McIntosh
_____
Dean of the Graduate School

119404

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PREFACE

Our attention was recently called to the relation between the kinetics of reversible reactions and their equilibrium constants by a rather surprising statement by Farrington Daniels (8) in his work "Chemical Kinetics". The relation between chemical kinetics and chemical equilibrium has long been stated in the equation
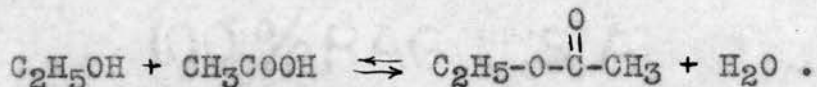
$$(1) \qquad K = \frac{k_1}{k_2} \, ,$$

where K is the equilibrium constant, k_1 is the velocity constant for the forward reaction and k_2 is the velocity constant for the back reaction. With reference to this equation he says, "It is surprising to realize that, except possibly in one or two cases, this important formula has not been subjected to complete experimental test by measuring all three quantities." The relation has been accepted for so long that it has become practically axiomatic in Physical Chemistry; nevertheless, such a statement by an authority in the field seemed to make further investigation of the matter imperative. This has been the purpose of the work reported in this thesis.

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INTRODUCTION

We have found five cases in which the relationship of re-
action kinetics to equilibrium constants have been studied.
The classical investigation was that made by O. Knoblauch (17)
and partially interpreted by van't Hoff. The reaction studied
was

$$C_2H_5OH + CH_3COOH \rightleftharpoons C_2H_5-O-\overset{\overset{\text{O}}{\|}}{C}-CH_3 + H_2O .$$

As reported in Mellor's "Chemical Statics and Dynamics" (21),
the velocity constant for the forward reaction, k_1, was found
to be 0.000238 and that of the reverse reaction, k_2, to be
0.0000815. The classical development of the law of chemical
equilibrium shows that the equilibrium constant, K, is equal
to k_1/k_2 or 2.92 in this case. This value agrees well with
the value of K as found by direct experiment.

Bodenstein (5) made a comprehensive research upon the re-
action $H_2 + I_2 \rightarrow 2HI$ and also $2HI \rightarrow H_2 + I_2$ and found that the
equilibrium constant is equal to the ratio of the two reaction
rates. In this research known quantities of hydrogen iodide
were sealed in glass bulbs, these were heated for a definite
length of time at some definite temperature (between 283° and
508° C.) and the bulbs were then cooled and opened, and their
contents submitted to chemical analysis.

Another reaction for which all three quantities have
been determined is that expressed by the equation

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + 2NO + H_2O.$$
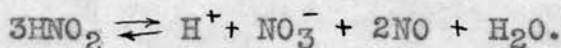
The equilibrium constant has been found to diminish with an

increase in dilution and is expressed by

$$K = \frac{[H^+][NO_3^-][NO]^2}{[HNO_2]^3} \quad .$$

Abel and Schmid (1) give the value of 29 for this equilibrium constant while Lewis and Randall (18) give the value 31:-- both in aqueous solution at 25° C. The kinetic expressions for the direct and reverse reactions are:

$$\frac{-d[HNO_2]}{dt} = k_1 \frac{[HNO_2]^4}{[NO]^2}$$

$$\frac{+d[HNO_2]}{dt} = k_2 [HNO_2][H^+][NO_3^-]$$

The ratio (k_1/k_2) of the two velocity constants change similarly with the dilution, the extrapolated value being about 35 as reported by Abel, Schmid, and Babab (2). Although the difference in K, as determined by the two methods varies 15% to 20%, it is regarded as proof of the equation: namely, that $K = k_1/k_2$.

Perhaps a more rigid proof is shown as a result of the work of Roebuck (28), Bray (6), and Liebhafsky (19) on the following equilibrium:

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 3I^- .$$
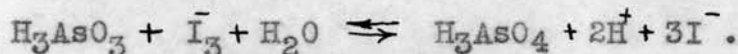
The results of their work shows that at 0° C., $k_1/k_2 = 0.15$, and $K = 0.16$.

The latest experimental proof we have uncovered is the work of Pease (24) who determined the reaction rates for the gas reaction

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$
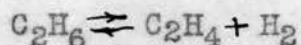
at various temperatures from 450° to 550° C. He used the

equation

$$K = \frac{p_{C_2H_4}p_{H_2}}{p_{C_2H_6}} = \frac{k_1}{k_2}$$

and found that k_2 could be expressed by the relation

$$\log_{10}k_2 = \frac{-43,150}{2.3RT} + 8.457.$$

The expression for the forward reaction is the work of Marek and McCluer (20) who give

$$\log_{10}k_1 = \frac{-73,170}{2.3RT} + 15.12.$$

Then from this follows that

$$\log_{10}K = \log_{10}k_1 - \log_{10}k_2 = \frac{-30,020}{2.3\ RT} + 6.66$$

Direct measurements at 600°-700° C. for the equilibrium constant gives

$$\log_{10}K = \frac{-31,244}{2.3\ RT} + 6.31.$$

This is very good agreement.

These studies seem to establish the validity of equation (1) very satisfactorily, especially when the experimental difficulties which are involved are considered.

Esterification in its narrow sense is the reaction between an organic acid and an alcohol to form an ester. Few if any chemical reactions have been the object of more extensive and intensive studies by both organic and physical chemists, yet we are still far from a satisfactory knowledge of its real nature. To quote E. E. Reid, "It has been one of the most useful reactions in preparative organic chemistry,

one of the best examples of the mass action law, and one of the most baffling problems in homogeneous catalysis." (26)

The classical investigations of the reaction between ethyl alcohol and acetic acid to form ethyl acetate were performed by Berthelot and St. Gilles (4). In it they brought together anhydrous ethyl alcohol and acetic acid and then allowed the reaction to go to equilibrium. This required several months, but they found that, ultimately, two thirds of the reactants disappeared with the formation of corresponding quantities of ethyl acetate and water when alcohol and acid were taken in equivalent proportions. On substituting into the equation expressing the law of chemical equilibrium the equilibrium constant was found to be:

$$(2) \qquad K = \frac{[ester] \times [water]}{[acid] \times [alcohol]} = \frac{2/3 \cdot 2/3}{1/3 \cdot 1/3} = 4$$

On varying the proportions of alcohol and acid, other yields of ester and water were found, yet the quantities of products and reactants at the end were found to be such that, when substituted into the equation (2) the same equilibrium constant was found. Others workers have verified this fact, but still others have been led to call it in question. Thus Carso and Durruty (7) found that for equivalent proportions $K = 3.80$, but that variation in the relative quantity of acetic acid caused large variations in this constant. Again, Poznanski (25) found $K = 3.79$ when equivalent quantities of acid and alcohol were taken; 4.73 when three parts of acid were taken to one of alcohol and

2.45 when these proportions were reversed. Further, he found that with equal proportions of alcohol and acid in the presence of 23 moles of water at the start the constant was 3.56. Similar results were found by Knoblauch (17). No explanation of these discrepancies is to be found in the literature.

Berthelot (loc. cit.) found that this reaction can be very greatly accelerated by the addition of small quantities of hydrochloric or sulfuric acid. Most investigators since his time have also employed these or other such catalysts. One of the best commercial syntheses of ethyl acetate is carried out in the presence of not more than 5% of either of these acids or of $CaCl_2$ (14). It is clearly recognized that the value of the equilibrium constant in this reaction is altered by the presence of electrolytes (12).

