KINETICS OF THE REACTION BETWEEN FORMIC ACID AND

PERMANGANATE IN AQUEOUS ACID SOLUTION

by

SANDRA MARGARET TAYLOR

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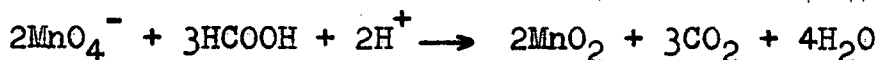
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ABSTRACT

The kinetics of the oxidation of formic acid by permanganate in aqueous perchloric acid solution, i.e.,

$$2MnO_4^- + 3HCOOH + 2H^+ \longrightarrow 2MnO_2 + 3CO_2 + 4H_2O$$

were studied in the temperature range 15 to 35°C. The variables examined included the reactant and hydrogen ion concentrations, ionic strength, the presence of various metal ions, and solvent and reactant deuterium isotope effects.

The reaction appears to proceed through two independent paths in which the rate-determining steps are bimolecular reactions of permanganate with formic acid and with formate ion, respectively. The kinetics are thus of the form

$$-d\left[MnO_4^-\right] / dt = \left[MnO_4^-\right] \left[HCOOH\right] (k_A + k_B K_1 / \left[H^+\right])$$

where k_A and k_B are rate constants of the two bimolecular reactions involving formic acid and formate ion, respectively, and K_1 is the ionization constant of formic acid. The Arrhenius expressions for the rate constants were found to be $k_A = 1.1 \times 10^9 exp. (-16400/RT)$ l.mole^{-1}sec^{-1} and $k_B = 7.8 \times 10^9 exp. (-13000/RT)$ l.mole^{-1}sec^{-1}.

The formate ion reaction exhibits a large deuterium (HCOO$^-$:DCOO$^-$) isotope effect which suggests cleavage of the C-H bond in the rate-determining step. The

absence of a corresponding isotope effect in the formic acid reaction suggests that it proceeds by a different mechanism.

Fe^{+++} (but not Ag^+, Cu^{++}, $C6^{++}$ or Na^+) was found to catalyze the reaction, possibly by a mechanism involving a $FeMnO_4^{++}$ complex.

Previous investigations of the formic acid-permanganate system have been confined to lower acidities than the present one, and only the formate ion contribution to the reaction had been detected.

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Department of _____Chemistry_____

The University of British Columbia,
Vancouver 8, Canada.

Date_____April 16, 1958._____

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INTRODUCTION

I. General

Considerable progress has been made in recent years toward the understanding of the kinetics and mechanism of simple oxidation-reduction reactions in aqueous solution. Some oxidizing agents whose reactions have been examined in some detail are Ag^+,[20,54] Cu^{++},[12,13,14] Hg^{++},[15,51] Hg_2^{++},[15,51] MnO_4^-,[18,32,47,54,57] Tl^{+++},[17] O_2[16] and $Cr_2O_7^=$.[14,25,41,42] Among the reducing agents subjected to study have been H_2,[12,23,54] U (IV),[16] HCO_2^-,[1,17,21,25,32,41,42,46,57] benzhydrol,[56] and other simple organic species.[5,7,10,20,31,34,53] The present study of the reaction between HCOOH and MnO_4^- is another contribution to this general field. The choice of this particular reaction was based, in part, upon the following considerations.

1. The kinetics of the reduction of MnO_4^- by various organic substances and by molecular H_2 have been thoroughly investigated.[32,54,56,57] A comparison of the reactions of H_2 and of HCOOH was considered to be of particular interest in view of certain similarities between the two molecules. Both are two-electron reductants with very similar oxidation potentials.[28]

2. It was anticipated that the stoichiometry of the reaction would be simple and clear cut; the reduction product of MnO_4^- being exclusively MnO_2, and the oxidation products of HCOOH, exclusively H_2O and CO_2.

3. The kinetics of the reaction between HCO_2^- and MnO_4^- have previously been investigated in some detail [19,32,57]. It was hoped, by extending these investigations to higher acidities, to establish also the kinetics of the reaction between undissociated HCOOH and MnO_4^-. In view of the important effects which various metal ions have been found to exert on several other oxidation-reduction reactions [12], it was proposed also to explore such effects in this reaction. It was also hoped to obtain some information about the mechanism of the reaction through an examination of kinetic isotope effects.

II. Previous Kinetic Work Leading to the Present Investigation

Among the oxidizing agents whose reactions with aqueous HCOOH have been kinetically examined are Hg^{++} [51], Hg_2^{++} [51], Co^{+++} [1,46], Tl^{+++} [17] and MnO_4^- [21,32,57]. The reactions of HCOOH with Hg^{++}, Hg_2^{++} and Co^{+++} have been postulated to involve a one-electron transfer from $HCOO^-$ to the oxidant resulting in formation of formyl radical ($HCOO\cdot$). These reactions are apparently second-order kinetically. The estimated Arrhenius frequency factors for these reactions

were abnormally high for bimolecular rate-determining steps (10^{15} - 10^{10} l-mole^{-1}sec^{-1}). [1,46,51] For the reaction between HCOOH and Tl^{+++} simple kinetics have been observed, and a mechanism was proposed involving formation of a complex (Tl·HCOOH^{+++}) which decomposes in the rate-controlling step to form the products, Tl$^+$, CO_2 and H$^+$. [17]

A number of kinetic investigations have also been made of the reaction between MnO_4^- and HCOOH (or HCO_2^-). Holluta, [22] Orlov, [35] Hatcher and West, [19] and later, Hill, Mann and Tompkins [21,32,50] studied this reaction in neutral and slightly acid solution. The overall kinetics observed were of second order: first order in MnO_4^- and in HCO_2^-; and the activation energy and frequency factor of the reaction were evaluated. It was found that the rate of oxidation was independent of pH when the acidity was low enough to ionize most of the formic acid. HCOO$^-$ was observed to be oxidized much more rapidly than HCOOH, and a primary salt effect indicated that the reaction involved two similarly-charged ions. The mechanism proposed involved oxygen transfer from MnO_4^- to HCO_2^-, with subsequent decomposition of the activated species to CO_2 and OH$^-$.

More recently, Wiberg and Stewart examined the kinetics of the reaction between MnO_4^- and HCO_2^- in basic solution, and found similar results. [57] The rate was found to be substantially independent of pH, and HCO_2^- reacted more rapidly than HCOOH. Through the use of O^{18}- labelled

MnO_4^- it was determined that considerable amounts of oxygen in the CO_2 product came from MnO_4^-. However, a large deuterium isotope effect (7.4) was also observed. These results suggested that the oxidative mechanism involved simultaneous oxygen transfer from MnO_4^- to HCO_2^-, and hydride transfer (or similar process) from HCO_2^- to MnO_4^-. Several possible mechanisms were considered.

The reduction of MnO_4^- in aqueous solution by H_2 was first reported in 1859.[2] Kinetic studies of this reaction were made in 1911 by Just and Kauko,[23] and more recently by Webster and Halpern.[54] The reaction proceeds by simple second-order kinetics and apparently involves Mn(V) as an intermediate. An interesting feature of this reaction is its marked susceptibility to catalysis by Ag^+. It has been suggested that the catalyzed reaction proceeds via a Mn(VI) intermediate. Some kinetic measurements have also been made on the reduction of MnO_4^- by CO.[24] The reaction is first order in each species. The observed rates of oxidation of CO are of similar magnitude to rates of H_2 oxidation, and the apparent activation energies are similar.

Reactions of MnO_4^- with various organic substances[29] have been examined, including ethylenes,[3,10,40,53] carbonyls,[7,47] alcohols[5,34,44,47] and acids.[31] Initial attack by Mn(III) or its complexes (MnX_2^+) is postulated for the oxidation of oxalate, followed by fast reduction in several stages to form Mn(II).[31] Oxidative attack of

enolized aldehydes and ketones by Mn(III) has also been suggested.[7] However, the majority of permanganate reactions are believed to proceed via conversion of MnO_4^- to Mn(V) (as $MnO_4^{\equiv}$ or MnO_3^-), either by two electron (or hydride ion) transfer from the substrate to MnO_4^-, or by transfer of an oxygen atom from MnO_4^- to the substrate.[8,32,37,40,43,48,54,57] On the basis of isotopic studies Wiberg and Stewart have suggested mechanisms for the permanganate oxidation of benzhydrol[43,56] involving simultaneous oxygen and hydrogen transfer. A number of these considerations are relevant to the present investigation.

EXPERIMENTAL METHODS

I. Materials

Baker and Adamson HCOOH was redistilled twice to remove impurities. $KMnO_4$ was an Analar product of high purity. This reagent was dissolved in distilled water and heated at the boiling point for several hours followed by filtration to remove MnO_2. Reagent grade $HClO_4$ from Merck (61%) and from Baker and Adamson (70%) were employed. Other chemicals were of reagent grade. Distilled water was used throughout. Deuterium oxide (99.5% isotopically pure) was obtained from Stuart Oxygen Co.; the isotopic purity was confirmed by N.M.R. measurements.

II. Preparation and Standardization of Reagents

Solutions of $KMnO_4$ were standardized against anhydrous sodium oxalate. HCOOH and $HClO_4$ solutions were standardized with carbonate-free NaOH solutions of known concentration. A $Fe(ClO_4)_3$ solution was prepared as follows:[30] to a solution containing 100 gm. $FeCl_3$, a solution of NaOH(6N) was added slowly with stirring. The precipitate of $Fe(OH)_3$ was purified by reprecipitating from $HClO_4$ and washing several times. The solid $Fe(OH)_3$ precipitate was added to 200 ml. $HClO_4$ (61%) and this mixture refluxed for 12 hours, after which the hydroxide was

completely dissolved. Fe^{+++} in the resulting $Fe(ClO_4)_3$
solution was determined by adding excess I^- (IO_3^- -free)
and titrating the I_2 liberated with standard thiosulphate.
The acidity of the $Fe(ClO_4)_3$ solution was determined
potentiometrically using a Beckman H-2 pH meter.

Deuterated Formic Acids

DCOOD and DCOOH were synthesized using the
procedure described by Stewart:[44]

Oxalic acid dihydrate (126 gm., 1 mole) was
equilibrated several times with D_2O. Glycerol (10 gm.) was
twice equilibrated with D_2O. After complete equilibration,
the deuterated oxalic acid (dideuterate) was slowly added to
the heated glycerol, and catalyzed decarboxylation of oxalic
acid occurred. The reaction mixture was continuously
distilled, and after purification the product of DCOOD in D_2O
contained 0.85 moles DCOOD (85% yield, 93 ml. containing
.00914 equivs. per ml.).

DCOOH was prepared by diluting a small quantity of
the DCOOD - D_2O solution with H_2O. The isotopic purity of the
DCOOD - D_2O solution was found to be over 99%, using N.M.R.
determination.

Deuterated perchloric acid was prepared by
equilibrating $HClO_4$ (165 gm., 70% $HClO_4$) five times with
30 ml. D_2O, excess water being removed by distillation under
reduced pressure after each addition of D_2O. An examination

of its N.M.R. spectrum showed it to be 85.5% isotopically pure. The final solutions employed in kinetic experiments were diluted to 1 M with D_2O, and thus had an isotopic purity of over 98%.

III. Kinetic Measurements and Analytical Determinations

The rates of the reactions were measured by the following methods:

A. Spectrophotometric Method

A blackened glass reaction vessel of 100 ml. capacity, containing known amounts of HCOOH, $HClO_4$ and $NaClO_4$ solutions, was immersed in a water bath thermostatically controlled to $\pm 0.05°C$. A separate vessel containing $KMnO_4$ and another containing distilled water were also allowed to come to the same temperature. An aliquot of $KMnO_4$ was subsequently pipetted into the reaction flask, and the reaction mixture made up to 100 mls. by adding water. At appropriate times, samples of the reaction mixture were withdrawn, quenched by cooling to 0°C, and centrifuged to remove MnO_2. MnO_4^- concentrations were measured using a Beckman D.U. Spectrophotometer at the MnO_4^- peak wavelength of 522 mμ.

This method was found to be unsatisfactory because of difficulty in removing all colloidal MnO_2 from the samples by centrifugation. Optical density measurements were inaccurate because of this.

B. Ferrous-Dichromate Titration Method

As in the preceding method, samples from a single reaction mixture were withdrawn at suitable times, cooled to $0°C$, and centrifuged to remove MnO_2. Aliquots of each solution were quenched with a known quanitity of ferrous sulphate. The quenched solutions were back-titrated with standard dichromate, using sodium diphenylamine sulphonate as the indicator. Again, difficulty in removing all MnO_2 from the samples was experienced, and the indicator proved unsatisfactory in cases where a large amount of MnO_4^- had been present in the sample. However, results obtained using this method agreed at least qualitatively with those obtained using the following method:

C. Iodide-Thiosulphate Titration Method

Brown glass reaction vessels, all containing known quantities of $HCOOH$, $NaClO_4$ and $HClO_4$ were immersed in the thermostatically-controlled water bath. A solution of $KMnO_4$ also was heated in the bath, and subsequently, aliquots of $KMnO_4$ were pipetted into the reaction flasks, which were shaken to ensure uniformity. Each reaction mixture was quickly quenched at the required time with an excess of KI. The I_2 liberated was titrated with standard sodium thiosulphate solution using starch indicator.

This method proved to be most satisfactory because instantaneous quenching could be achieved, and analysis for

MnO_4^- does not necessitate removal of MnO_2. Quenching time did not exceed two seconds.

Concentrations of KI and $Na_2S_2O_3$ solutions were suited to reaction concentrations, and ranged as follows: KI - 0.025N to 0.5N; $Na_2S_2O_3$ - 0.01N to 0.1N. Uncertainty at the end point did not exceed 0.003 ml. of 0.01N thio-sulphate for most of the titrations. Experimentally measured rates were reproducible to within 5% in most cases. Reactions were conducted in the temperature range 15 to 35°C; most of the experiments being conducted at 30°C.

The reaction rate was found to be unaffected by glass wool (evidence for homogeneous character) and by light. (These results are shown in Table VIII.) Acidic solutions of the separate reactants (HCOOH and MnO_4^-) were found to be stable.

Ionization constants for DCOOH and HCOOH were determined over the temperature range 15° to 36°C by measuring the pH of solutions of known HCOOH - $HCOO^-$ concentration ratios (concentrations ranging from 0.2 to 0.05 M) with a Beckman Model G pH meter. The ionic strength was maintained constant at 1.0M with $NaClO_4$.

