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ABSTRACT

The kinetics of the reaction of ferricyanide with borohydride
(in the concentration ranges for both reactants of $0.1-0.5\underline{M}$) has
been studied in alkaline aqueous solution at room temperature.
The reaction was found to be catalyzed by glass surfaces. This
catalysis, however, can be avoided by using wax-coated-surfaces.
The rate of change of the hydroxide ion concentration was found
to be first order in both ferricyanide and borohydride and
independent of the hydroxide ion, at least in the high pH region,
with a rate constant of $4.93\times10^{-4}\underline{M}^{-1}min.^{-1}$. This result is
different from that found by Freund for very dilute ferricyanide
and borohydride ion in buffered aqueous solution. Under the
conditions of Freund's experiments, no glass catalysis was
observed.

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I. INTRODUCTION

The recent study of complex hydrides of boron, aluminum and gallium is one of the most important developments in inorganic chemistry in view of the broad usefulness of these compounds as reducing agents. In the process of complex ion formation, the hydride ion coordinates, or donates a share in its pair of electrons to the central atom of the acceptor molecule:

$$:H^- + \overset{\text{H}}{\underset{\text{H}}{\ddot{X}}}\text{H} \ \text{-----}\ \left[\overset{\text{H}}{\underset{\text{H}}{\text{H}:\ddot{X}:\text{H}}} \right]^- \tag{1}$$

where X = B, Al or Ga. Since the hydride ion is not a strong electron donor, the acceptor component must necessarily be strong if compound formation is to take place. All of these XH_4^- ions are believed to be tetrahedral, i.e., the four bonds to the hydrogen atoms are equivalent. This structure has been established for the BH_4^- ion.[1,2] The stability of a complex hydride salt depends not only on the strength of the electron

acceptor but also on the strength of the metallic component as
an electron acceptor. The alkali metal borohydrides are fairly
stable since the alkali metal ion can offer very little competi-
tion to the BH_3 group for the electron associated with hydride
ion. The salts most widely used as reducing agents are $NaBH_4$
and KBH_4.

The reactions of borohydride with iodine, permanganate and
hypochlorite in aqueous solution have been investigated from an
analytical standpoint by Jensen.[3] Several other reactions of
borohydride have been surveyed by other workers.[4] However, water
is the first inorganic oxidising agent for borohydride which has
been studied kinetically.[5,6,7] In this case, the rate of the
hydrolysis of borohydride may be represented by the expression:

$$- \frac{d(OH^-)}{dt} = k_1(H^+)(BH_4^-) + k_2(BH_4^-) \qquad (2)$$

over the pH ranges 3.8-14.[7] The rate-determining step of the
acid hydrolysis is believed to be the formation of a short-lived
intermediate, BH_5,

$$BH_4^- + H^+ \xrightarrow{\text{slow}} BH_5 \qquad (3)$$

followed by,

$$BH_5 \longrightarrow BH_3 + H_2 \qquad (4)$$
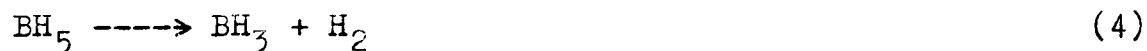
In order to get more information of the general behavior of boro-
hydride as a reducing agent, it seems worthwhile to do extensive
investigation of the kinetics of the redox reactions of boro-
hydride with other inorganic species. Among them, the ferri-

cyanide ion should be an attractive choice because both ferri-
cyanide and ferrocyanide are extremely stable with respect to
dissociation and have the same octahedral geometry and chemical
composition.   Therefore, we can expect that only a one-electron
transfer is involved.[8]   The reaction of borohydride with ferri-
cyanide to give borate and ferrocyanide has been previously
studied in buffered aqueous solution by Freund.[9]   The con-
centration ranges in his experiments were: initial borohydride
from 1×10^{-3} to $70 \times 10^{-3} \underline{M}$, ferricyanide from 1.5×10^{-4} to $18 \times 10^{-4} \underline{M}$
and hydrogen ion from 6×10^{-10} to $3 \times 10^{-3} \underline{M}$.   The over-all
stoichiometry is,