Turning now for a moment to the kinetics of this reaction under these conditions, we find that great irregularities exist. "If we consider a dilute solution of acetic acid in ethyl alcohol (no water being present) and we pass in dry hydrogen chloride, the normal behavior would be for the rate to be proportional to the concentration of acetic acid. Actually we find that as the acetic acid reacts the rate of the reaction falls much more rapidly. We might find for example that when half the acetic acid is esterified, the rate, instead of being one half of the initial rate, is only one tenth to one hundredth of the initial rate. This is due to the extremely high negative catalytic

action of small quantities of water, the mechanism of which is not yet understood." (27) It may well be that water in small concentrations in an organic medium and in the presence of an electrolyte, has such an activity as to cause considerable alteration in the equilibrium constant. At any rate, it would not be safe to conclude that in such cases the constant as found by Berthelot and St. Gilles holds.

The kinetics of the reaction between ethyl alcohol and acetic acid, as well as the equilibrium which is reached in the reaction, have, for the most part, been studied in the presence of relatively large excess of water. The reaction proceeds more smoothly under these conditions; and results are more readily reproduced. The rate of hydrolysis of ethyl acetate has been studied much more than the rate of esterification; chiefly because, in the presence of much water, only a small fraction of the alcohol and acid present can react. For this reason the change which can be detected in titration of acid in the solution is relatively small.

Schreiner (30) compiled the data upon rate of hydrolysis of ethyl acetate in the presence of HCl as found by several investigators at concentrations up to about 0.5 moles per liter. His data are shown in Table I. k_2' is the simple constant calculated for a first order reaction according to the equation $k_2' = \frac{1}{t} \ln \frac{a}{a-x}$. As will be seen, the velocity constant increases at approximately the same rate as that of the catalyst throughout this range of concentration.

TABLE I

Hydrolysis of Ethyl Acetate

in the presence of HCl-- 25° C.

Moles HCl per liter C	$k_2' \times 10^5$	$\dfrac{k_2'}{C} \times 10^5$
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
0.479	138	288
0.493	145	296

Kendall and King (16), on the other hand, in agreement with the work of others, found that the rate of hydrolysis of ethyl acetate in hydrochloric acid solutions increases much more rapidly than does the molecular concentration of the acid.

We have found but one study of the rate of formation of ethyl acetate from alcohol and acid in the presence of an excess of water. This study was made by Knoblauch (loc. cit.). We cannot give any of the details, since we have been unable to secure a photoprint of the article.

A number of acids have been employed as catalysts in this reaction. Goldschmidt and his students (11) employed hydrochloric, picric, trichloroacetic, trinitrobenzoic, tri-chlorobutyric and dichloroacetic acids as catalytic agents. In general, the weaker acids prove to be poor catalysts.

In very dilute solutions hydrochloric, hydrobromic, hydriodic, methyl sulfuric, nitric and chloric acids, which are strongly ionized are powerful catalysts. In the same concentrations these acids seem to give the same velocity of hydrolysis, and the velocity of hydrolysis is proportional to the concentration. (29) Sulfuric acid, if counted as dibasic, is about half as effective as is hydrochloric acid. The sulfonic acids, particularly ethyl sulfonic acid, are as good as the best catalysts. Phosphoric acid is a poor catalyst. (12)

Attempts have been made to correlate the rate of hydrolysis of ethyl acetate with the total acid concentration, with the concentration of hydrogen ion as determined by conductivity methods, with pH as determined electrometrically, with mean ion activity and with acidity as measured by means of simple acid indicators without much success in general. The theories as to the manner in which the catalyst promotes the reaction involve addition of the reactants to (a) the acid, (b) the unhydrated hydrogen ion or (c) the hydronium ion to form an unstable intermediate compound. The final products are then formed by decomposition of the complex. Each of these theories has its adherents, and it is probably not possible to choose between them as yet.

In Bernthsen and Sudborough (3) the statement is made that in hydrolysis of esters the action of a mineral acid is purely catalytic, and that the same result (i. e., the

same equilibrium) would ultimately be obtained by reaction with water alone. This is in direct conflict with the findings of numerous workers. Thus, Michaelis (23) found that, while various acids accelerated the hydrolysis of ethyl acetate, they also raised the equilibrium constant. This means that the presence of the acid may affect the degree to which the reaction goes.

Harned and Pfanstiehl (13) have determined the equilibrium constants reached in the hydrolysis of ethyl acetate in the presence of HCl at various concentrations. Their data are given in Table II. For the range of concentrations covered this constant shows practically no change.

TABLE II

Equilibrium constant in Hydrolysis of
Ethyl Acetate. Harned and Pfanstiehl. 25° C.

Molal Concentration HCl	K
0.01	3.39
0.03	3.87
0.05	3.50
0.07	3.89
0.10	3.87
0.15	3.61
0.20	4.01
0.30	4.00
0.50	3.93
0.70	3.68
1.00	3.35

Jones and Lapworth (15) have made very careful determinations of the equilibrium constants reached by the hydrolysis of ethyl acetate in solutions containing little water. In these experiments there were present from

0.013 to 0.070 moles of HCl. The water at the start varied from about 0.085 to about 0.47 moles, and the ethyl acetate at the start varied from about 0.14 moles to about 0.038 moles. Calculations from their data give the values set forth in Table III.

TABLE III

Equilibrium Constants in Hydrolysis of Ethyl Acetate
Jones and Lapworth   25° C.

Mole fraction of HCl	K
0.116	6.35
0.115	6.45
0.113	6.62
0.109	6.94
0.099	7.09
0.094	7.30
0.083	7.62
0.080	7.73
0.077	7.81
0.054	8.90
0.053	8.83

When these data are plotted they are found to lie fairly well on a straight line, whence it follows that, for these conditions, the equilibrium constant is inversely proportional to the mole fraction of the hydrochloric acid present as catalyst.

Jones and Lapworth have shown that if it be assumed that each mole of HCl is combined with two moles of water, which is thus rendered inactive in the reaction, the equilibrium constant is approximately four for these cases.

Students in the course in Physical Chemistry in this College, following the directions given in Daniels, Mathews

and Williams (9) have secured very high values for the equilibrium constant in this reaction during the past several years. They also used HCl as catalyst, at concentrations well below those employed by Jones and Lapworth, yet the constants varied from 6 to 15. This fact has lent interest to the present study.

The references to the literature which have been given are only a fraction of those which may be found; yet they serve to indicate the confusion, the incompleteness and the general unsatisfactory state which exists in this field despite the great amount of work which has been done on it. With particular reference to the kinetics of the reaction and the relation of the velocity constants to the equilibrium constant, we have found no case in which all three constants have been determined over a considerable range of concentration of the catalyst. The work of Knoblauch was apparently rather indirect and covered only a small range of concentration. It seemed, then, very much worth while to repeat this work, with various modifications in procedure.

It has been suggested by several workers that perchloric acid should be an excellent catalyst for esterification reactions though we have found no record of its use in this connection. It has been used to good advantage by Smith and Orton (31) in acetylation of phenols with acetic anhydride. A few preliminary experiments showed us that perchloric acid acts quite as well as hydrochloric, if not better, for

esterification and that the results gained by its use are very regular and readily reproducible. For these reasons, and because its use would enable us to contribute data upon a new catalyst for this reaction, it was decided to use it in this study.

REAGENTS AND APPARATUS

Perchloric Acid.

The perchloric acid used in this work was Merck's Reagent 70%. The media for the reactions were made by diluting this acid with ordinary distilled water. The solutions prepared in this manner for the several reactions were titrated to determine their actual concentrations.

Ethyl Acetate.