RESULTS AND DISCUSSION

I. Stoichiometry of the Reaction

When HCOOH was present in excess, MnO_4^- was found to be reduced quantitatively to MnO_2. (Table I.) Further reduction of MnO_2 by HCOOH was slow. When MnO_4^- was present in excess, that amount of MnO_4^- reduced to MnO_2 was found to be two-thirds of the initial HCOOH concentration. Further reduction of MnO_4^- was slow and could be neglected in the time taken for the kinetic experiments. Results are shown in Table I, page 12. These observations are consistent with the expected stoichiometry of the reaction represented by:

$$2MnO_4^- + 3HCOOH + 2H^+ \longrightarrow 2MnO_2 + 3CO_2 + 4H_2O \quad . \quad . \quad . \quad . \quad . \quad 1$$
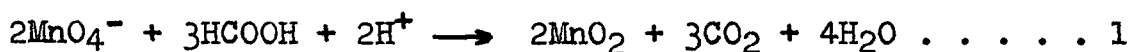
II. Kinetics of the Reaction: Effect of Reactant
    Concentration

A series of experiments was made in which the concentration of $HClO_4$ was maintained at 0.601M. The initial concentration of MnO_4^- was varied from 0.0004M to 0.0016M while the initial concentration of HCOOH was in large excess (0.0970M). Ionic strength was maintained constant at 1.0M by the addition of $NaClO_4$. Typical first order rate plots (the reaction is pseudo-first order since the concentration of HCOOH which is in large excess is essentially constant throughout the reaction) are shown in Figure 1, page 13. No

TABLE I

STOICHIOMETRY OF THE REACTION BETWEEN MnO_4^- AND HCOOH

| Temperature = 30.1°C | | | Ionic strength = 1.0M | |
| Expt. No. | Initial Conc. ($M \times 10^3$) | | $HClO_4$ | MnO_2 formed |
	MnO_4^-	HCOOH	(M)	($M/L \times 10^3$)
A_3	1.002	97.0	0.601	0.948
A_5	0.502	97.0	0.601	0.486
A_6	0.252	97.0	0.601	0.250
R_1	40.18	10.29	1.02	6.76
R_2	40.18	10.29	1.02	6.84
R_4	40.18	10.29	1.02	6.80

Figure 1
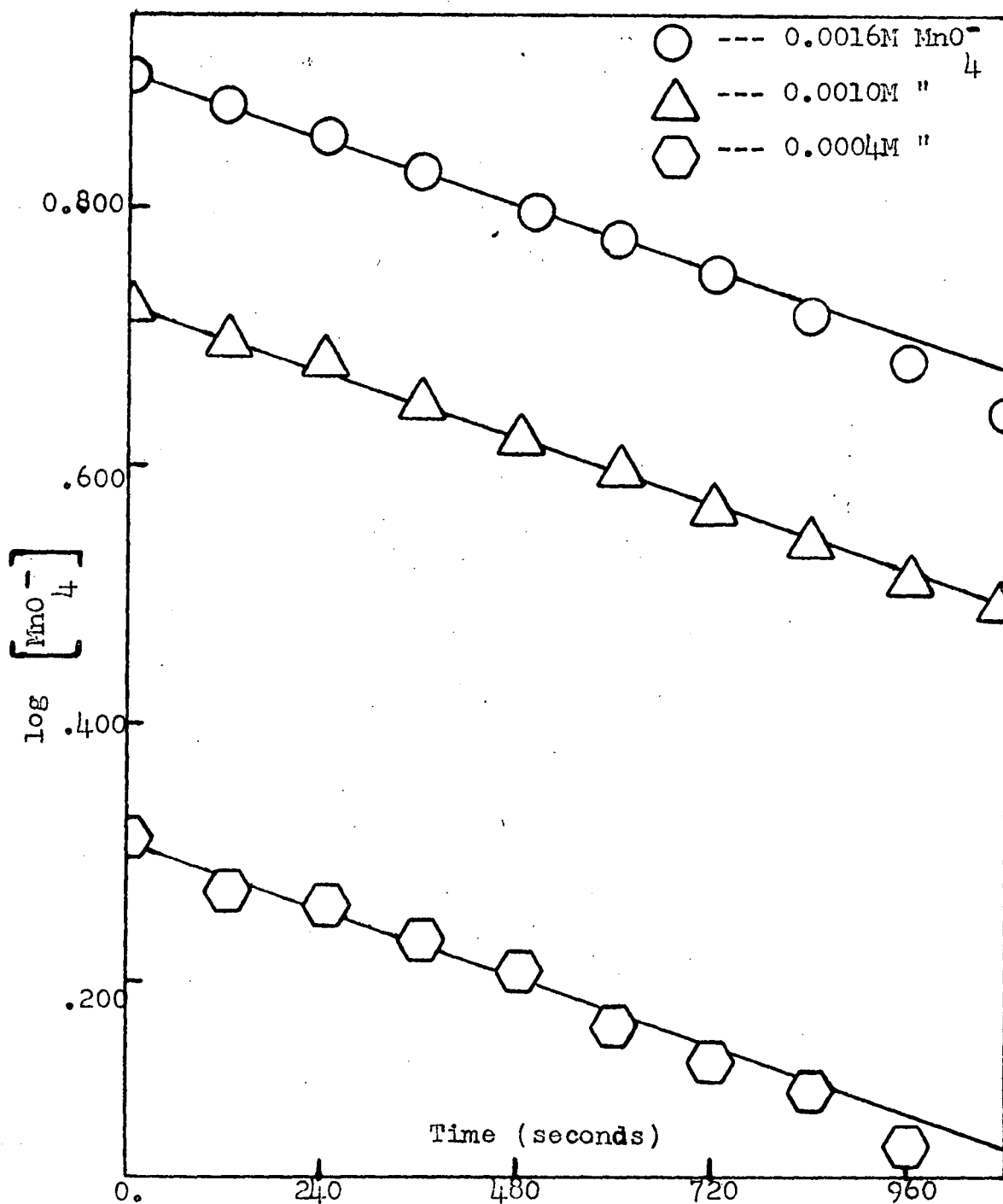
First- Order Rate Plots at Constant HCOOH and Varying

MnO$_4$ Initial Concentrations. HCOOH--0.0970M. HClO$_4$ --0.601M.

μ--1.0 M. Temperature--30.1°C.

observable change in the slopes was apparent over the range of initial MnO_4^- concentrations employed. The results showed the reaction to be first order in MnO_4^- under these conditions.

A second series of experiments was conducted in which the initial MnO_4^- concentration was maintained constant at 0.0010M, while the initial HCOOH concentration was varied from 0.00 to 0.1212M. Solutions were 0.601M in $HClO_4$ and the ionic strength was held constant at 1.0M using $NaClO_4$. The results of these experiments are shown in Table II, page 15, and Figures 2 and 3, pages 16 and 17 respectively. The pseudo-first order rate plots (Figure 3) were again linear; however the slope varied with the HCOOH concentration. Pseudo-first order rate constants (k') were found to be directly proportional to the HCOOH concentrations. (See Figure 4.) Thus the overall kinetics are seen to be of second order (first order both in HCOOH and in MnO_4^-), i.e.,

$$-\frac{d[MnO_4^-]}{dt} = k'' \; [MnO_4^-] \; [HCOOH] \quad \ldots \ldots \ldots \ldots 2$$

When the concentration of HCOOH remains effectively constant during a given experiment, this reduces to

$$-\frac{d[MnO_4^-]}{dt} = k' \; [MnO_4^-] \quad \ldots \ldots \ldots \ldots \ldots 3$$

where $k' = k'' \; [HCOOH]$.

In these and subsequent experiments, values of k', and hence

TABLE II

EVIDENCE FOR SECOND ORDER KINETICS

Expt. No.	Temperature = 30.1°C Initial Conc. (M)			Ionic strength = 1.0M $k'x10^4$	$k''x10^3$
	MnO_4^-	HCOOH	$HClO_4$	sec^{-1}	$1-m^{-1}s^{-1}$
J_1	–	0.0970	0.601	–	–
S_1	0.0004	0.0970	0.601	5.10	5.25
N_1	.0010	0.0970	0.601	4.87	5.02
M_1	.0010	0.0970	0.601	4.90	5.05
R_1	.0016	0.0970	0.601	4.90	5.05
K_1	.0010	–	0.601	–	–
U_1	.0010	0.0485	0.601	2.45	5.06
M_1	.0010	.0970	0.601	4.90	5.05
N_1	.0010	.0970	0.601	4.87	5.02
T_1	.0010	.1212	0.601	6.18	5.06

Figure 2
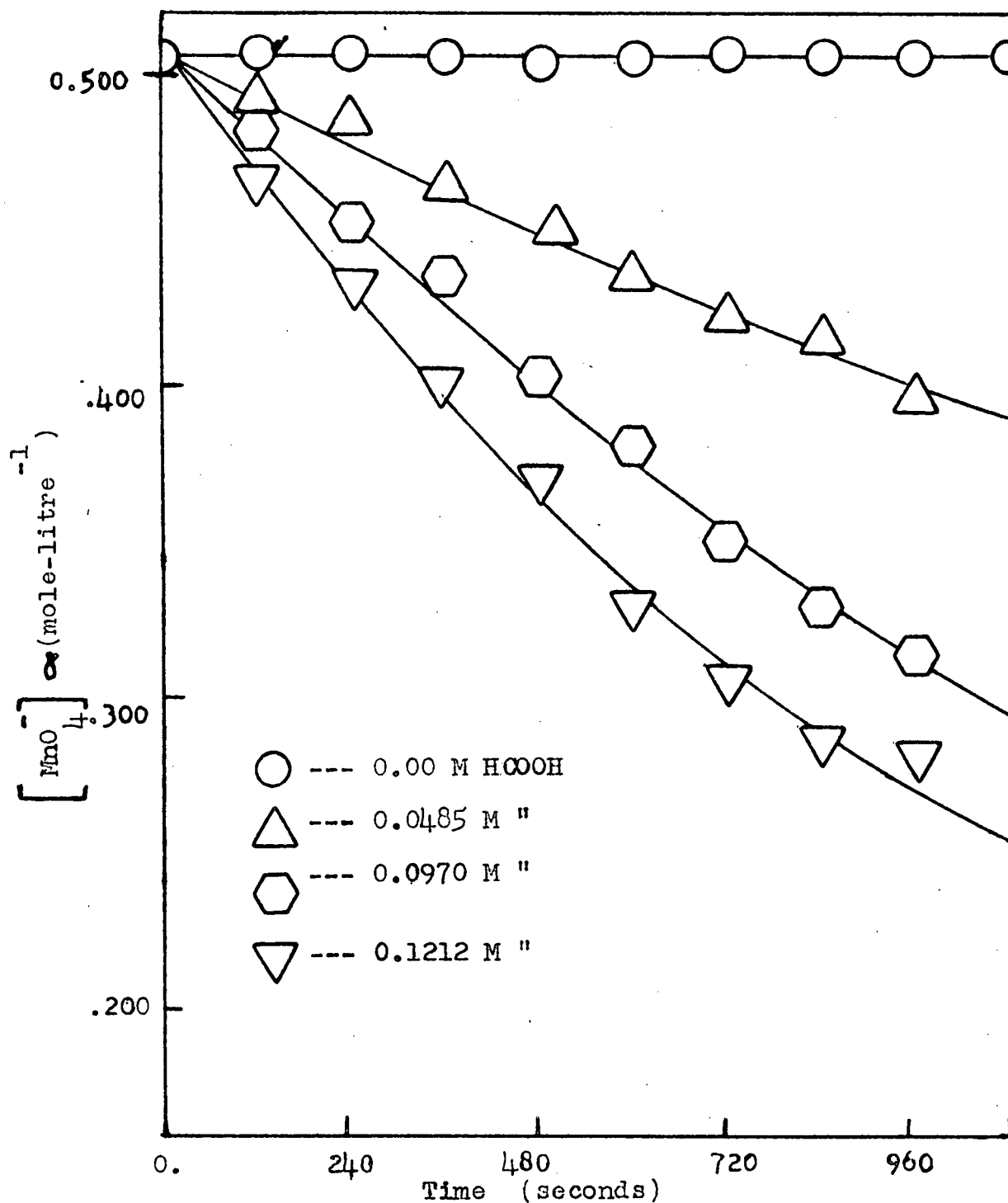
Typical Rate Plots for Reaction in Solutions Containing Different (Excess) HCOOH Concentration. Initial MnO$_4^-$-- 0.0010 M. HClO$_4$ --0.601 M. μ--1.0M. T---30.1°C.
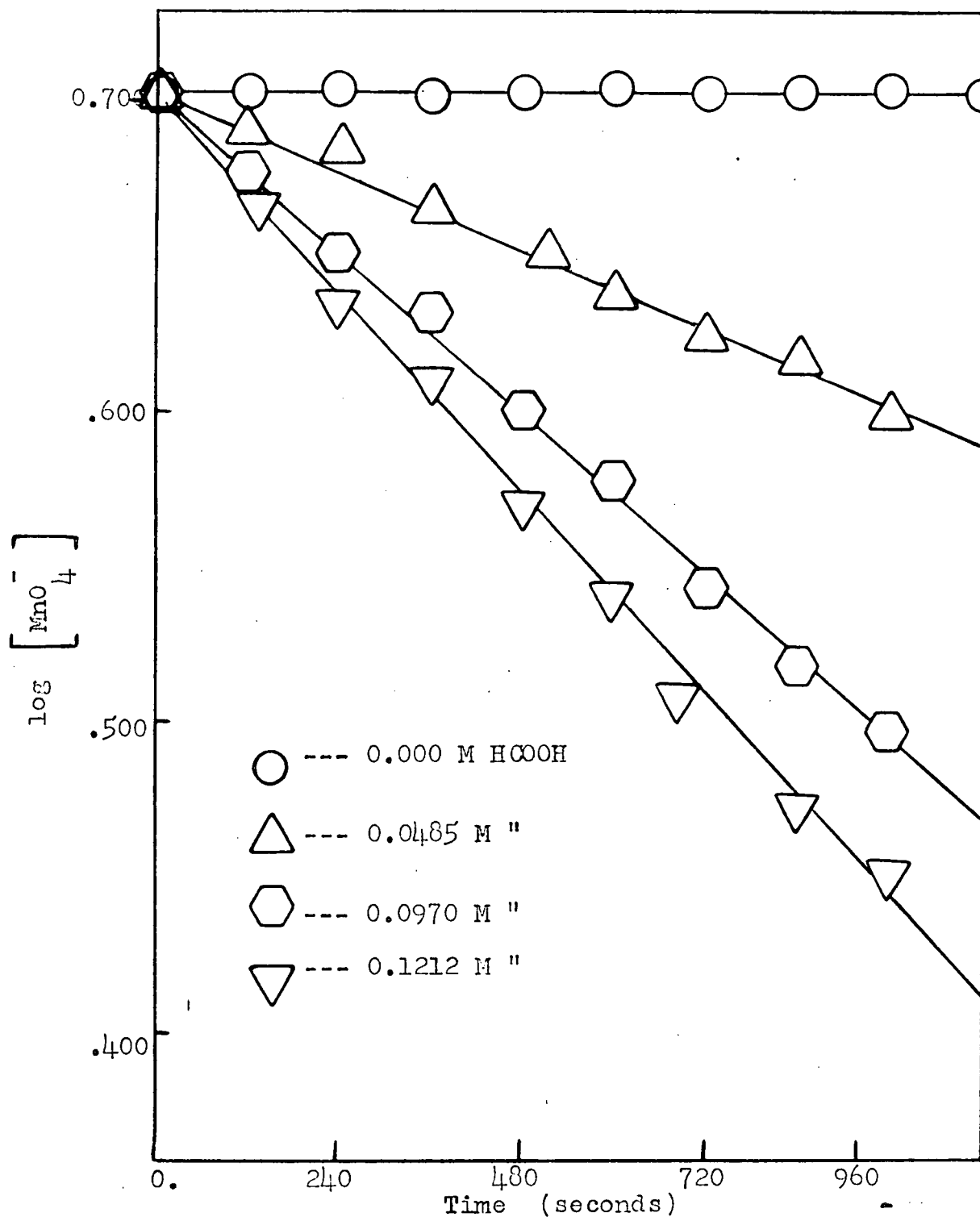
Figure 3