$$8Fe(CN)_6^{3-} + BH_4^- + 8OH^- \longrightarrow 8Fe(CN)_6^{4-} + H_2BO_3^- + 5H_2O \quad (5)$$
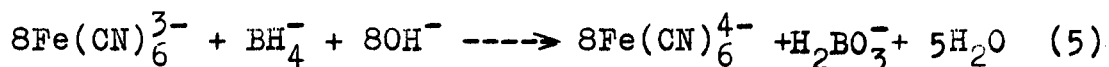
The rate of disappearance of the ferricyanide ion was measured
from its absorption with a spectrophotometer to be first order
in both borohydride and hydrogen ion and independent of the
ferricyanide ion,

$$- \frac{d(Fe(CN)_6^{3-})}{dt} = k(BH_4^-)(H^+) \quad (6)$$

This kinetics suggests that the activated complex for the rate-
determining step of the oxidation of borohydride by ferricyanide
is probably the same as the hydrolysis, in the absence of
ferricyanide, of borohydride alone.

While extending to higher concentration ranges of both boro-
hydride and ferricyanide in alkaline aqueous solutions, however,
it was found in this laboratory that obvious deviation in rate

law of this redox reaction from that of dilute concentration case occurred. Several observations from preliminary experiments were: (i) the reaction was quite unreproducible without stirring; (ii) the rate of change of hydroxide ion concentration with excess borohydride and ferricyanide ion increased with increasing ferricyanide ion concentration; and (iii) the glass-surface catalytic effect was extremely influential. Therefore, more work has been done on these aspects. The results showed that a different mechanism must exist.

II. EXPERIMENTAL

A. Preparation of Solutions

Metal Hydrides potassium borohydride ($KBH_4 > 97\%$) was used without further purification. It is a white crystalline material which is stable in dry air. General Chemical potassium ferricyanide ($K_3Fe(CN)_6 > 99\%$) was recrystallized from water and dried under vacuum at room temperature. The aqueous solution of ferricyanide thus obtained was slightly acidic because of dissolved carbon dioxide. Both solid reactants were separately dissolved in 0.01$\underline{M}$ sodium hydroxide up to 100 ml., in order to stabilize the borohydride and to get roughly the same initial hydroxide ion concentrations. These two solutions were then mixed together in a 400 ml. beaker with vigorous stirring, especially at the beginning of mixing.

In these experiments, the ferricyanide and borohydride ion concentrations were kept essentially constant by using a large excess, i.e., both of them from 0.1 to 0.5$\underline{M}$ while initial hydroxide ion was 1.4×10^{-2} to $2.4 \times 10^{-2}\underline{M}$.

B. Reaction in Glass Beaker
a. Reaction without Stirring in an Open Vessel

The kinetic studies were carried out at room temperature by continuously following the concentration of hydroxide ion with a Radiometer pH meter, using a Type G222B glass electrode. A Radiometer Type S1001 buffer solution (pH = 6.50) was used as

a pH standard.

When the reaction mixture was allowed to stand still after
bringing the two reagents together, quite peculiar and unre-
producible results were obtained. The pH value of the solution
dropped slowly until it reached somewhere around 8 to 9 after
a period of time which varied from a few seconds to one hour
from the start of the reaction, then a spontaneous foaming
occurred. After the foaming, the solution became acidic. An
example of these unreproducible results was shown in Fig. 1.
In fact, it was this observation which led to the performance
of this work. Such phenomena were not expected if the reactions
were the same as that reported by Freund for the low concentration
case.

b. <u>Reaction with Stirring in an Open Vessel</u>

When the reaction proceeded with constant stirring in a glass
beaker, a more satisfactory result was obtained. Typical runs
were shown in Fig. 2. The hydroxide ion concentration vs. time
plot was linear in the high concentration region, but began to
curve toward the time axis after a turning point was reached.
This point occurred at an approximate hydroxide ion concentration
of 5×10^{-3} to $7 \times 10^{-3} \underline{M}$ in all runs with different ferricyanide
and borohydride concentration. Spontaneous foaming followed
as before.