Two different grades of ethyl acetate were used; about half of that used was Merck's U.S.P. grade and the rest was Merck's Reagent grade. After purification both grades were found to be of equal purity and acid free. Purification was accomplished by washing each pound of ethyl acetate with three portions of distilled water each of 100 ml. This procedure removes all of the acid impurities and other water soluble products of decomposition. After the final portion of water has been drawn off, the acid free ethyl acetate is allowed to stand over fused K_2CO_3 until ready for use. This removes the water left in the reagent. When ready for use (not before 4 or 5 days after putting over fused K_2CO_3), an ordinary distillation gave a product which analyzed 95% pure. The analysis was carried out by the addition of a 50 ml. portion of standard base to a weighed sample of the ethyl acetate. After allowing two or three days for the reaction to go to completion, the solution was back-titrated with a solution of standard hydrochloric acid.

Ethyl Alcohol

The alcohol was prepared from ordinary 95% U.S.P. grade ethyl alcohol. To remove the aldehydes, Dunlap (10) proposed a method which was found to be satisfactory. 1.5 g. of $AgNO_3$ are dissolved in about 3 ml. of water and added to a liter of the 95% alcohol in a glass stoppered flask and mixed thoroughly; 3 g. of KOH are dissolved in 10 to 15 ml. of warm alcohol, and, after cooling this solution, is poured into the alcoholic silver nitrate solution without shaking. The Ag_2O is precipitated in a very finely divided state and slowly distributes itself through the contents of the flask but after standing over-night, the precipitate settles and the supernatant liquid is filtered and distilled to produce a product which tested 91.5% pure. The purity was tested by an accurate determination of the density at 30° C.

Acetic Acid.

The acetic acid used was Du Pont's Reagent grade. Since the presence of water was not harmful if the amount was known, no further purification was attempted. Analysis by titration with standard base showed the acetic acid to be 99.8% pure.

Sodium Hydroxide.

The sodium hydroxide used was Baker and Adamson's Reagent grade. The solution was mixed in bottles of 5 gallon capacity and standardized by titration with potassium acid phthalate and constant boiling hydrochloric acid; both methods giving identical results. A small amount of $BaCl_2$

was added to keep the solution free of carbonates. In addition, the solution was protected from carbon dioxide by passing all air admitted to the bottle through soda lime.

Apparatus.

Ordinary precision burettes and pipettes were used in this research. All reaction vessels used for kinetics experiments were glass stoppered flasks of 225 ml. capacity. The vessels used to determine the equilibrium constants were glass stoppered bottles of 100 ml. capacity. Before being used, the flasks and bottles were cleaned, rinsed with distilled water, and dried thoroughly in an oven at 200° C. to remove all traces of water.

The thermostat used held the temperature at 30° C.$\pm.02^{\circ}$ as measured by a mercurial thermometer that had been calibrated against a Bureau of Standards thermometer. The thermostat had a capacity of approximately 100 gallons and the temperature was controlled by a mercury-regulator. Time was measured during the experiments on velocity of reaction by means of accurate stop watches.

EXPERIMENTAL

All experiments were run at 30° C. since this temperature is easily maintained, and it is high enough for reactions to take place rapidly and yet low enough so that the reactions do not go with a rapidity which would make accurate measurements difficult.

The Kinetics of Hydrolysis.

In each of the 13 experiments for which results are presented, 10 ml. of ethyl acetate were added to 150 ml. of $HClO_4$ of known strength; the time of addition being taken as zero time. At intervals of from 2 to 6 mins., depending on the extent to which the reaction had proceeded, 10 ml. samples of the reaction mixture were withdrawn and pipetted into about 50 ml. of distilled water at 0° C. in order to stop the reaction. The solution was titrated immediately with approximately N/2 sodium hydroxide. Table IV gives the data on a representative experiment in which the concentration of the perchloric acid was 0.912 moles per liter.

The first experiments were continued until equilibrium was reached but it was soon found that measurements made after the first 40 minutes were entirely useless in the calculation of the velocity constants. During the latter part of the reaction the acid, through whose titration the rate of the reaction was being followed, was being used up by reacting with alcohol to reform ester and water. Because

of this fact and also because a more accurate determination of the equilibrium constant could be effected by entirely separate experiments, the later experiments were studied and data collected for only 40 to 60 minutes.

TABLE IV

Hydrolysis of Ethyl Acetate at 30° C.

0.912   moles $HClO_4$ per liter
52.81   moles H_2O per liter
(a) 0.6015 moles ethyl acetate per liter at beginning.

Time in mins.	moles HAc/liter(x)	Log(a-x)
0	0.0000	-.2208
2	0.0106	-.2285
4	0.0211	-.2363
6	0.0313	-.2440
8	0.0409	-.2513
10	0.0506	-.2589
15	0.0744	-.2781
20	0.0964	-.2966
25	0.1176	-.3152
30	0.1378	-.3338
40	0.1766	-.3717
50	0.2109	-.4083
65	0.2593	-.4657
75	0.2871	-.5125

To get the best values for each run the numbers of ml. of the standard NaOH solution required to neutralize the 10 ml. samples of the reaction mixture at various times were plotted against the times in minutes and the best curve drawn through the points and extrapolated to zero time. Fig. 1 is a representative graph; the points shown are those experimentally determined when the perchloric acid in the reacting solutions was 3.29 N and 2.97 N. respectively. From the curve were read the best values for the ml. required to neutralize the sample at 0, 1, 2, 4, 6, 10, 20, 30, and 40 minutes after the reaction had started. From
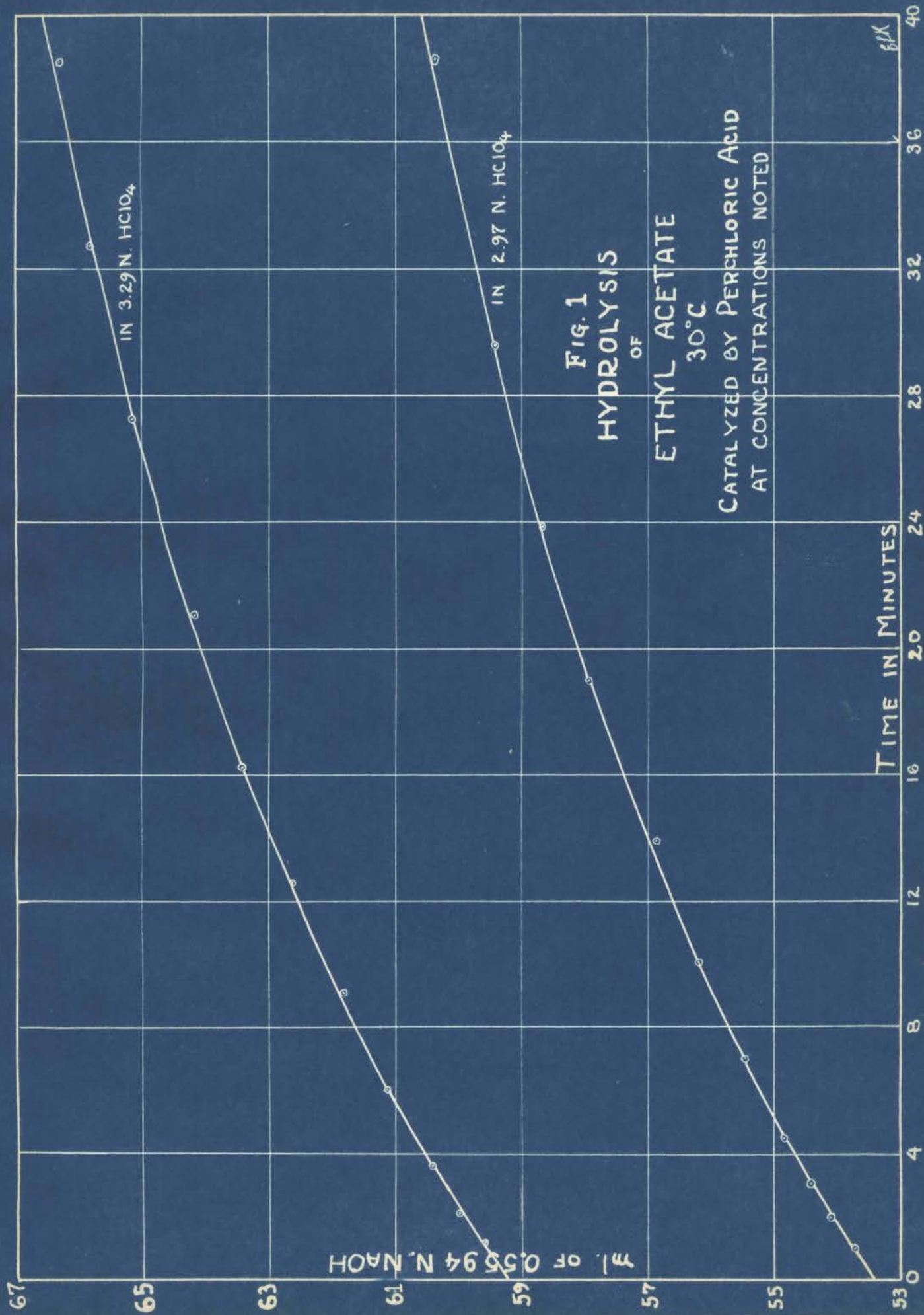
Fig. 1
HYDROLYSIS
of
ETHYL ACETATE
30°C
Catalyzed by Perchloric Acid
at concentrations noted