First- Order Rate Plots at Constant Initial MnO₄⁻ and Varying HCOOH (Excess) Concentrations. Initial MnO₄⁻ -- 0.0010 M. HClO₄ --0.601 M. μ --1.0M. T ---30.1°C.
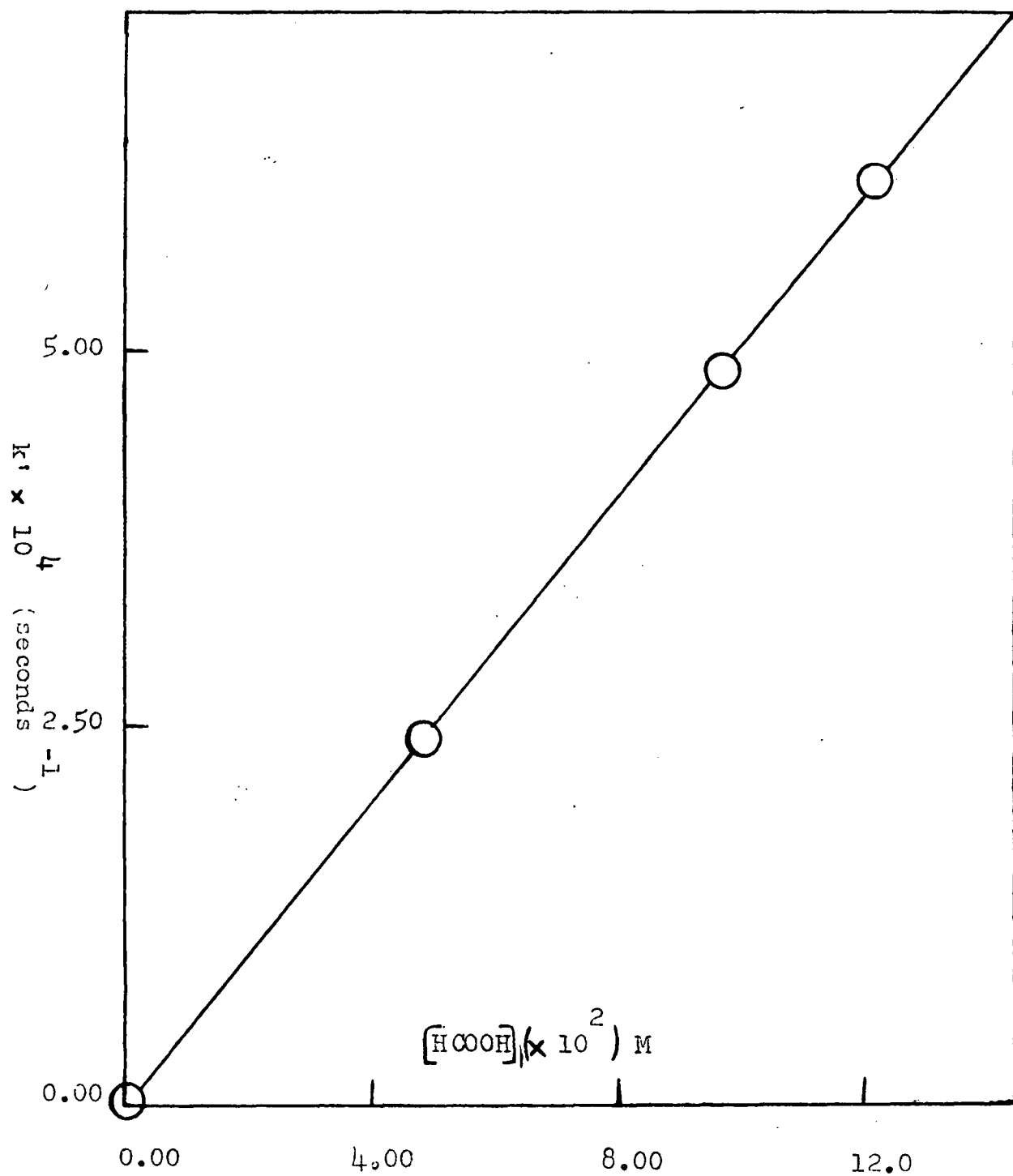
Figure   4

Plot of Pseudo- First Order Rate Constant (k') Against HCOOH

Concentration. Ionic strength—1.0 M. Temperature -- 30.1°C.

of k'' were determined from the slopes of pseudo-first order rate plots of the type shown in Figures 1 and 3.

III. Effect of Hydrogen Ion Concentration

To determine the effect of hydrogen ion concentration on the reaction, a series of kinetic experiments was conducted as follows: the initial HCOOH concentration was maintained at 0.0970M, and the initial MnO_4^- concentration at 0.0010M. The $HClO_4$ concentration was varied from 0.10M to 1.202M. Ionic strength was maintained at 1.0M, where possible, by the addition of $NaClO_4$. In these experiments, the pseudo-first order rate constants were found to vary with H^+ concentration as shown in Figures 5 and 6, pages 20 and 21 respectively, and in Table III, page 22. The measured rates steadily decreased with increasing $HClO_4$ concentration, approaching a finite limiting value at high H^+ concentration. (Figure 7.)

In Figure 8, a plot of k'' against $1/[H^+]$ is seen to be linear. Similar relationships were obtained at several other temperatures. (Figure 8 and Table III.)

In an attempt to explain this pattern of kinetic behaviour the following mechanism has been proposed:

1. HCOOH, in aqueous solution, ionizes in an equilibrium process to form $HCOO^-$ (formate ion) and H^+; viz

$$HCOOH \; \underset{\longleftarrow}{\overset{K_1}{\longrightarrow}} \; HCOO^- + H^+ \;\; \ldots \ldots \ldots \ldots 4$$
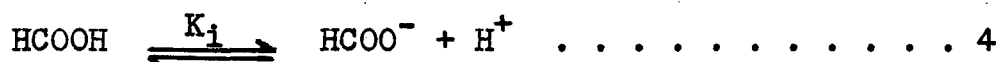
where K_1 is the ionization constant for HCOOH at a particular

Figure 5
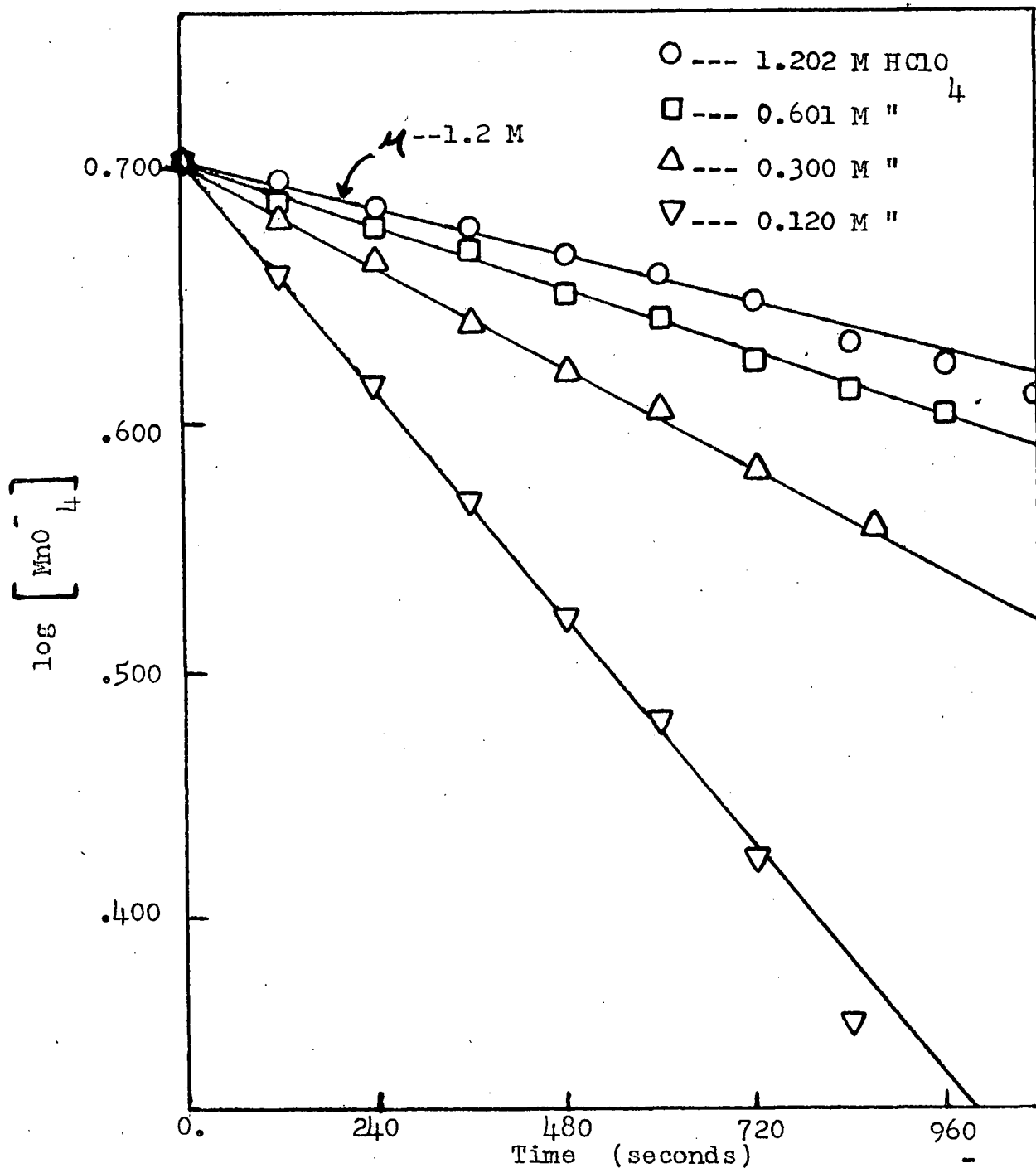
First- Order Rate Plots at Constant HCOOH and MnO$_4^-$
Initial Concentrations and Varying HClO$_4$ Concentration.
Initial MnO$_4^-$ --0.0010M. HCOOH --0.0970M. μ --1.0M. T--30.1°C.

Figure 6
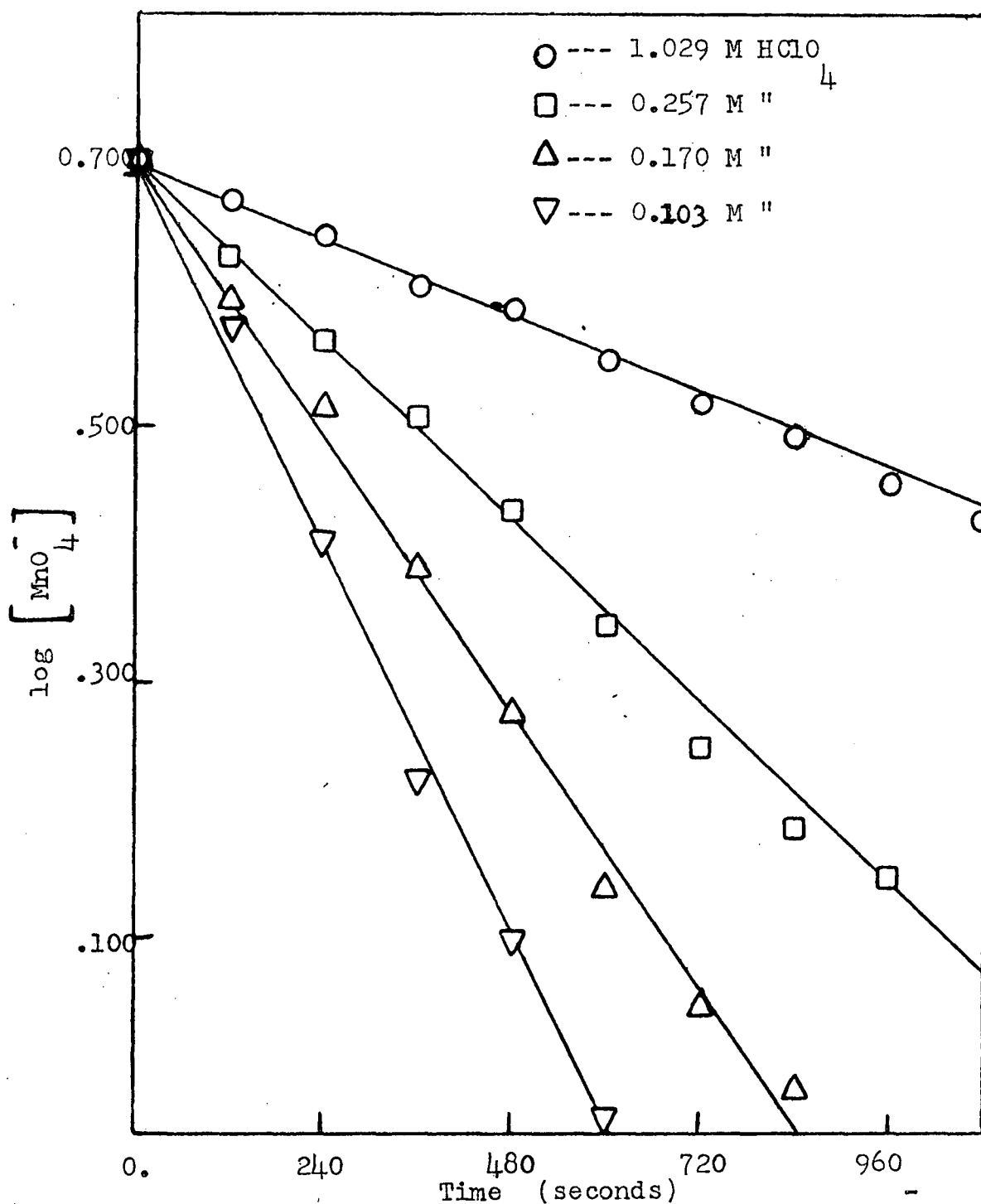
First- Order Rate Plots at Constant HCOOH and MnO$_4^-$ Initial Concentrations and Varying HClO$_4$ Concentration. Initial MnO$_4^-$ --0.0010M. HCOOH--0.0970M. μ --1.0M. T--35.0°C.