these values and the known normality of the NaOH solution, the amount of acetic acid in moles per liter that had formed was calculated.

The reaction is pseudo-first-order because it can be described by the equation for first order reactions:

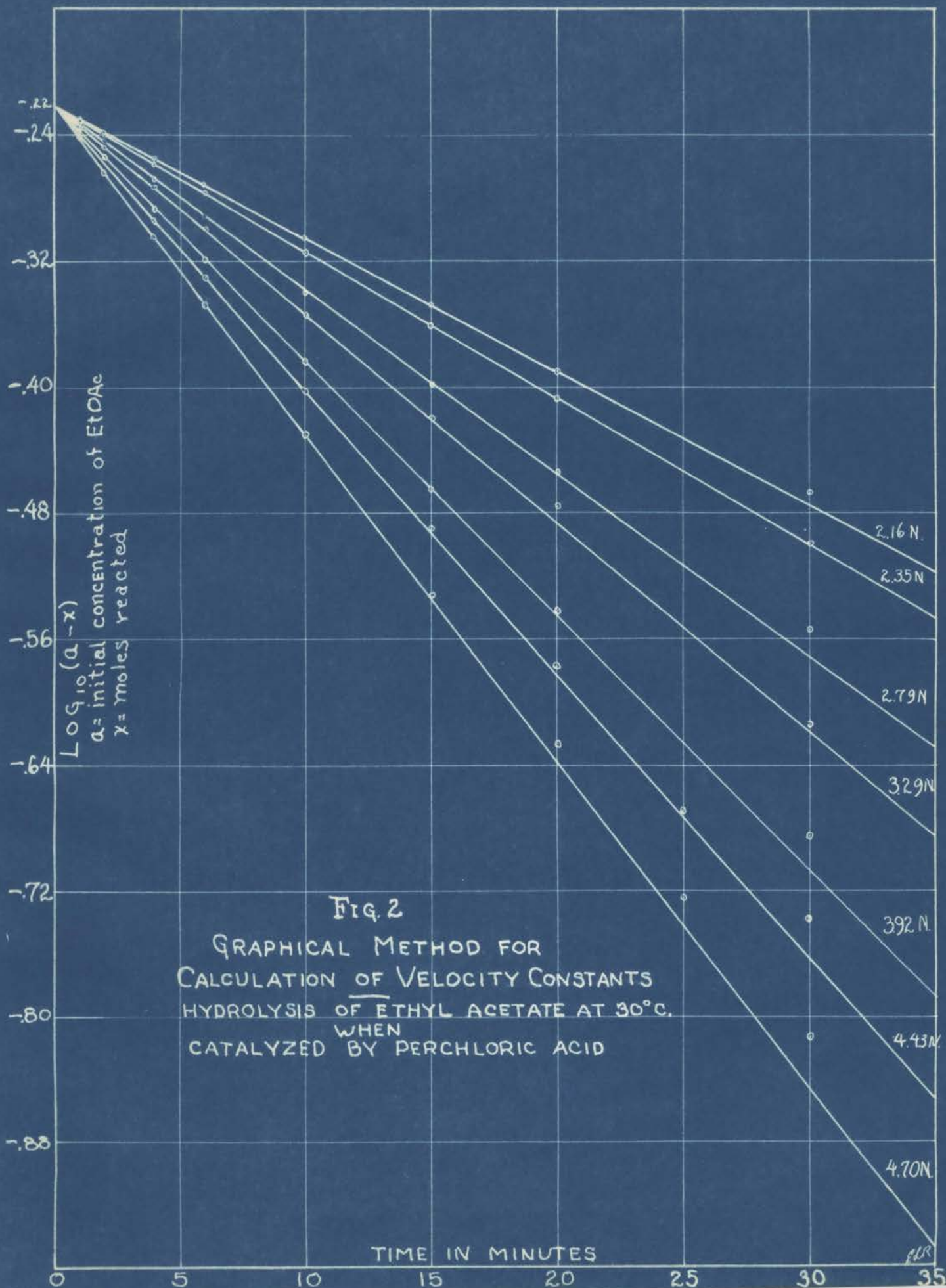$$(3) \qquad k' = \frac{1}{t} \ln \frac{a}{a - x} \quad .$$

Actually, however, the water present enters into the reaction and this fact must be taken into account. Without a knowledge of the concentration of the water, the measurement would be valueless. Thus we must use the equation

$$(4) \qquad k = \frac{1}{bt} \ln \frac{a}{a - x} \quad .$$

From equations (3) and (4) is seen that $k' = kb$. Therefore the true bimolecular constant for the reaction is obtained by dividing the "pseudo-unimolecular" constant, kb, by b, the concentration of the water in moles per liter.

Two methods for calculating the constant are possible: first, by substituting the data into the equation; second, by plotting $\log_{10} (a - x)$ against time and multiplying the slope of the line so obtained by 2.303. This last calculation gives kb, from which k is found by dividing by b. The two methods check well, but the latter method is simpler, hence it was used in all cases. Fig. 2 is a graph used to determine the velocity constants.

The final results of the hydrolysis experiments are shown in Table V which gives the concentration of the perchloric acid in the reacting solution, the "pseudo-

FIG. 2

GRAPHICAL METHOD FOR
CALCULATION OF VELOCITY CONSTANTS

HYDROLYSIS OF ETHYL ACETATE AT 30°C.
WHEN
CATALYZED BY PERCHLORIC ACID

unimolecular" constant, the amount of water present and the true constant calculated as described above. The constant k is in moles liter^{-1} min^{-1}.

TABLE V

Hydrolysis of Ethyl Acetate
Velocity Constants at 30° C.

Exp. No.	HClO$_4$ moles/liter (N)	kb (calculated)	H$_2$O moles/liter (b)	True k	k/N x 10^4
1	4.70	0.0480	43.66	0.001100	2.34
2	4.43	0.0418	44.50	0.000939	2.12
3	3.92	0.0376	45.51	0.000826	2.11
4	3.29	0.0307	46.97	0.000654	1.99
5	2.79	0.0270	48.09	0.000561	2.01
6	2.35	0.0214	49.21	0.000435	1.85
7	2.30	0.0213	49.33	0.000432	1.88
8	2.16	0.0193	49.67	0.000389	1.80
9	2.09	0.0197	49.83	0.000395	1.89
10	1.88	0.0173	50.38	0.000343	1.82
11	1.31	0.0125	51.74	0.000241	1.83
12	1.22	0.0116	52.02	0.000223	1.83
13	0.91	0.0087	53.09	0.000164	1.81

The final column of Table V gives the ratio of the velocity constant to concentration of HClO$_4$ x 10^4. It indicates that below about 2.5 N HClO$_4$ the rate of hydrolysis of the ethyl acetate is approximately proportional to the concentration of the acid. Above 2.5 N the reaction velocity increases more rapidly than does the concentration. This fact is shown graphically by Fig. 3, in which the velocity constants are plotted against time. This is in accord with the findings of Kendall and King (loc. cit.).

FIG. 3

HYDROLYSIS
OF
ETHYL ACETATE
30° C.

CATALYZED BY PERCHLORIC ACID

HClO₄ IN MOLES/LITER
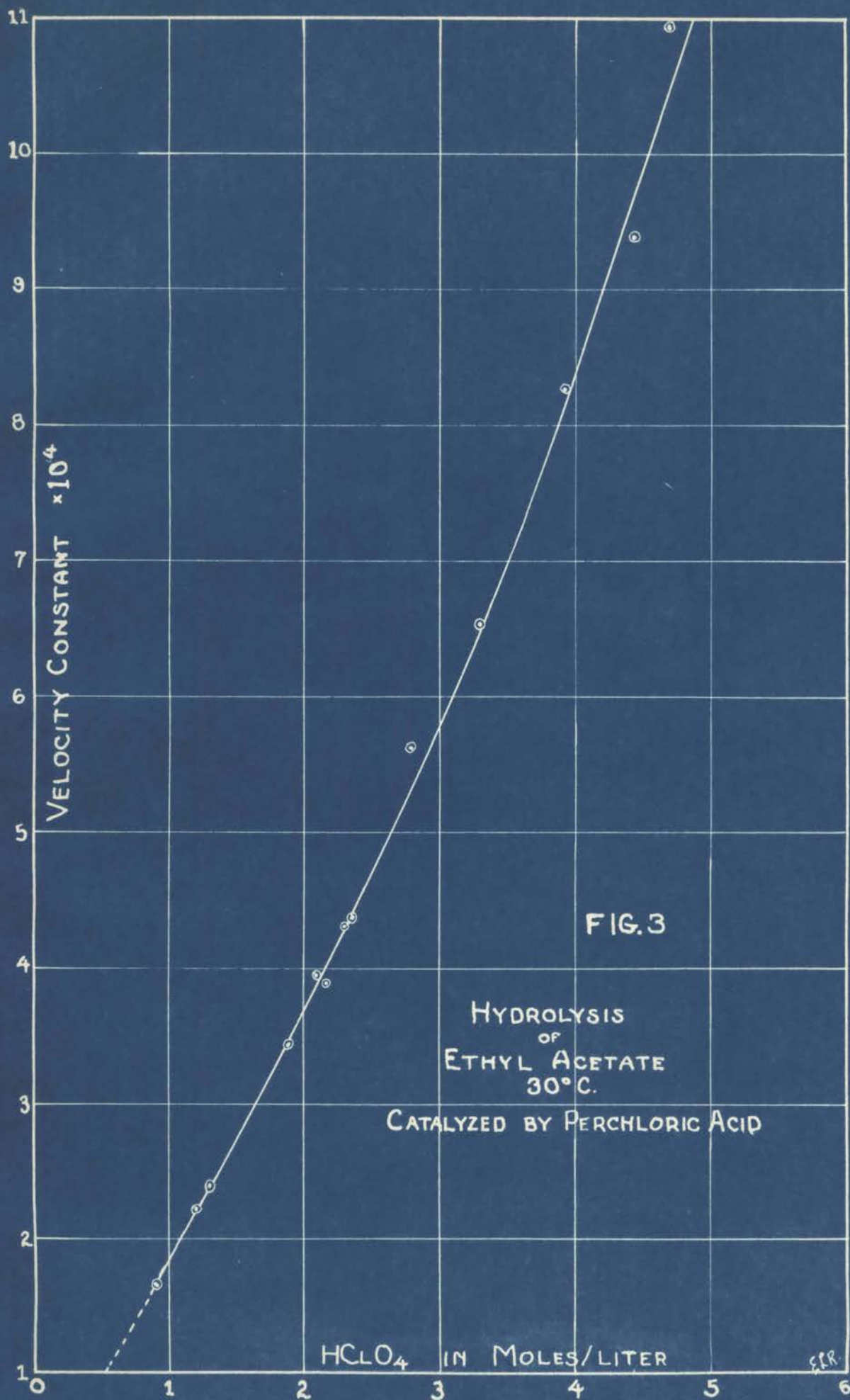
Kinetics of Esterification.

In each reaction studied, 10 ml. each of purified ethyl alcohol and acetic acid were added to 150 ml. of $HClO_4$ solution of known strength; the acetic acid was added first and the time of addition of the ethyl alcohol was taken as zero time. Samples were removed and titrated with approximately N/2 sodium hydroxide solution in the same manner as explained in the description of the hydrolysis experiments. Table VI gives the data on a representative experiment in which the concentration of the perchloric acid was 1.002 N. As in the case of the hydrolysis experiments, we found it needless to study the reactions further than the first 40 or 60 minutes in order to calculate the velocity constant.

The best values for the quantity of acetic acid which had reacted at definite times was found as described under "Kinetics of Hydrolysis". A typical graph is shown in Fig 4 for reactions in $HClO_4$ solutions of 2.70 and 2.52 N. From these graphs were read the ml. required at 0, 5, 10, 15, 20, 30, and 40 minutes. From these values and the known normality of the NaOH solution, the amount of acetic acid in moles per liter that had reacted was calculated.