TABLE III

DEPENDENCE OF THE RATE ON PERCHLORIC ACID CONCENTRATION

	Ionic strength = 1.0M					
Temperature	Initial Conc. (M)			$1/H^+$	$k'x10^4$	$k''x10^3$
($°C$)	MnO_4^-	HCOOH	$HClO_4$	(M^{-1})	sec^{-1}	$1-m^{-1}s^{-1}$
15.6	0.0010	0.0989	1.029	0.973	1.17	1.18
15.6	0.0010	0.0989	0.2573	3.89	3.27	3.31
15.6	0.0010	0.0989	.1698	5.90	4.57	4.61
15.6	0.0010	0.0989	.1029	9.73	7.38	7.46
22.8	0.0010	0.0989	1.029	0.973	2.03	2.05
22.8	0.0010	0.0989	0.2573	3.89	5.40	5.46
22.8	0.0010	0.0989	.1698	5.90	8.01	8.22
22.8	0.0010	0.0989	.1029	9.73	12.6	12.7
25.8	0.0010	0.0970	1.029	0.973	2.57	2.64
25.8	0.0010	0.0970	0.2569	3.90	7.57	7.28
25.8	0.0010	0.0970	.1696	5.90	10.3	10.6
25.8	0.0010	0.0970	.1028	9.73	15.7	16.2
30.1	0.0010	0.0970	1.202*	0.833	3.57	3.68
30.1	0.0010	0.0970	0.6010	1.67	4.90	5.05
30.1	0.0010	0.0970	.3004	3.33	7.97	8.22
30.1	0.0010	0.0970	.1202	8.33	17.5	18.1
32.7	0.0010	0.0989	1.029	0.973	4.58	4.63
32.7	0.0010	0.0989	0.2573	3.89	11.5	11.6
32.7	0.0010	0.0989	.1698	5.90	16.0	16.7
32.7	0.0010	0.0989	.1029	9.73	25.8	26.1
35.0	0.0010	0.0970	1.029	0.973	5.12	5.26
35.0	0.0010	0.0970	0.2573	3.89	13.6	14.0
35.0	0.0010	0.0970	.1698	5.90	19.1	19.7
35.0	0.0010	0.0970	.1029	9.73	29.7	30.7

*Ionic strength = 1.2M.

temperature. In strongly acid solution, most of the formic acid will exist as the undissociated HCOOH molecule. The equilibrium concentration of $HCOO^-$ is given by

$$[HCOO^-] = K_1 [HCOOH] / [H^+] \ldots \ldots \ldots 5$$

where $[HCOOH]$ may be approximated by the total formic acid concentration.

2. MnO_4^- reacts with both HCOOH and $HCOO^-$, in bimolecular rate-determining steps, i.e.

$$MnO_4^- + HCOOH \xrightarrow{k_A} \text{intermediates} \ldots \ldots \ldots 6$$
$$MnO_4^- + HCOO^- \xrightarrow{k_B} \text{intermediates} \ldots \ldots \ldots 7$$
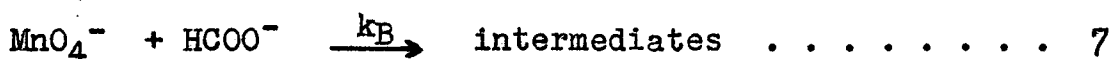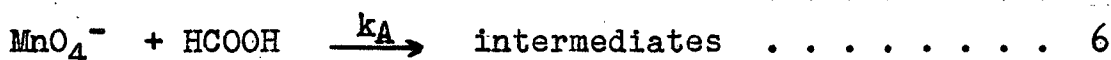
where k_A and k_B are second order rate constants for the oxidation of HCOOH and $HCOO^-$ respectively. (The nature of the intermediates will be discussed later.) Hence the total rate of reaction is given by

$$-\frac{d[MnO_4^-]}{dt} = k_A [HCOOH] [MnO_4^-] + k_B [HCOO^-] [MnO_4^-] \ldots \ldots \ldots 8$$

Substituting for $[HCOO^-]$ from equation 5 and rearranging, the rate expression becomes

$$-\frac{d[MnO_4^-]}{dt} = [HCOOH] [MnO_4^-] \left(k_A + k_B K_1 / [H^+] \right) \ldots \ldots 9$$

Thus it is seen that

$$k'' = k_A + k_B K_1 / [H^+] \ldots \ldots \ldots 10$$

and

$$k' = [HCOOH] \left(k_A + k_B K_1 / [H^+] \right) \ldots \ldots \ldots 11$$

At any temperature a plot of k'' against $1/[H^+]$ should

Figure 7
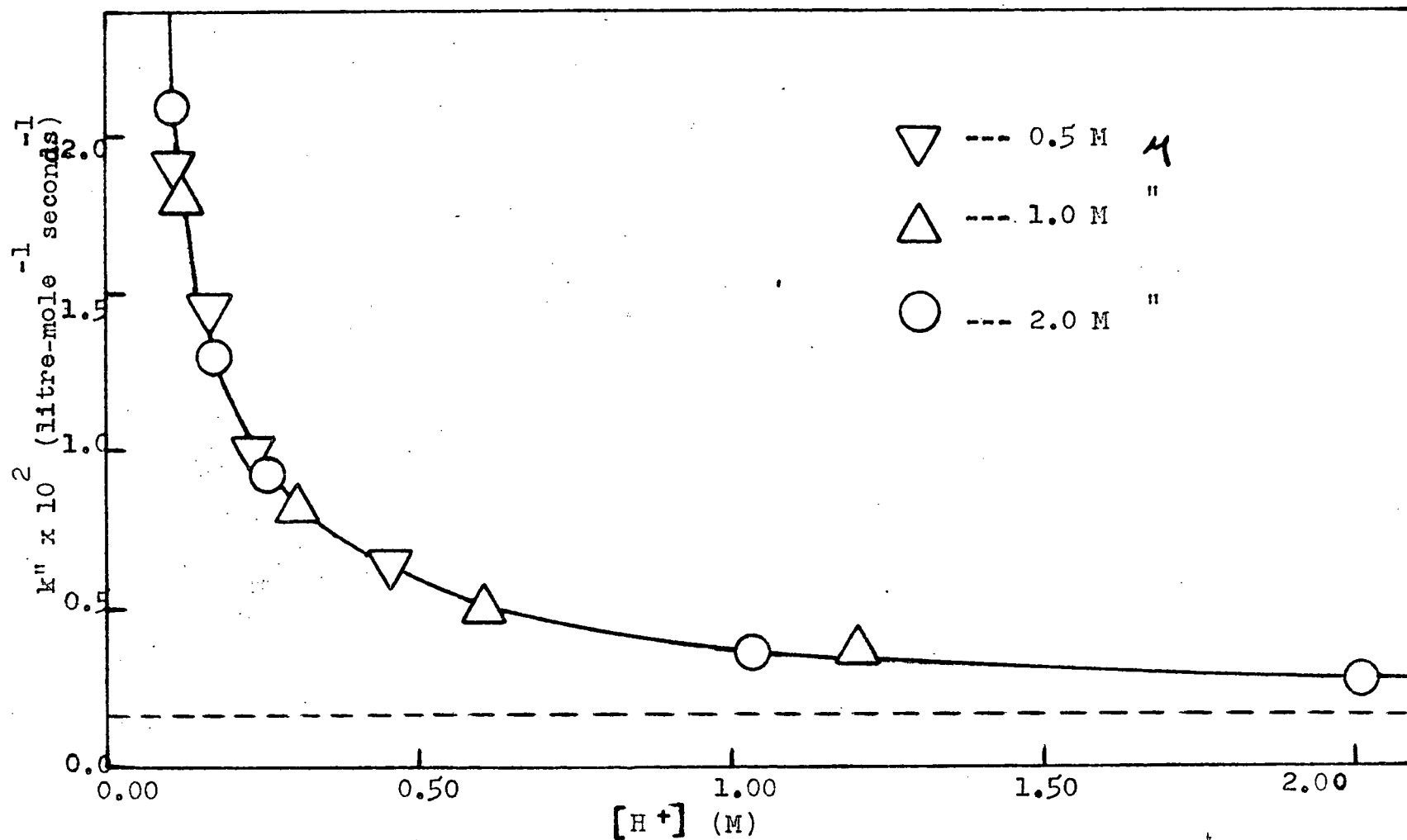
Plot of Apparent Second- Order Rate Constant (k") Against $[H^+]$ at Different Ionic Strengths. Temperature—30.1° C.

then be linear with a slope of $k_B K_1$ and an intercept of k_A.
Such plots for various temperatures are shown in Figure 8,
page 28, and were used to obtain the values of k_A and $k_B K_1$
listed in Table V, page 27. Values of k_B were then
calculated using separately measured values of K_1, listed in
Table IV, page 26.

IV. Evaluation of K_1, the Ionization Constant of Formic
    Acid

In 1943, Harned and Embree[18] determined K_1
values for HCOOH using electrochemical methods. These
measurements were conducted in solutions having ionic
strengths up to 0.25M. There appeared to be a slight increase
in K_1 with increasing ionic strength, in keeping with the
predictions of the Debye-Hückel theory. Since the present
kinetic investigations were carried out in solutions of
μ = 1.0, values for K_1 in 1.0M NaclO$_4$ were determined
potentiometrically using a Beckman G pH meter. K_1 values
were observed to be about three times greater than those
previously reported at low ionic strengths. (Table IV.)
However, the same type of temperature dependence (although
much more pronounced) was found, (Figure 9) with a maximum
in K_1 occurring at about 25°C. Similar maxima in K_1 have
been observed at 25°C for acetic and propionic acids.

TABLE IV

TEMPERATURE DEPENDENCE OF THE IONIZATION CONSTANT OF FORMIC ACID

Acid	Temperature (°C)	Reported* K_1 (M/L)	Experimental** K_1 (M/L)
HCOOH	15.2	1.750×10^{-4}	4.12×10^{-4}
HCOOH	20.9	1.767×10^{-4}	5.7×10^{-4}
HCOOH	24.7	1.772×10^{-4}	6.2×10^{-4}
HCOOH	29.9	1.768×10^{-4}	5.6×10^{-4}
HCOOH	36.1	1.740×10^{-4}	4.2×10^{-4}
DCOOH	29.9	-	8.0×10^{-4}

*Harned and Embree,[18] 1934. $\mu < 0.01M$

**Mean of two measurements at different $[HCOOH] / [HCOO^-]$ ratios. $\mu = 1.0M$.

TABLE V

DEPENDENCE OF k_A AND k_B ON TEMPERATURE

Temperature		$k_A \times 10^3$	$k_B K_1 \times 10^3$	$K_1^* \times 10^4$	k_B
°C	°K	1-mole^{-1}sec^{-1}	sec^{-1}	M/1	1-m^{-1}s^{-1}
15.6	288.8	0.450	0.718	4.25	1.69
22.8	296.0	0.881	1.22	6.05	2.01
25.8	299.0	1.15	1.59	6.20	2.56
30.1	303.3	1.70	1.95	6.04	3.23
32.7	305.9	2.15	2.47	4.95	4.99
35.0	308.2	2.69	2.87	4.45	6.46

*Experimental values from Figure 9.

Figure 8
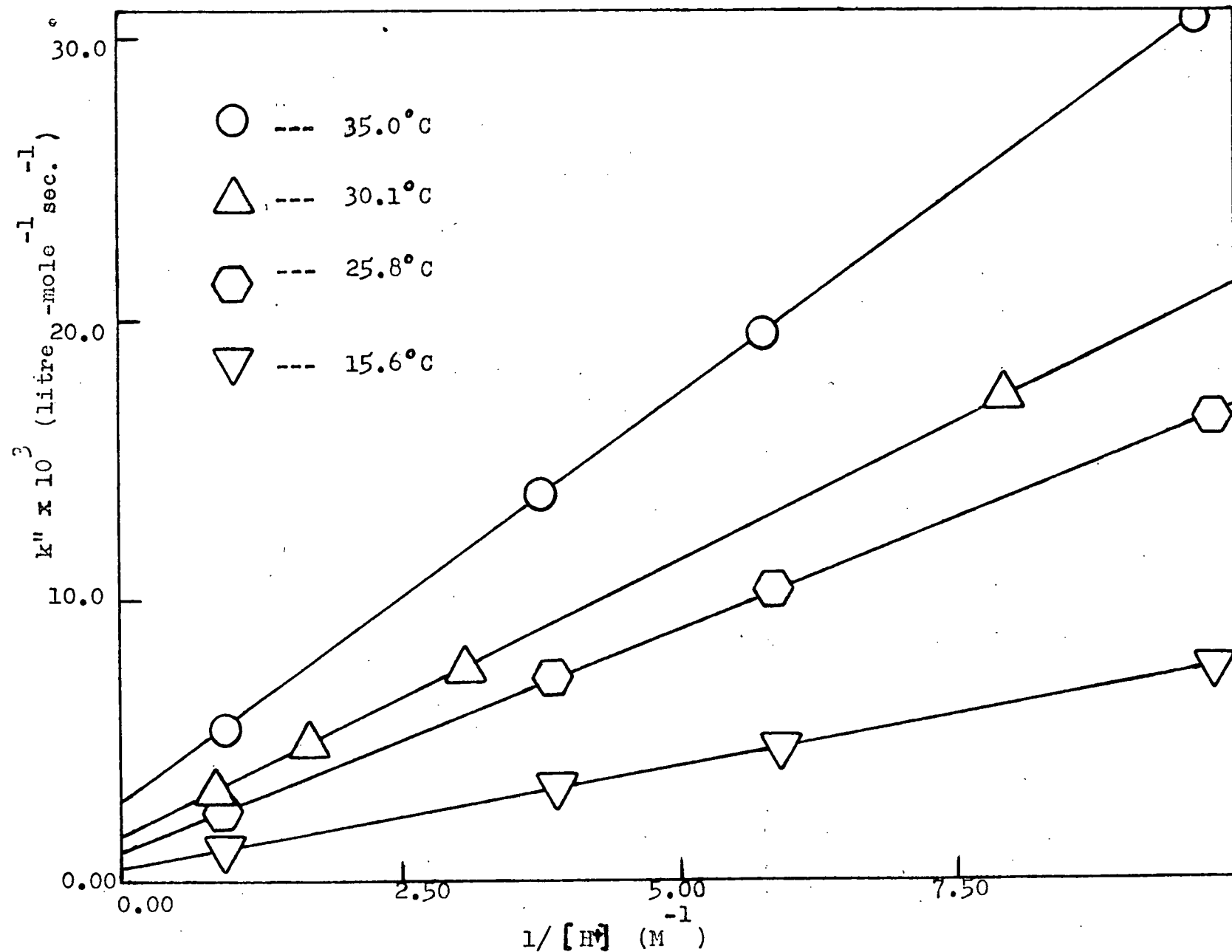
Plots of Second- Order Rate Constants (k") Against 1/[H⁺] at Several Temp-
-eratures. $\mathcal{A}$ --- **1.0 M.**