To be certain that no oxidation of the ethyl alcohol by perchloric acid at the concentrations used was taking place, 10 ml. of the ethyl alcohol was added to about 150 ml. of the most concentrated acid used and tested for presence of chloride, which presumably would be formed, at intervals for over seven hours; the tests were negative. Also to make
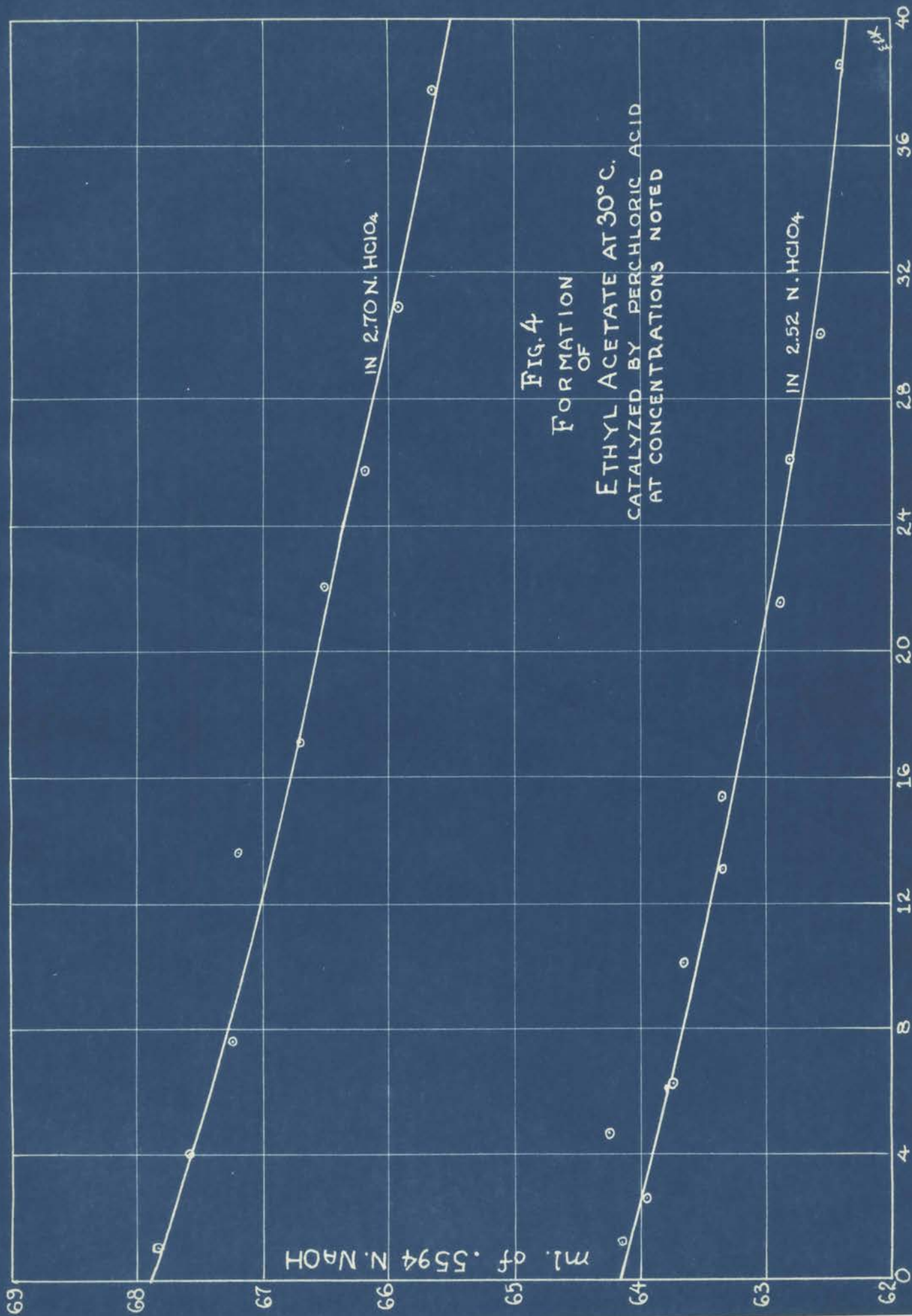
Fig. 4
Formation
of
Ethyl Acetate at 30°C.
catalyzed by perchloric acid
at concentrations noted

In 2.70 N. HClO₄

In 2.52 N. HClO₄

ml. of .5594 N. NaOH

sure that no chemical reaction between the $HClO_4$ and acetic acid was taking place that would invalidate the results, 10 ml. of the acetic acid used were added to 150 ml. of the most concentrated acid used: tests for over seven hours showed that there was no change in acidity.

Meyer, Julius and Sporman (22) found that ethyl perchlorate could be formed directly from ethyl alcohol and perchloric acid only in an anhydrous medium. Therefore no ethyl perchlorate was formed in our experiments because of the large amount of water present. Also Jones and Lapworth (loc. cit.) found that no appreciable amount of ethyl chloride was formed under the conditions of their experiments.

Two methods for the calculation of the velocity constants were possible. The first and conventional method is to substitute in the equation for reactions of the second order. This equation in its commonly accepted form is

$$(5) \qquad k = \frac{1}{t(a - x)} \ln\frac{b(a - x)}{a(b - x)}$$

where a and b are the initial concentrations in moles per liter of ethyl alcohol and acetic acid, respectively, and x is the number of moles per liter of either that have reacted in time t. However when the initial concentrations of acid and alcohol are close together the equation may be simplified to the following:

$$(6) \qquad k = \frac{1}{t} \frac{x}{a'(a - x)'},$$

where a' represents the geometric mean of a and b and (a-x)'
represents the geometric mean of (a-x) and (b-x). It was
found much more convenient to use equation (6) as the use of
equation (5) would necessitate the use of seven place log-
arithms. Table VI gives the constants as determined in this
way.

TABLE VI

Esterification
of Acetic Acid with Ethyl Alcohol-- 30° C.

$HClO_4$ 1.002 moles per liter
$HC_2H_3O_2$ 1.032 moles per liter (initial concentration)
C_2H_5OH 0.9224 moles per liter (initial concentration)

Time mins	ml. of .4475 N NaOH	diff.	moles/liter of acetic acid reacted (x).	k (equation 6)
0	45.31	0.00	0.00000	
5	45.23	0.08	0.00358	0.00075
10	45.15	0.16	0.00716	0.00076
15	45.07	0.24	0.01074	0.00074
20	45.00	0.31	0.01387	0.00073
30	44.86	0.45	0.02014	0.00072
40	44.75	0.56	0.02506	
50	44.65	0.66	0.02954	Average
60	44.57	0.74	0.03312	0.00074
70	44.50	0.81	0.03625	
80	44.44	0.87	0.03893	
100	44.36	0.95	0.04251	

The second possible method of calculation was graphical:
$\log_{10}$ (a-x)/(b-x) was plotted against time and the slope
of the straight line produced multiplied by 2.303/a-b. The
value of k for the same reaction tabulated in Table VI as
determined by this graphical method was 0.000732. This is
an excellent check and justifies the use of equation (6).

Table VII gives the results of the study of the ester-
ification reactions. The constant k is in moles liter^{-1} min^{-1}.

The final column again gives the relation between the velocity constant and the concentration of the $HClO_4$: this also increases abnormally with increase in molar concentration of the perchloric acid.

TABLE VII

Esterification
Velocity Constants at 30° C.

Exp. No.	$HClO_4$ (N) moles/liter	k	k/N x 10^4
1	4.26	0.02117	49.5
2	3.03	0.00497	16.4
3	2.83	0.00528	18.7
4	2.70	0.00401	14.8
5	2.52	0.00350	13.9
6	2.31	0.00304	13.2
7	1.98	0.00202	10.2
8	1.77	0.00159	9.00
9	1.46	0.00136	9.31
10	1.15	0.00099	8.62
11	1.002	0.000732	7.32
12	0.855	0.000626	7.32

These data are presented graphically in Fig. 5. The values of the velocity constants are plotted against time and the best curve drawn through the points. The point as determined in Experiment 1 is not plotted as the abnormal increase in the velocity constant at the higher concentrations of catalyst would make the rest of the curve insignificantly small if the scale was decreased so as to include that point on the graph.