Figure 9
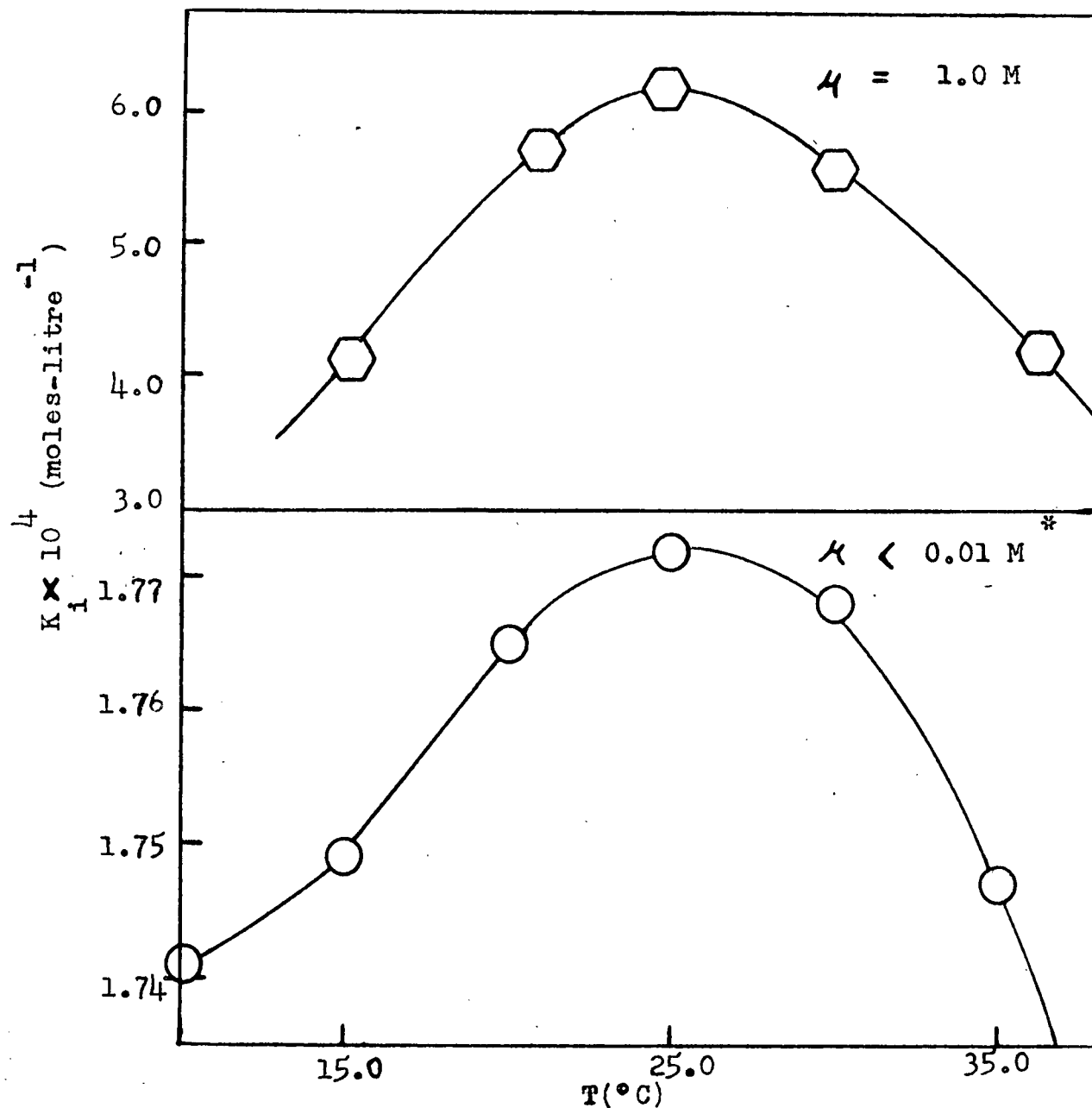
Dependence of K_i on Temperature.

($*$--Data of Harned and Embree[18])

V. Effect of Temperature on the Reaction

An Arrhenius plot for k_A in the temperature range 15.6° to 35.0°C is shown in Figure 10, page 31. The slope corresponds to an apparent activation energy E_A of 16.4 kCal mole^{-1}. Using this value and the experimental values of k_A, the Arrhenius frequency factor A_A was estimated to be 1.1×10^9 litre-mole^{-1}-sec^{-1} (corresponding to an entropy of activation $\Delta S_A^{\ddagger}$ of -19.3 eu.).

Although a plot of log $k_B K_i$ versus 1/T gave a good straight line (Figure 11, page 32), the Arrhenius plot for k_B (based on values of K_i measured at different temperatures) showed pronounced curvature (Figure 11). It seems likely that this is an apparent effect arising from a systematic error in the determination of the temperature dependence of K_i. This is suggested by the fact that the magnitude of the apparent temperature dependence of K_i is much greater than that found by Harned and Embree[18] (at ionic strengths up to 0.25M in which range there was no indication of an increase in this magnitude with ionic strength). Furthermore it would be most unlikely that the dependencies of log k_B and log K_i on 1/T were both non-linear and that the departures from linearity were exactly compensating to account for the resultant linearity of the log $k_B K_i$ vs. 1/T plot. It is believed that while the pH method used is sufficient to yield approximate K_i values, more refined methods, such as those employed by Harned and Embree[18] would be necessary to measure the

Figure 10

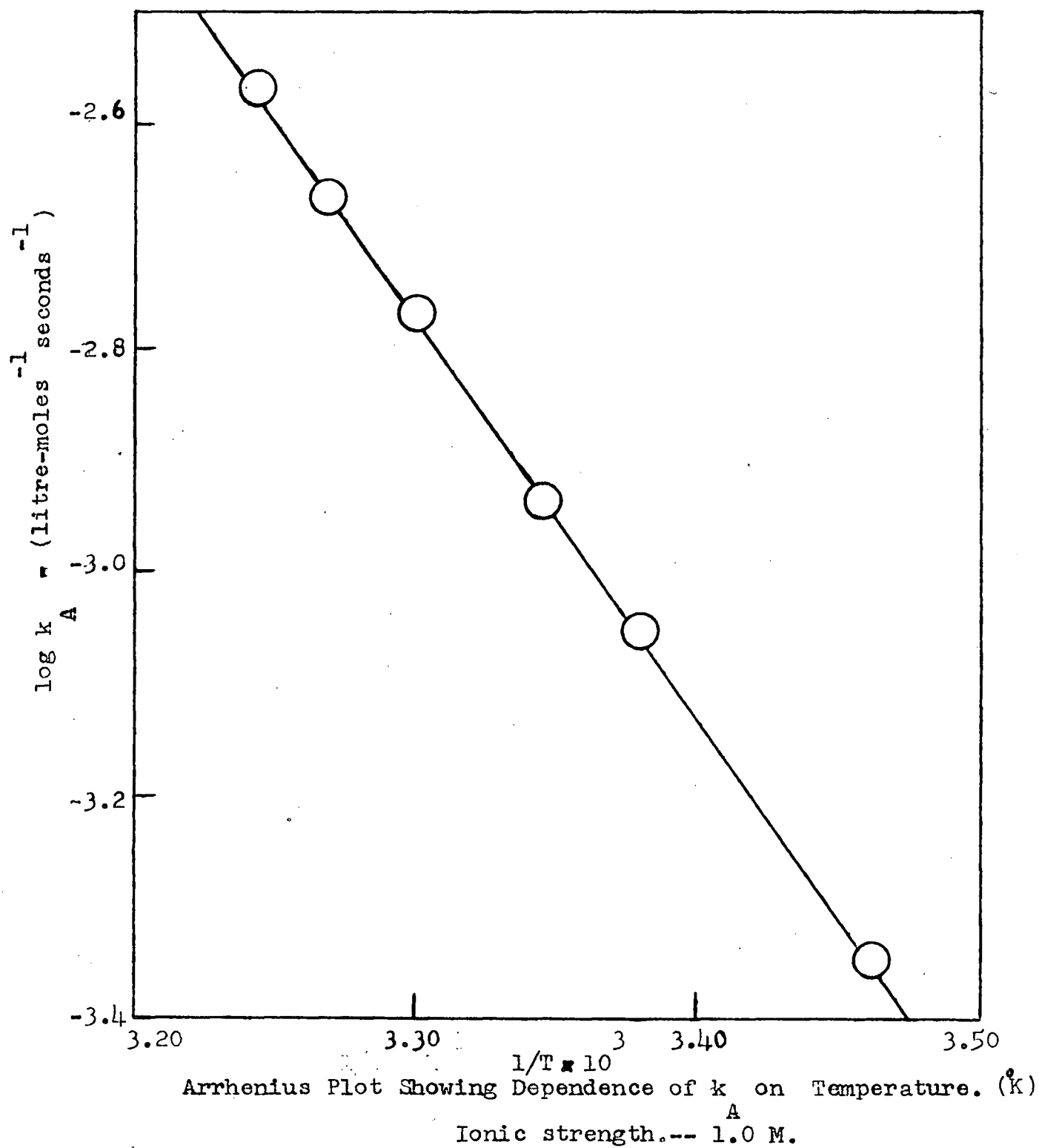Arrhenius Plot Showing Dependence of k_A on Temperature. (°K)

Ionic strength.-- 1.0 M.

Figure 11
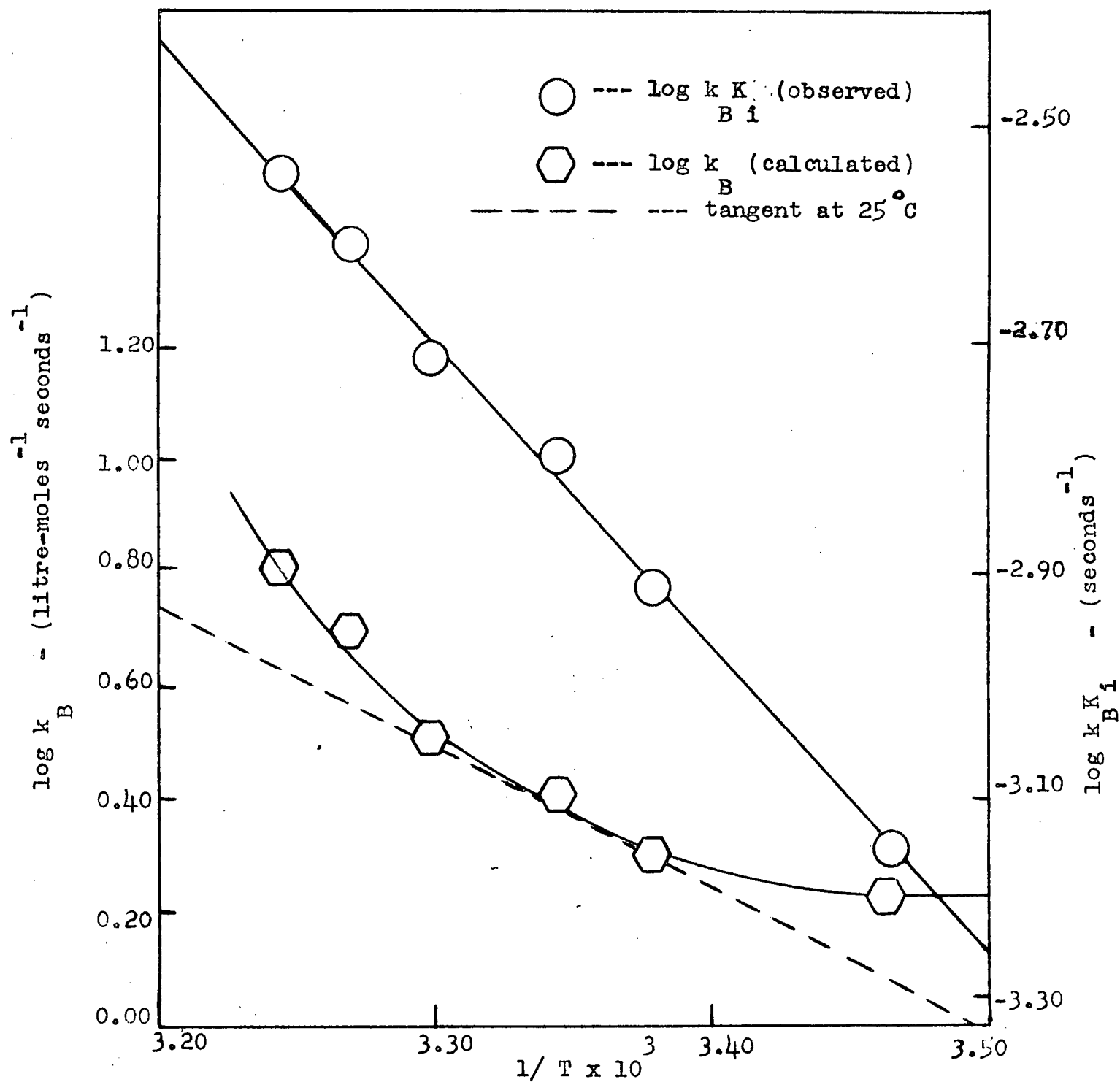
Arrhenius Plot Showing Dependence of $k_B K_i$ on Temperature (°K).
(Right Ordinate)

Arrhenius Plot Showing Dependence of k_B on Temperature (°K).
(Left Ordinate)

Ionic strength -- 1.0M.

temperature dependence precisely. However, the maximum in K_1 at 25°C which was observed both in the earlier and present measurements appears to be real; hence for the purpose of determining k_B it seems safe to assume that the heat of ionization of formic acid (ΔH_1) is zero at this temperature. Using this assumption, a value of 13.0 kCal/mole is obtained for E_B from the slope of the log $k_B K_1$ vs. 1/T plot. This corresponds to the value estimated from the slope of the k_B Arrhenius plot at 25°C. (See Figure 11.) The Arrhenius frequency factor A_B was estimated to be 7.8×10^9 litre mole^{-1} sec^{-1}, corresponding to an entropy of activation $\Delta S_B^{\ddagger}$ of -15.3 eu. (A Summary of Temperature Parameters is shown in Table VI, page 34.)

The uncertainties in E_A and E_B are estimated to be ± 0.5 and ± 2.0 kCal/mole respectively. The uncertainty of $\Delta S_A^{\ddagger}$ is estimated at ± 1.5 eu. The absolute uncertainty of K_1, and hence of $\Delta S_B^{\ddagger}$ are difficult to estimate. However, the values of the kinetic parameters determined above are in reasonable agreement with those reported by Tompkins[32] ($E_B = 11.8$ kCal/mole; $\Delta S_B^{\ddagger} = -20.8$ eu.) on the basis of measurements at lower acidities and ionic strength. The value of 2.30 l.mole^{-1}sec^{-1} found for T = 25°C and $\mu = 1.0M$, compares with the value of 3.06 l.m^{-1}s.$^{-1}$ reported by Tompkins[32] at $\mu = .0859M$ and the value of $0.927\pm.015$ l-m^{-1}s^{-1} reported

TABLE VI

KINETIC PARAMETERS FOR THE REACTION

Reaction	E (Cal/mole)	A (1-mole^{-1}sec^{-1})	$\Delta S^{\ddagger}$ (eu)	k (1-mole^{-1}sec^{-1})
HCOOH+ $MnO_4^-\rightarrow$	16,400	1.1×10^9	-19.3	$k_A = 1.1 \times 10^9 \exp(-16400/RT)$
HCOO$^-$+ $MnO_4^-\rightarrow$	13,000	7.8×10^9	-15.3	$k_B = 7.8 \times 10^9 \exp(-13000/RT)$