FIG. 5
FORMATION OF
ETHYL ACETATE AT 30°C.
CATALYZED BY PERCHLORIC ACID
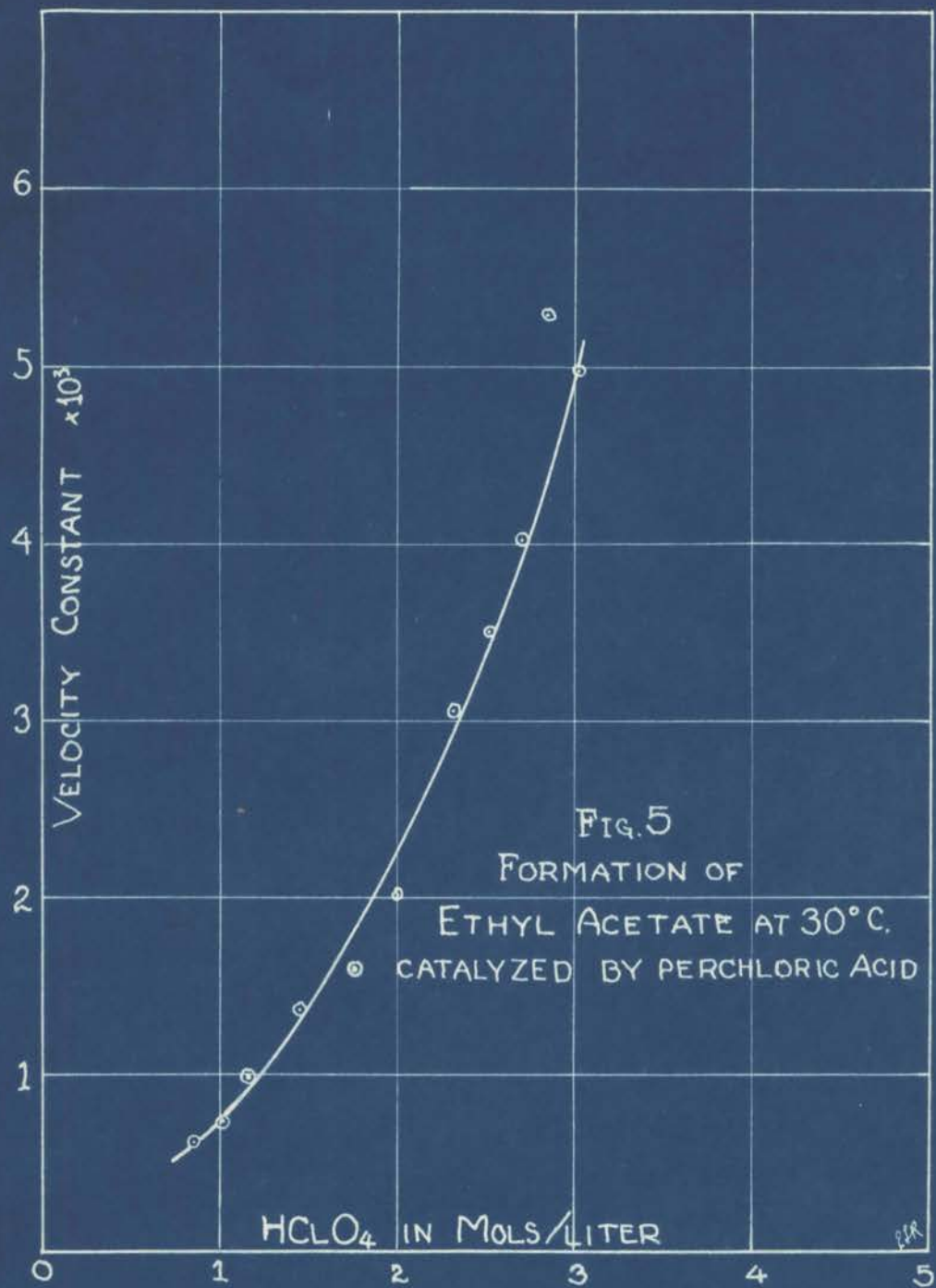
<u>Determination of the Equilibrium Constants.</u>

The determination of the equilibrium constants was carried out by a method similar to the one outlined by Daniels, Mathews, and Williams in "Experimental Physical Chemistry" (9). Essentially, this method consists in weighing the amount of the various constituents put into the reaction vessel and then, after sufficient time for the reaction to reach equilibrium, the reaction mixture is titrated with a standard solution.

In our experiments the reaction vessels were glass stoppered bottles of approximately 100 ml. capacity. In each case the weights of the reagents delivered by the pipette were determined. From these weights the quantities of $HClO_4$, ethyl alcohol, acetic acid and water at the start were calculated. In the greater number of experiments, 5 ml. of the $HClO_4$ solution whose concentration had already been determined were added to the bottle with a calibrated 5 ml. pipette. In a few experiments 10 ml. of the solution were added in like manner. To the acid was then added one ml. each of the purified ethyl alcohol and acetic acid and the bottle sealed air-tight to prevent loss by evaporation by covering the glass stopper with stop-cock grease. The bottles were then suspended in the thermostat at 30° C. for two or three days before titrating with the standard sodium hydroxide solution.

The equilibrium constants as determined by the hydrolysis reaction were somewhat erratic. On analysis of the

calculations we found that a very small error, even within the limits of experimental error, in the determination of the purity of the ethyl acetate, would be sufficient to cause the discrepancy found. For this reason, only those constants found as a result of the esterification reaction are presented.

The calculation was straightforward. The number of ml. of the sodium hydroxide solution required to neutralize the initial 5 ml. (or 10 ml.) of the perchloric acid solution was substracted from that amount required to neutralize the final mixture at equilibrium. This was a measure of the acetic acid left in solution, and since, in each case, the initial amount of acetic acid added was known (0.01595 moles), the moles of acetic acid which had disappeared was also the number of moles of ethyl alcohol reacted and the number of ethyl acetate formed. A simple calculation of the equilibrium constant followed from the equation:

(7)
$$K = \frac{[\text{water}] \times [\text{ethyl acetate}]}{[\text{acetic acid}] \times [\text{ethyl alcohol}]}$$

The water in the solution was that added with the reagents plus that formed by the reaction; the latter being almost insignificant.

Table 8 gives the results of the runs. The data are also presented in graphical form in Fig. 6 and the best line drawn through the points.
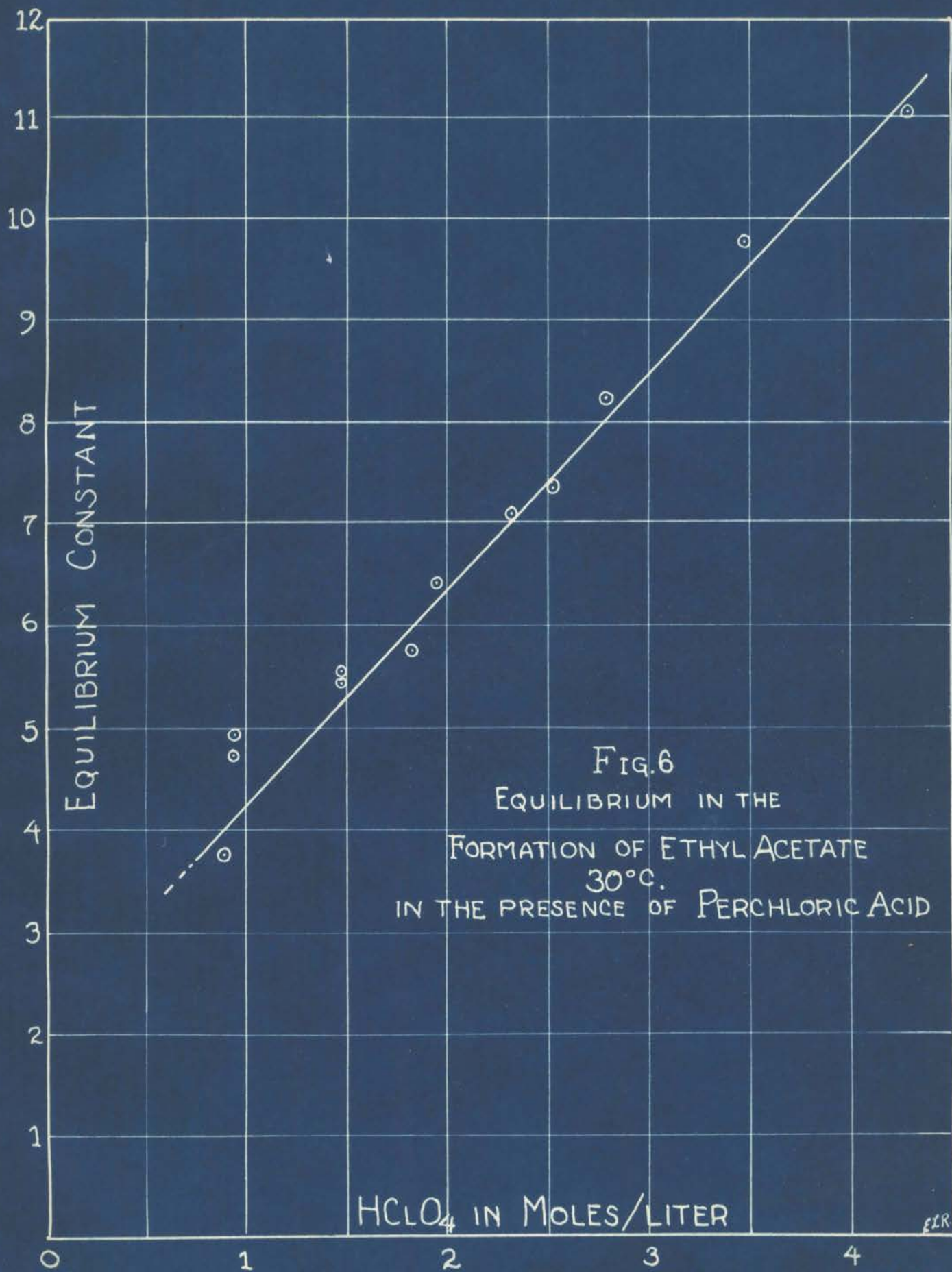
FIG. 6
EQUILIBRIUM IN THE
FORMATION OF ETHYL ACETATE
30°C.
IN THE PRESENCE OF PERCHLORIC ACID

TABLE VIII

Equilibrium Constants at 30° C.
as determined by Esterification Reaction

Ethyl Alcohol added-- 0.01728 moles
Acetic Acid added -- 0.01595 moles
Sodium Hydroxide solution--.4403 N.

Run No.	$HClO_4$ in react. sol. (moles/l)	Excess NaOH (ml.)	Moles EtOH left	Moles HAc left	Moles EtOAc formed	Moles H_2O (final)	K
7-8	0.88	37.26	.01508	.01641	.00087	1.0603	3.73
47	0.93	31.78	.01266	.01399	.00329	0.2664	4.95
48	0.93	31.99	.01276	.01409	.00319	0.2664	4.73
43	1.47	30.98	.01231	.01364	.00364	0.2575	5.58
44	1.47	31.10	.01236	.01369	.00359	0.2575	5.46
15-16	1.82	33.95	.01362	.01495	.00233	0.5033	5.76
39-40	1.94	30.01	.01188	.01321	.00407	0.2502	6.49
35-36	2.32	29.35	.01159	.01292	.00436	0.2438	7.10
31-32	2.52	28.84	.01137	.01270	.00458	0.2399	7.32
28	2.79	28.22	.01110	.01243	.00485	0.2356	8.28
23-24	3.47	26.92	.01052	.01185	.00543	0.2195	9.80
19-20	4.26	25.82	.01004	.01137	.00591	0.2130	11.03

When these data are plotted, a straight line may be drawn through the points as shown in Fig. 6.

DISCUSSION AND CONCLUSIONS

The results we have gained by this research are shown graphically: the velocity constants for the forward reaction in Fig. 5, those for the back reaction in Fig. 3, and the equilibrium constants in Fig. 6. Reading off the values of the three constants at concentration intervals of 0.25 moles per liter we find the data of Table IX. Here n is normality of the perchloric acid, k_1 is the constant of the forward reaction and k_2 the constant for the back reaction. The fourth column gives the values of the ratio k_1/k_2 while the fifth column gives the values of K, the equilibrium constant as determined by direct experiment.

TABLE IX

Relation of k_1/k_2 to K

n	k_1 x 10^4	k_2 x 10^4	k_1/k_2	K
1.00	7.4	1.82	4.06	4.05
1.25	10.2	2.26	4.51	4.60
1.50	13.8	2.73	5.06	5.17
1.75	18.0	3.20	5.63	5.70
2.00	22.6	3.67	6.02	6.24
2.25	27.8	4.23	6.57	6.80
2.50	33.0	4.70	7.03	7.32
2.75	40.3	5.26	7.57	7.86
3.00	48.2	5.84	8.25	8.40
3.25	(57.7)*	6.45	----	8.95
3.50	(67.5)	7.10	----	9.50
3.75	(77.0)	7.70	----	10.00
4.00	(88.6)	8.36	----	10.60

*Calculated

As will be seen, the values of columns four and five agree well; showing that, for this reaction, the ratio of velocity constants is equal to the equilibrium constants within the

limits of experimental error. This, then, verifies the relation set forth in Equation (1) for this reaction.

In order to show the probable values of the constant of the forward reaction, a number of values have been calculated from Equation (1) for concentrations of acid between 3 and 4 moles per liter. These values are given in parenthesis in column 2.

It is impossible to compare our results with those of others because we have found no data determined under conditions comparable to ours. There is no doubt, however, that $HClO_4$ is an excellent catalyst for this reaction.

SUMMARY

1. We have found in the literature five cases in which the generally accepted equation $k_1/k_2 = K$ has been proved true by measuring experimentally all three quantities.

2. We have added more complete data upon one of these reactions: namely, the reversible reaction;

$$C_2H_5OH + CH_3COOH \rightleftharpoons C_2H_5\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + H_2O.$$

We have made a study of this reaction at 30° C. using perchloric acid as catalyst over a wide range of concentrations.

3. The velocity of esterification increases with concentration of the catalyst, $HClO_4$, more rapidly than does this concentration. The rate of increase of velocity is greater at the higher concentrations. The velocity constants range from 0.00074 at 1 n. to 0.00482 at 3 n., i.e., the reaction goes 6.5 times as rapidly when the catalyst is 3 n. as when it is 1 n.

4. We also find that the velocity of hydrolysis of ethyl acetate increases faster than the increase in concentration of perchloric acid catalyst. The velocity constants for hydrolysis range from 0.000182 at 1 n. to 0.000836 at 4 n., i.e., the reaction goes 4.6 times as fast when the catalyst is 4 n. as when it is 1 n.

5. We find a straight line relation between the equilibrium constant and the concentration of the catalyst. At 1 n. in perchloric acid we find that K is 4.05 while at 4 n. K is 10.60.

6.   As suggested by other workers, we find that perchloric
acid is an excellent catalyst for esterification and hy-
drolysis reactions.

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AUTOBIOGRAPHY

I, Earl Leroy Richardson, was born in Lebanon, Missouri on the twenty first day of March, 1917. I received my elementary and secondary education in the public schools of Springfield, Missouri. I graduated from Springfield Senior High School in June, 1933. In February, 1934, I enrolled in Drury College in Springfield, Missouri. My undergraduate work was completed in January, 1938, and I received my Bachelor of Science degree, cum laude, from that institution in June, 1938.

In February, 1938, I enrolled in the Graduate School of the Oklahoma Agricultural and Mechanical College. I will complete the requirements for the Master of Science degree in Physical Chemistry in July, 1939.

TYPIST:

Earl L. Richardson