Figure   12
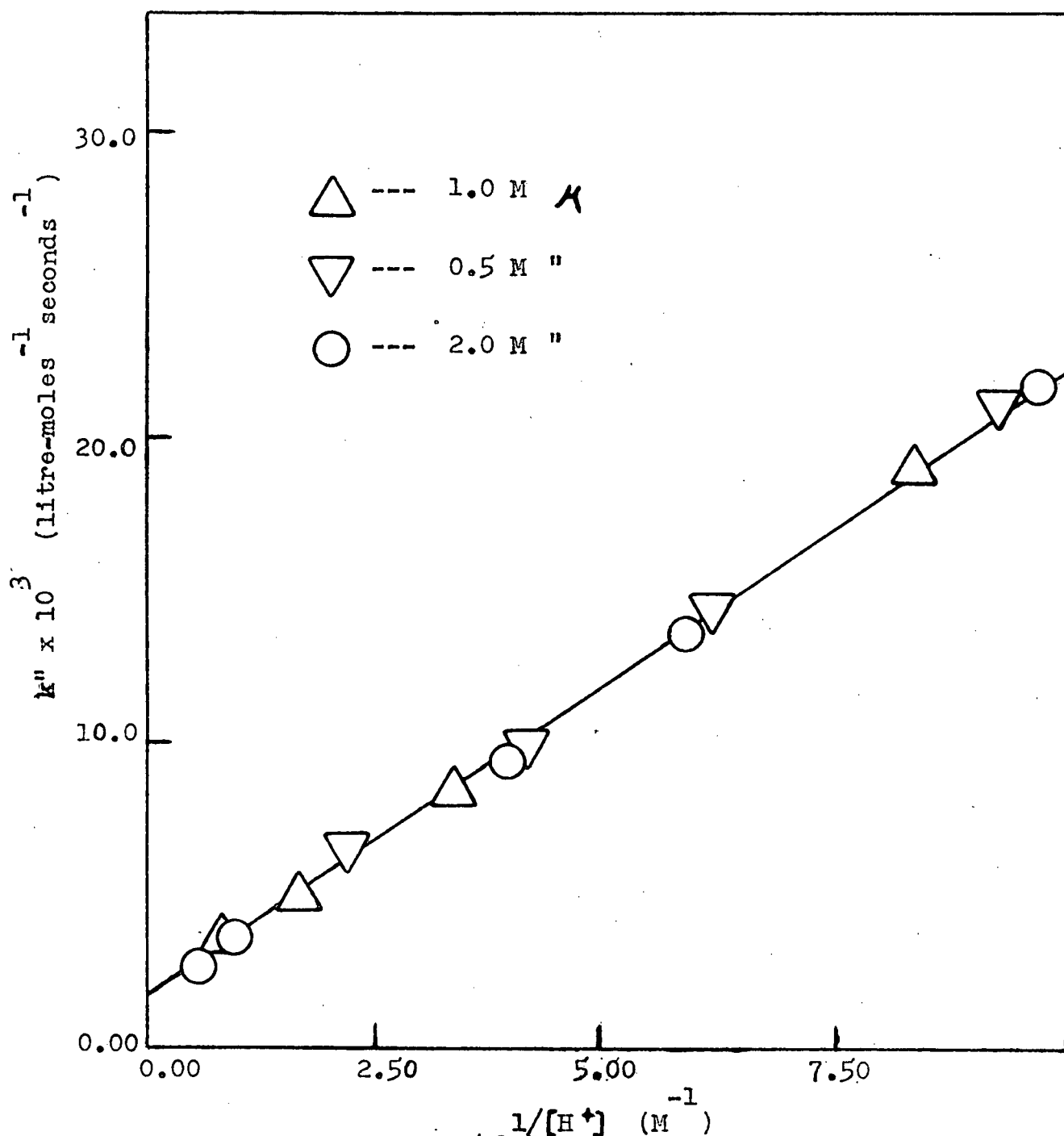
Plot of k" Against 1/ [H] Showing Effect of Varying Ionic
Strength on k_A and $k_B K_i$.   Temperature -- 30.1°C.

by Stewart at μ = 0.2M.[57]   (All at 25°.)*

VI. Effect of Ionic Strength

Varying the ionic strength of reaction solutions
from 0.5 to 2.0M by changing the $NaClO_4$ concentration had no
detectable effect on reaction rates over an acid concentration
range of 0.10 to 2.1M. Results of these measurements are
summarized in Table VII, page 37 and in Figures 7 and 12.
The absence of an ionic strength effect on k_A is not surprising
since k_A refers to a reaction between an ion and a neutral
molecule. The absence of an apparent ionic strength effect
on the formate ion contribution is probably due to the fact
that the measurements were made in the region of high ionic
strengths where ionic activity coefficients tend to be fairly
independent of ionic strength. At low ionic strengths, k_B
has been reported[32,57] to increase with ionic strength in
accordance with the predictions of the Bronsted-Bjerrum
theory.

VII. Effect of Metal Ions

The addition of $Co(ClO_4)_2$, $AgClO_4$ and $Cu(ClO_4)_2$ had
no effects on the rates of reaction (Table VIII). Considering
the marked catalytic activity which Ag^+ exhibits in the

---

*Kinetic calculations of E, A and$\Delta S^{\ddagger}$ employ the standard
Arrhenius and Eyring rate equations:
$$k = A \exp.(-E/RT)$$
$$k' = KkT/h \exp.(\Delta S^{\ddagger}/R) \exp.(-\Delta H^{\ddagger}/RT)$$

TABLE VII

DEPENDENCE OF RATE ON IONIC STRENGTH

Temperature = 30.1°C

	Initial Conc. (M)			$\mathcal{M}$	$k' x 10^4$	$k'' x 10^3$
MnO_4^-	HCOOH	$HClO_4$	$NaClO_4$	(M)	sec^{-1}	$1-m^{-1}s^{-1}$
0.0010	0.0970	1.20	-	1.2	3.57	3.68
0.0010	0.0970	0.601	.40	1.0	4.90	5.05
0.0010	0.0970	0.300	.70	1.0	7.98	8.22
0.0010	0.0970	0.120	.88	1.0	17.6	18.1
0.0010	0.0970	2.06	-	2.1	2.65	2.73
0.0010	0.0970	1.03	1.0	2.0	3.45	3.56
0.0010	0.0970	0.257	1.7	2.0	9.10	9.39
0.0010	0.0970	0.170	1.8	2.0	12.6	13.0
0.0010	0.0970	0.103	1.9	2.0	20.3	20.9
0.0010	0.0970	0.451	.05	0.5	6.37	6.55
0.0010	0.0970	0.238	.26	0.5	9.55	9.84
0.0010	0.0970	0.163	.34	0.5	14.0	14.5
0.0010	0.0970	0.108	.39	0.5	18.6	19.1

reaction of MnO_4^- with H_2 in aqueous solution,[54] this is of interest.

The addition of $Fe(ClO_4)_3$ was observed to increase reaction rates to a considerable extent. That Fe^{+++} displays true catalytic activity (rather than "trivial" catalytic activity arising from the oxidation of HCOOH by Fe^{+++}, followed by the reoxidation of Fe^{++} by MnO_4^-) may be shown by the following evidence:

In acid solution containing HCOOH and Fe^{+++}, but no MnO_4^-, the concentrations of HCOOH and Fe^{+++} remained constant for several hours. When MnO_4^- is added, reaction starts, and the rate of this reaction is proportional to the concentration of Fe^{+++}. Furthermore, during this reaction the Fe^{+++} concentration remains constant.

Acceleration of the reaction by Fe^{+++} is illustrated in Figure 13, page 41, and in Table VIII, page 39.

If the pseudo-first order rate constant k_c is plotted against concentration of Fe^{+++}, the resulting curve is found to level off at high Fe^{+++} concentration. (Figure 14, page 42.) This behaviour is consistent with the following interpretation:

Fe^{+++} in aqueous solution is assumed to associate with MnO_4^- to form a complex $FeMnO_4^{++}$ (there is no evidence for this but analogous complexing of Fe^{+++} with HSO_4^- and ClO_4^- has been reported):[45]

$$Fe^{+++} + MnO_4^- \underset{}{\overset{K_c}{\rightleftharpoons}} FeMnO_4^{++} \quad \ldots \ldots \ldots 12$$

TABLE VIII

EFFECT OF SOLUTION COMPOSITION ON THE RATE

Temperature = 29.9°C   Ionic strength = 1.0M

| Initial Conc. (M) | | | | $k' \times 10^4$ | $k'' \times 10^3$ |
MnO_4^-	HCOOH	$HClO_4$	Added Material	sec^{-1}	$1-m^{-1}s^{-1}$
0.0008	0.0989	1.017	–	3.70	3.75
0.0008	0.0989	1.017	–	3.60	3.65
0.0008	0.0938	1.022	.001M $Cu(ClO_4)_2$	3.53	3.76
0.0008	0.0938	1.022	.010M $Cu(ClO_4)_2$	3.45	3.67
0.0008	0.0939	1.022	.010M $Co(ClO_4)_2$	3.57	3.80
0.0008	0.0939	1.022	.001M $AgClO_4$	3.50	3.72
0.0008	0.0939	1.022	.010M $AgClO_4$	3.48	3.71
0.0008	0.0989	1.017	.0017M $Fe(ClO_4)_3$	5.13	5.20
0.0008	0.0989	1.017	.0075M $Fe(ClO_4)_3$	6.73	7.16
0.0008	0.0989	1.017	.0170M $Fe(ClO_4)_3$	7.52	8.00
0.0008	0.0989	1.017	glass wool	3.37	3.58
0.0008	0.0989	1.017	exposure to light	3.67	3.70

The equilibrium constant for this process may be expressed as

$$K_c = \frac{[FeMnO_4^{++}]}{[Fe^{+++}]\,[MnO_4^-]} \quad \ldots\ldots\ldots\ldots\ldots 13$$

Since $[Fe^{+++}]$ is in large excess over $[MnO_4^-]$ it may be approximated by the total Fe^{+++} concentration. If the overall reaction involves independent reactions of MnO_4^- and of $FeMnO_4^{++}$ with $HCOOH$ (or $HCOO^-$), the rate equation will be of the form:

$$\text{Rate} = k_c\,[MnO_4^-] = k'\,[MnO_4^-] + k^*\,[FeMnO_4^{++}] \quad \ldots\, 14$$

where k' is the apparent rate constant for the reduction of uncomplexed MnO_4^- (uncatalyzed rate) and k^* is the apparent rate constant for reduction of $FeMnO_4^{++}$ (catalyzed rate).

Rearranging equation 14 gives

$$\text{Rate} = k'\,[MnO_4^-] + (k^* - k')\,[FeMnO_4^{++}] \quad \ldots\ldots\ldots 15$$
$$\text{(total)}$$

Solving for $[FeMnO_4^{++}]$ in equation 13 gives

$$[FeMnO_4^{++}] = K_c\,[Fe^{+++}]\,[MnO_4^-]_{(total)}\big/\left(1 + K_c\,[Fe^{+++}]\right)\, \ldots\, 16$$

Hence equation 15 will become

$$\text{Rate} = k'\,[MnO_4^-]_{(total)} + \frac{(k^* - k')\,K_c\,[Fe^{+++}]\,[MnO_4^-]}{1 + K_c\,[Fe^{+++}]} \quad \ldots\ldots\ldots 17$$

$$\text{and } k_c = k' + (k^* - k')\,K_c\,[Fe^{+++}]\big/\left(1 + K_c\,[Fe^{+++}]\right). \quad \ldots\ldots 18$$

Figure 13
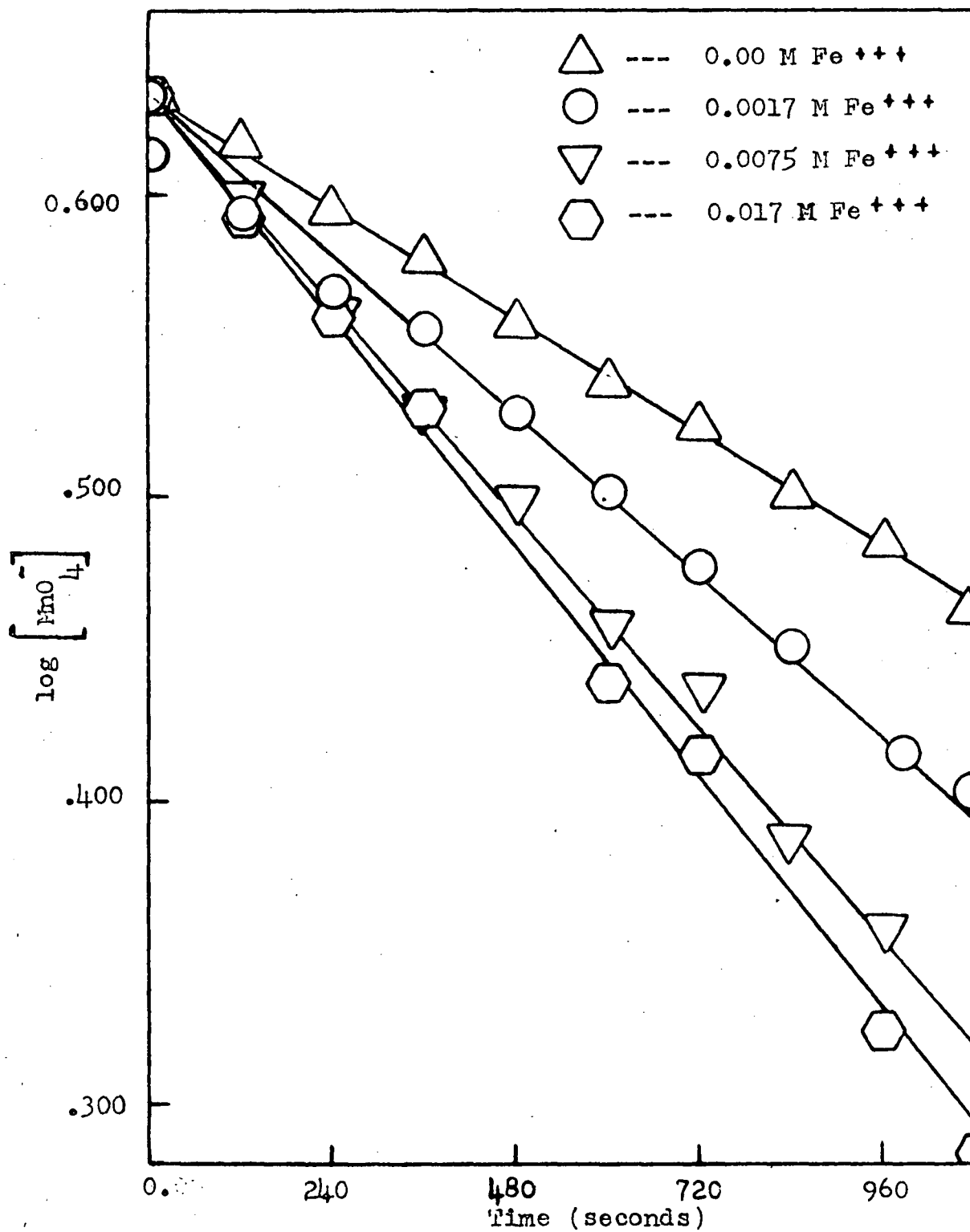
First-Order Rate Plots Showing Effect of Fe+ + +

Concentration on the Rate(k_c). HCOOH --- 0.0989 M.

Initial MnO_4^---0.0008M. $HClO_4$--1.017M. μ --10M. T--29.9°C

Figure 14
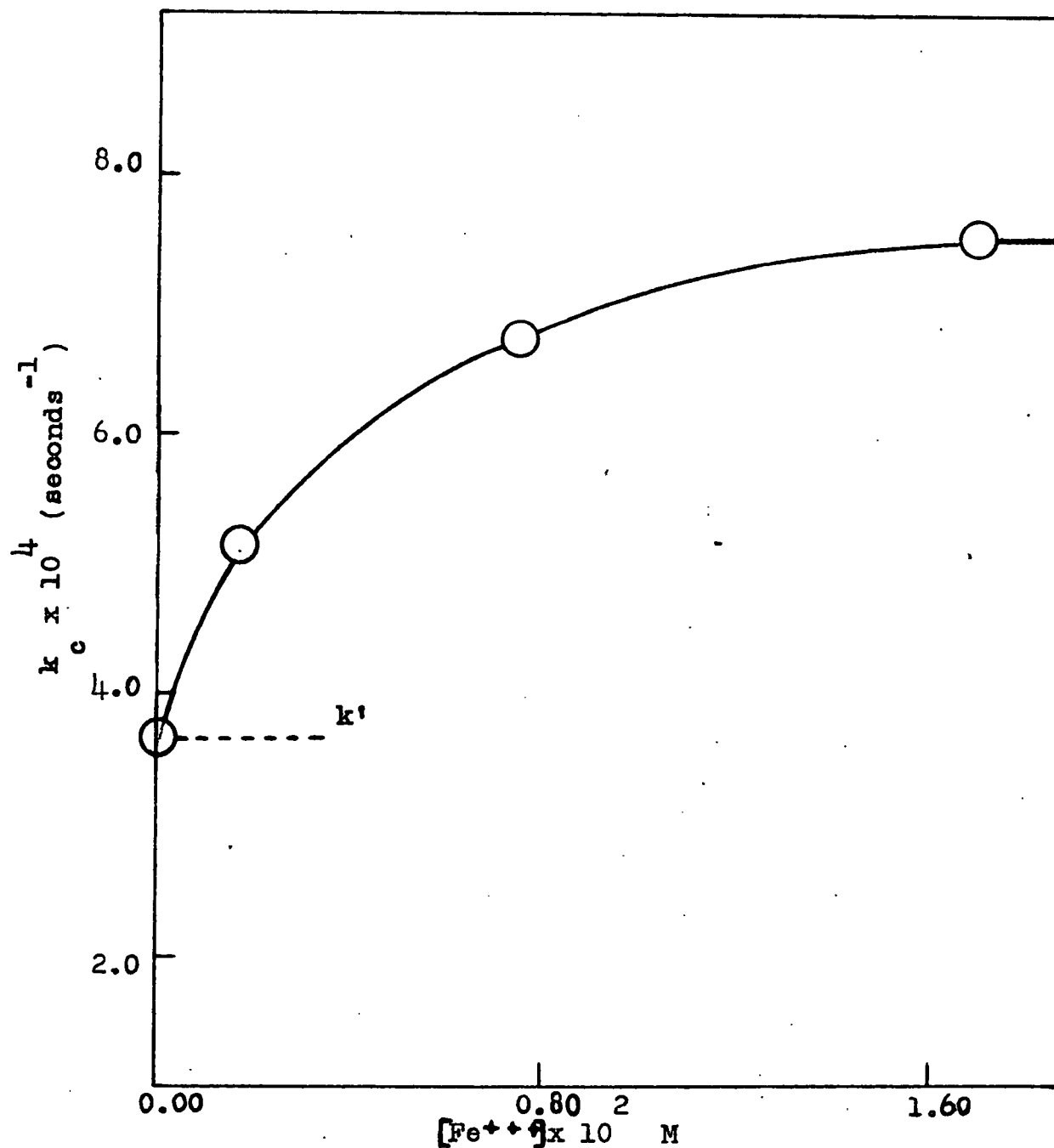
Plot of Apparent First- Order Rate (k) Against
Fe^{+++} Concentration. Ionic strength -- 1.0 M.
Temperature -- 29.9°C.

Figure 15
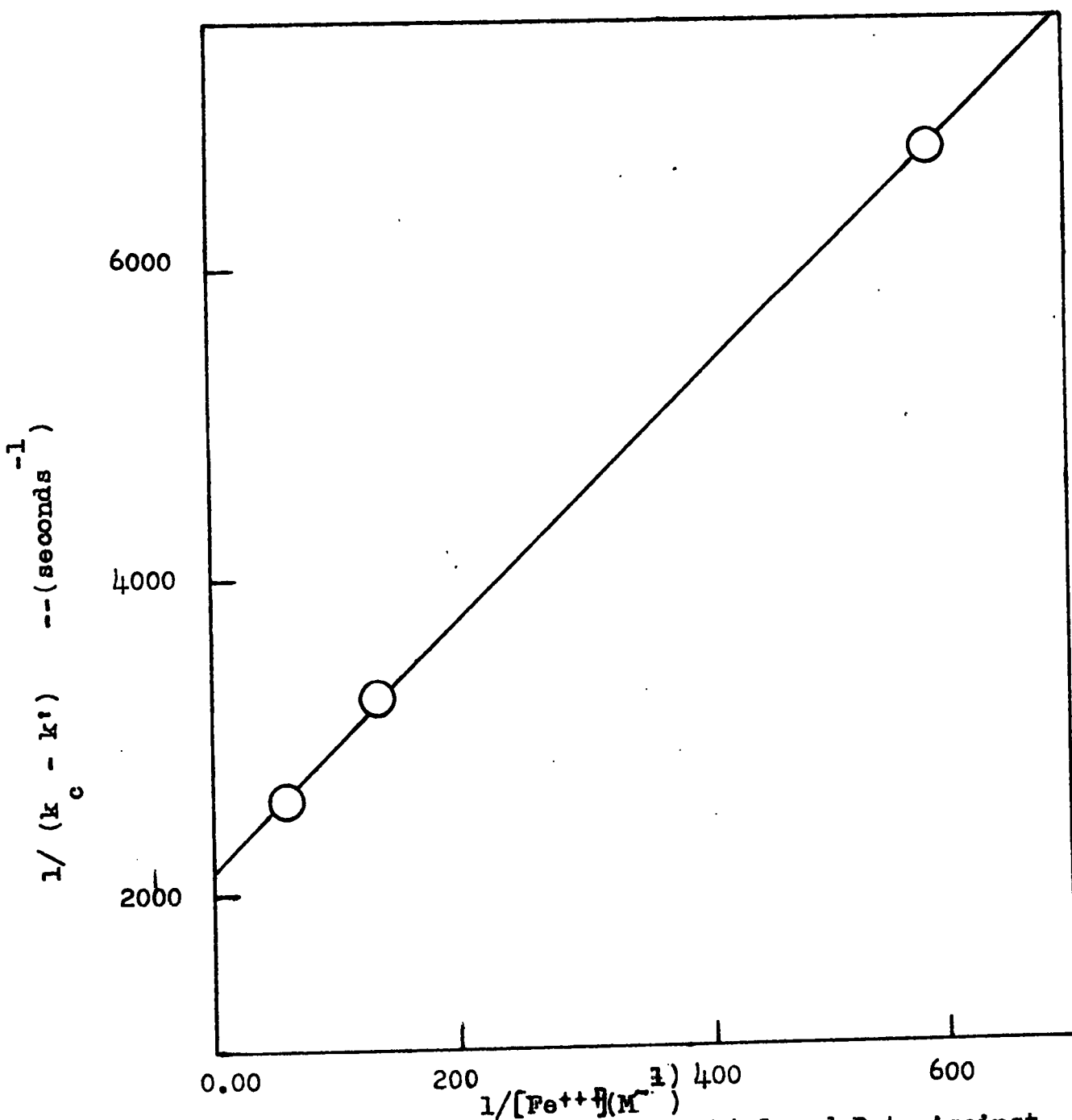
Plot of Reciprocal of Fe^{+++}— Catalyzed Rate Against

Reciprocal of Fe^{+++} Concentration.   Ionic strength--1.0 M.

Temperature--29.9°C.

Rearrangement of equation 18 gives

$$\frac{1}{k_c - k'} = \frac{1}{(k^* - k') K_c [Fe^{+++}]} + \frac{1}{(k^* - k')} \quad \dots \quad 19$$

According to this, a plot of $\frac{1}{k_c - k}$, against

$\frac{1}{[Fe^{+++}]}$ should be linear with an ordinate intercept of

$\frac{1}{k^* - k'}$, and a slope, $\frac{1}{(k^* - k')K_c}$. The plot in Figure 15 is

consistent with this interpretation, and yields values of

$k' = 3.65 \times 10^{-4} sec^{-1}$; $k^* = 8.30 \times 10^{-4} sec^{-1}$; and $K_c = 273$

litre/mole. Here k' and k^* are apparent rate constants only,

since the dependence on the HCOOH concentration is not

considered in the above rate calculation.

The above value of K_c is not unreasonable for the

formation constant of a complex such as $FeMnO_4^{++}$. However,

there is no corroborating evidence for the existence of this

complex. For example, the addition of $0.017M Fe^{+++}$ did not

produce any detectable change in the absorption spectrum of a

$0.0002M MnO_4^-$ solution. The proposed explanation for the

catalytic effect of Fe^{+++} must therefore be considered as very

speculative.

VIII. Deuterium Isotope Effects

To obtain further insight into the mechanism of the

reactions, an investigation was made of the kinetic isotope

effects arising from the substitution of reactant (HCOOH) and

solvent (H_2O) hydrogen by deuterium. Measurements of the

kinetic isotope effect (HCOO:DCOO rates) have been previously reported for the HCOO⁻-MnO₄⁻ reaction [58] (also Aebi, Buser and Luthi, Helv. Chim. Acta., 112:944.1956). Four series of experiments were conducted.

Series a). Reactions in which the reductant was HCOOH; the solvent, H_2O; the acid, $HClO_4$.

Series b). Reductant, DCOOH; solvent, H_2O; acid, $HClO_4$.

Series c). Reductant, HCOOD; solvent, D_2O; acid, $DClO_4$.

Series d). Reductant, DCOOD; solvent, D_2O; acid, $DClO_4$.

All experiments were made at ionic strength of 1.0M by the addition of $NaClO_4$, and temperature was maintained at 29.9°C. Initial MnO_4^- concentration was always 0.0008M, and perchloric acid concentrations were varied within each series from 0.1 to 1M.

Linear first order rate plots were obtained for each series. The experimental results are summarized in Table IX, page 46. Pseudo-first order rate constants (k') were used to calculate k'' values and these were plotted against $1/[H^+]$ (or $1/[D^+]$) as illustrated in Figure 16, page 47. For each series a fairly good straight line could be drawn, and k_A and $k_B K_1$ determined as described previously.

The ionization constant K_1 for DCOOH in H_2O was determined potentiometrically to be 8.0×10^{-4} mole/litre

TABLE IX

ISOTOPE EFFECTS ON THE RATE

		Temperature = 29.9°C				Ionic strength = 1.0M	
Solvent	Formic Acid	F.A. Conc. (M)	MnO_4^- (M)	Acid	Acid Conc. (M)	$k' \times 10^4$ sec^{-1}	$k'' \times 10^3$ 1-m^{-1}s^{-1}
H_2O	HCOOH	0.1029	0.0008	$HClO_4$	1.20*	3.52	3.42
H_2O	HCOOH	0.1029	0.0008	$HClO_4$	0.330	7.93	7.71
H_2O	HCOOH	0.1029	0.0008	$HClO_4$	.155	14.7	14.3
H_2O	HCOOH	0.1029	0.0008	$HClO_4$	.111	19.9	19.3
H_2O	DCOOH	0.1005	0.0008	$HClO_4$	1.11*	1.92	1.90
H_2O	DCOOH	0.1005	0.0008	$HClO_4$	0.300	3.07	3.05
H_2O	DCOOH	0.1005	0.0008	$HClO_4$	.150	4.13	4.12
H_2O	DCOOH	0.1005	0.0008	$HClO_4$	.107	5.38	5.35
D_2O	HCOOD	0.1036	0.0008	$DClO_4$	1.51*	2.60	2.51
D_2O	HCOOD	0.1036	0.0008	$DClO_4$	0.350	6.72	6.48
D_2O	HCOOD	0.1036	0.0008	$DClO_4$	.162	12.3	11.9
D_2O	HCOOD	0.1036	0.0008	$DClO_4$	.112	17.3	16.7
D_2O	DCOOD	0.1253	0.0008	$DClO_4$	1.03	2.15	1.72
D_2O	DCOOD	0.1253	0.0008	$DClO_4$	.590	2.80	2.23
D_2O	DCOOD	0.0888	0.0008	$DClO_4$	.296	2.22	2.50
D_2O	DCOOD	0.0888	0.0008	$DClO_4$	.216	2.88	3.24

*Ionic strength > 1.0M.

Figure   16
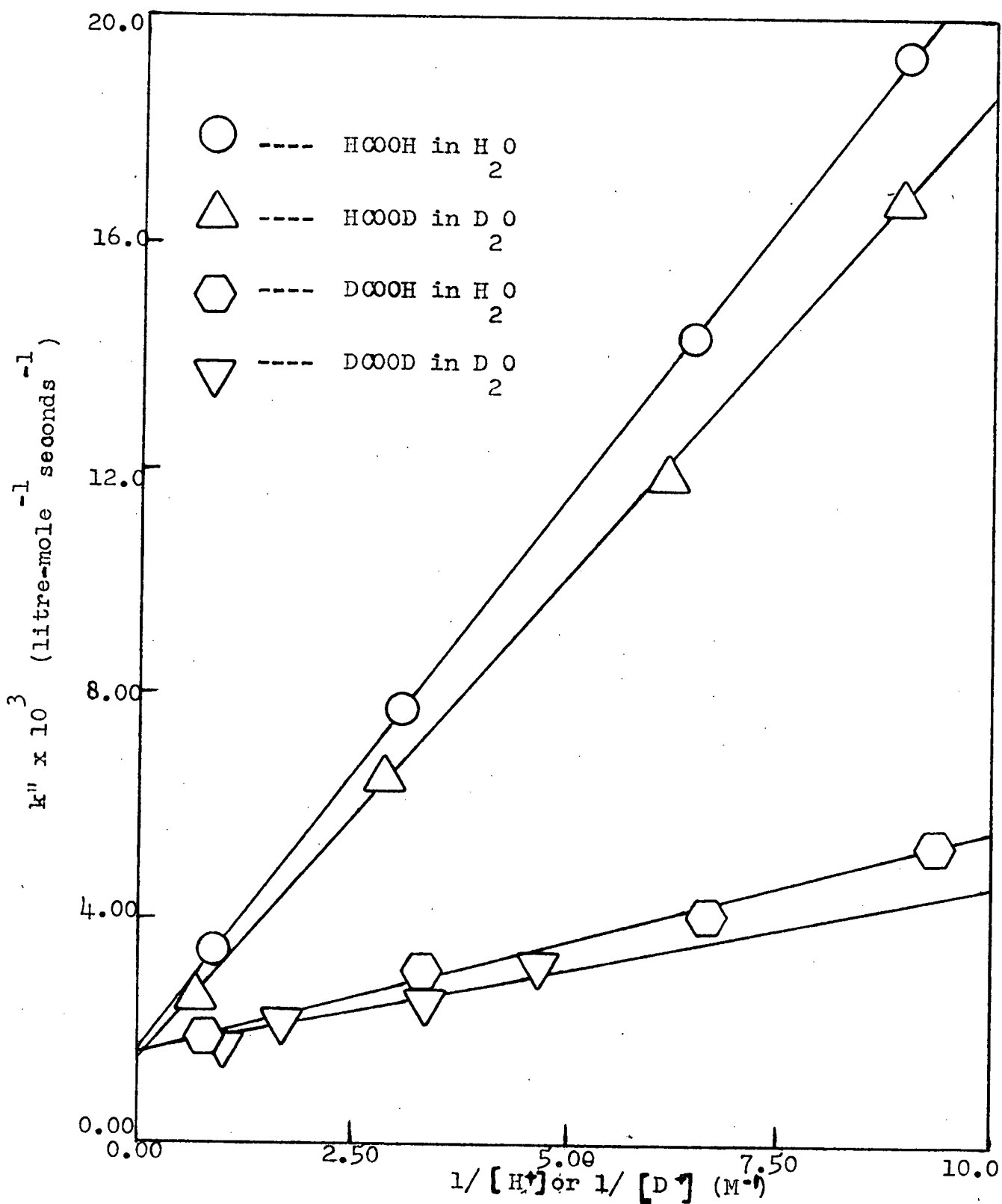
Plots of Apparent Second- Order Rate Constant (k") Against

1/ [H⁺] or 1/ [D⁺] for the Isotopic Systems. μ --1.0M. T--29.9°C.

(Table IV) and hence k_B for series (b) was calculated. Butler and co-workers [33,36] have determined ionization constants for HCOOH in D_2O to be about one-third of K_i in H_2O under the same conditions, or

$$K_i(D_2O) = 0.340 K_i(H_2O) \quad \ldots \ldots \ldots \ldots \quad 20$$

This relationship was employed to estimate K_i for HCOOD and DCOOD in D_2O, and hence k_B for series (c) and (d). Table X, page 49, lists the values obtained for k_A and k_B for series (a) to (d).

Obviously (within experimental accuracy) substitution of the hydrogen attached to carbon in HCOOH by deuterium has little effect on k_A, and hence it appears that cleavage of the C-H bond probably does not play an important role in the rate-controlling step of the oxidation of HCOOH. This is applicable in H_2O as well as in D_2O, as is seen in Tables X and XI. Ratios of k_A (A) and (C) are approximately unity in the two solvents, showing that rates of oxidation of undissociated HCOOH are unaffected by deuterium substitution in either solvent.

Moreover, apparently there is very little solvent isotope effect on k_A; values in H_2O being close to those in D_2O for HCOOH and DCOOH. This is seen by examining ratios (B) and (D), Table XI. Hence it seems that H-O bonds of the solvent also do not play an important part in the oxidation rate-controlling process.

On the other hand, oxidation of $HCOO^-$ is observed to be greatly affected by deuterium substitution. In H_2O,

TABLE X

RATE CONSTANTS IN VARIOUS ISOTOPIC SYSTEMS

System	$k_A \times 10^3$ $\text{l-m}^{-1}\text{s}^{-1}$	$k_B K_1 \times 10^3$ sec^{-1}	$K_1 \times 10^4$ m/l	k_B $\text{l-m}^{-1}\text{s}^{-1}$
HCOOH in H_2O	1.69	1.94	5.6	3.50
DCOOH in H_2O	1.60	0.40	8.0	0.50
HCOOD in D_2O	1.50	1.74	1.9*	9.1
DCOOD in D_2O	1.57	0.348	2.7*	1.29

*Calculated from $K_1(D_2O) = 0.340 K_1(H_2O)$.[36]

TABLE XI

RATIOS OF RATE CONSTANTS FOR VARIOUS ISOTOPIC SYSTEMS

Reaction	$k^{HC-}_{H_2O}/k^{DC-}_{H_2O}$	$k^{H-}_{H_2O}/k^{H-}_{D_2O}$	$k^{H-}_{D_2O}/k^{D-}_{D_2O}$	$k^{D-}_{H_2O}/k^{D-}_{D_2O}$
"H"COO"H"+MnO$_4^-$→	1.06(A)	1.13(B)	.974(C)	1.04(D)
"H"COO$^-$+MnO$_4^-$→	7.0 (E)	0.38(F)	7.1 (G)	0.39(H)

reactions of $HCOO^-$ are 7.0 times faster than reactions of $DCOO^-$ (Table X and ratio E, Table XI), in agreement with the values of 7.4 and 6-10 previously reported by Wiberg and Stewart,[57] and Aebi, Buser and Luthi (Helv. Chim. Acta., 112:944.1956), respectively. In the solvent D_2O the ratio $k_{HCOO^-}:k_{DCOO^-}$ is 7.1, (Ratio G, Table XI), indicating that in forming the activated complex cleavage or weakening of the C-H bond occurs.[11,26,27,55]

Also, a noticeable solvent isotope effect is seen for the $HCOO^-$ oxidation. Oxidation of $HCOO^-$ in H_2O is 0.38 times that in D_2O. Similarly, oxidation of $DCOO^-$ in H_2O is 0.39 times that in D_2O. (Ratios F and H, Table XI.) Apparently H-O bonds of the solvent play some part in the rate-controlling step. The experimental uncertainties of k_A and k_B are estimated to be as follows: series (a) $\pm 2\%$; series (b) $\pm 3\%$; series (c) $\pm 10\%$; series (d) $\pm 15\%$. The large possible error in the latter two series are due to the very small slopes: these are reflected in large uncertainties in k_B.

CONCLUSIONS

I. Mechanism of the Formate Ion Reaction

The observed entropy of activation ($\Delta S_B^{\ddagger} = -15$ eu.) is within the normal range for a bimolecular reaction between two similarly-charged ions.

The occurrence of a deuterium isotope effect implies C-H bond weakening or breakage in the rate-controlling step. The present observations are consistent with those of Aebi et. al. (Helv. Chim. Acta., 112:944.1956), and Wiberg and Stewart.[57] The results imply a hydride transfer to MnO_4^- during the rate-controlling step. However, Wiberg and Stewart have also shown that oxygen from MnO_4^- appears in the CO_2 product in this reaction.[57] Hence a combination of the two processes is probable. Possibly the transition complex is a cyclic species, e.g.

$$O = C \underset{\diagdown H \diagup}{\overset{\diagup O^-}{- - - - - O}} - - - MnO_3^-$$
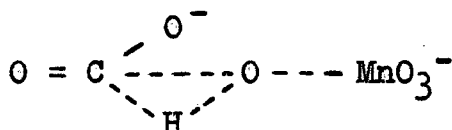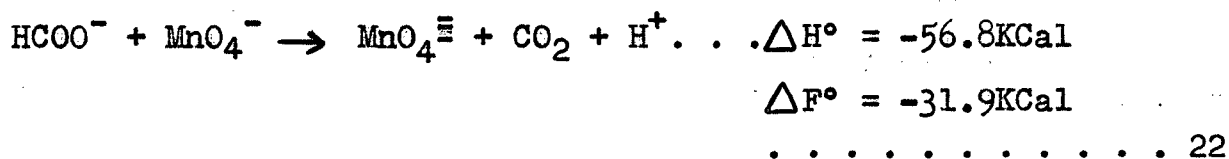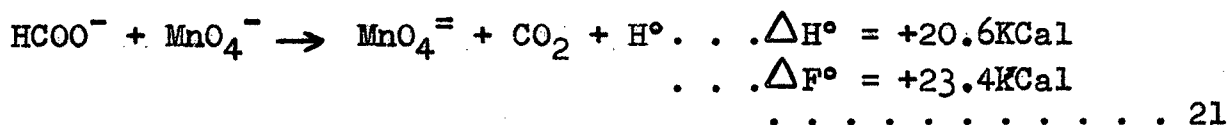
In forming this activated complex the C-H bond will be greatly weakened, reflected in a deuterium isotope effect. Subsequent decomposition of the activated complex may proceed in two ways: a) complete cleavage of the C-H bond, with transfer of hydride ion to MnO_4^- forming $HMnO_4^=$ b) cleavage of the O-Mn bond; and hence transfer of a MnO_4^- oxygen to the CO_2 product

or to the solvent. Formation of other types of cyclic transition intermediates will also be consistent with the observed behaviour; for example, complete cleavage of the C-H bond in the rate-determining step to form a "cage" type of transition species:

$$O = C \begin{array}{c} \diagup O \diagdown \\ H^- \\ \diagdown O \diagup \end{array} MnO_3^-$$
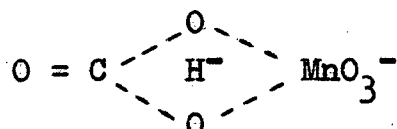
in which hydride ion may subsequently be transferred to MnO_4^-, or else the O-Mn bond is broken, oxygen appearing in CO_2.[57]

Possible intermediates in the reaction mechanism are Mn(VI) and Mn(V),[8,37,47] both of which would be expected to react rapidly under the experimental conditions to give the observed products. The latter species is considered more likely on thermodynamic grounds:

$$HCOO^- + MnO_4^- \longrightarrow MnO_4^= + CO_2 + H^\circ \quad . \quad . \quad .\Delta H^\circ = +20.6 KCal$$
$$. \quad . \quad .\Delta F^\circ = +23.4 KCal$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 21$$

$$HCOO^- + MnO_4^- \longrightarrow MnO_4^{\equiv} + CO_2 + H^+ \quad . \quad . \quad .\Delta H^\circ = -56.8 KCal$$
$$\Delta F^\circ = -31.9 KCal$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 22$$

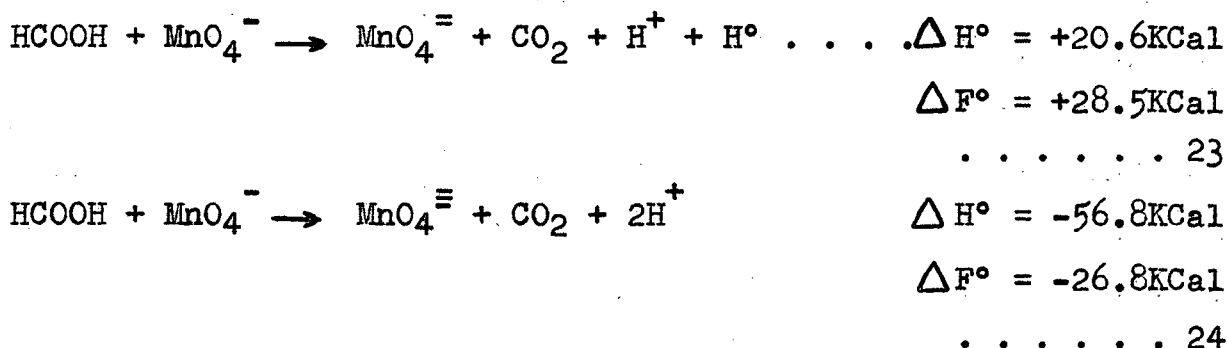ΔH° values used here for $MnO_4^=$ and $MnO_4^{\equiv}$ were those evaluated by Symons in basic solution.[48] Other values were obtained from Latimer.[28] Formation of a H atom in equation 21 is considered energetically inconsistent with the observed activation energy ($E_B = 13$ kCal/mole). However, the formation

of Mn(V), as shown in equation 22, seems possible. This species has been postulated for this reaction, and for the reaction between MnO_4^- and benzaldehyde.[56,57] Furthermore, since Mn(V) can be regarded to form either by a two electron (or hydride ion) transfer from $HCOO^-$ to MnO_4^- (to give $HMnO_4^=$), or by oxygen transfer from MnO_4^- to $HCOO^-$ (to give MnO_3^- or a related species), this postulate is consistent with the isotopic observations.[57]

II. Mechanism of the Formic Acid Reaction

Under the conditions described, oxidation of undissociated HCOOH apparently does not involve C-H bond cleavage in the rate-controlling step, as indicated by the absence of a deuterium isotope effect. Possibly the mechanism of oxidation proceeds by oxygen transfer from MnO_4^- to HCOOH, or by electron transfer from HCOOH to MnO_4^-. This is an interesting demonstration that ionized and unionized forms of a substance may react by different mechanisms.

The entropy of activation ($\Delta S_A^{\ddagger} = -19$ eu.) is abnormally low for a bimolecular reaction between an ion and a neutral molecule. A similarly low $\Delta S^{\ddagger}$ is observed for the reaction between H_2 and MnO_4^- in solution. This suggests that $MnO_4^=$ may be involved as an intermediate, reflected in a transition state which is more highly hydrated than the reactants because of a greater charge. That Mn(V) and not Mn(VI) is formed in the rate-controlling step is supported thermodynamically:
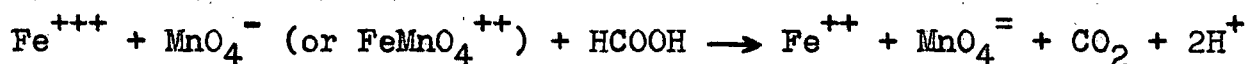
$$HCOOH + MnO_4^- \longrightarrow MnO_4^= + CO_2 + H^+ + H° \quad \ldots \ldots \Delta H° = +20.6 KCal$$

$$\Delta F° = +28.5 KCal$$

$$\ldots \ldots 23$$

$$HCOOH + MnO_4^- \longrightarrow MnO_4^\equiv + CO_2 + 2H^+ \qquad \Delta H° = -56.8 KCal$$

$$\Delta F° = -26.8 KCal$$

$$\ldots \ldots 24$$

Again, formation of Mn(VI) accompanied by formation of a H atom in equation 23 leads to a value of $\Delta H°$ (and $\Delta F°$) which appears inconsistent with the observed activation energy (16 kCal/mole), while formation of Mn(V) by equation 24 appears to be energetically plausible.

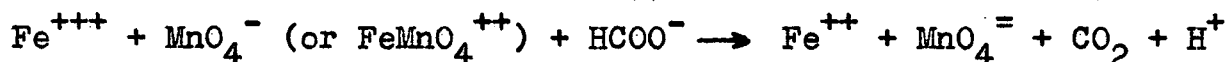## III. Ferric--Catalyzed Reaction

In view of the observed activation energies, and the comparably large energy required to form H atoms, it is suggested that formation of Mn(V) rather than Mn(VI) is more probable in the uncatalyzed reaction schemes. From an examination of equations 21 and 23, it might be predicted that formation of Mn(VI) would be favored by the presence of another species which readily accepts an electron (or combines with a H atom).

The catalytic activity of Fe^{+++} in this reaction may be due to its fulfilling this role, so that the rate-determining steps of the catalyzed reactions can be expressed as

$$Fe^{+++} + MnO_4^- \text{ (or } FeMnO_4^{++}\text{)} + HCOOH \longrightarrow Fe^{++} + MnO_4^= + CO_2 + 2H^+$$

$$\text{where } \triangle H^\circ = -41.1kCal$$

$$\triangle F^\circ = -37.9kCal \ldots\ldots\ldots\ldots 25$$

$$Fe^{+++} + MnO_4^- \text{ (or } FeMnO_4^{++}\text{)} + HCOO^- \longrightarrow Fe^{++} + MnO_4^= + CO_2 + H^+$$

$$\text{where } \triangle H^\circ = -41.1kCal$$

$$\triangle F^\circ = -43.0kCal \ldots\ldots\ldots\ldots 26$$

Here the energetics of formation of $Mn(VI)$ are apparently favorable, since $\triangle H^\circ$ and $\triangle F^\circ$ for both reactions are negative. This mechanism is analogous with the proposed mechanism for Ag^+ catalysis of the reaction between H_2 and MnO_4^- [54] where Ag^+ acts as a hydrogen atom acceptor, and hence energetically promotes formation of $Mn(VI)$. It is of interest that Ag^+ apparently does not catalyze the reaction of MnO_4^- with HCOOH or HCOO$^-$.

Fe^{+++} has also been reported to cause a slight increase in the rate of the H_2-MnO_4^- reaction [54] which was attributed to induced decomposition by MnO_4^- rather than to catalysis. In view of the present study, it would be of interest to examine this effect further.

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