The linear relationship in high concentration region indicated
a zero order with respect to hydroxide ion of the reaction. It
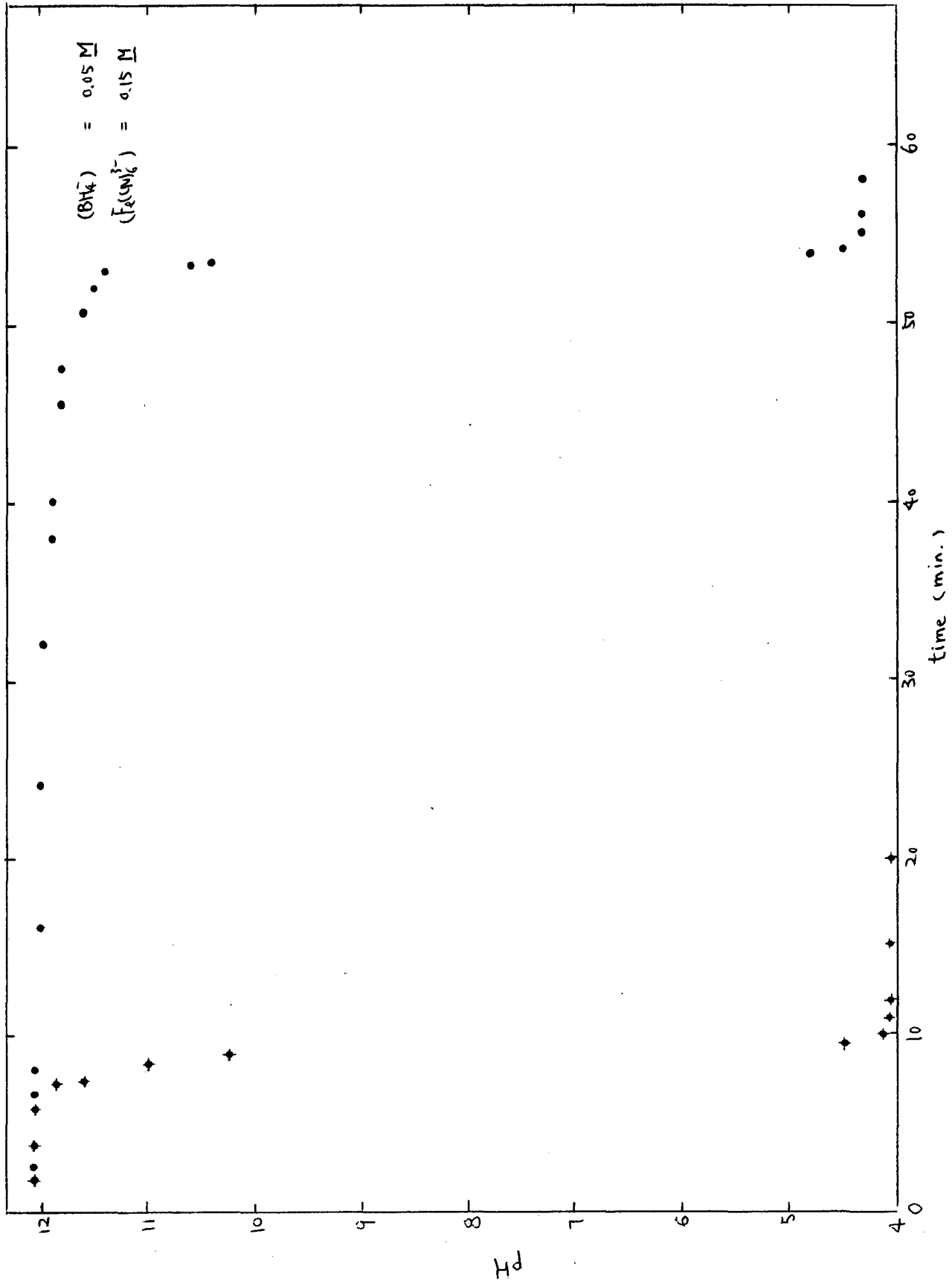was also noticed that, with constant borohydride, $-d(OH^-)/dt$

Fig. 1. pH vs. time for reactions in glass beakers without stirring. Both runs at the same concentrations, $(BH_4^-)=0.05\ \underline{M}$, $(Fe(CN)_6)^{3-}=0.15\underline{M}$.
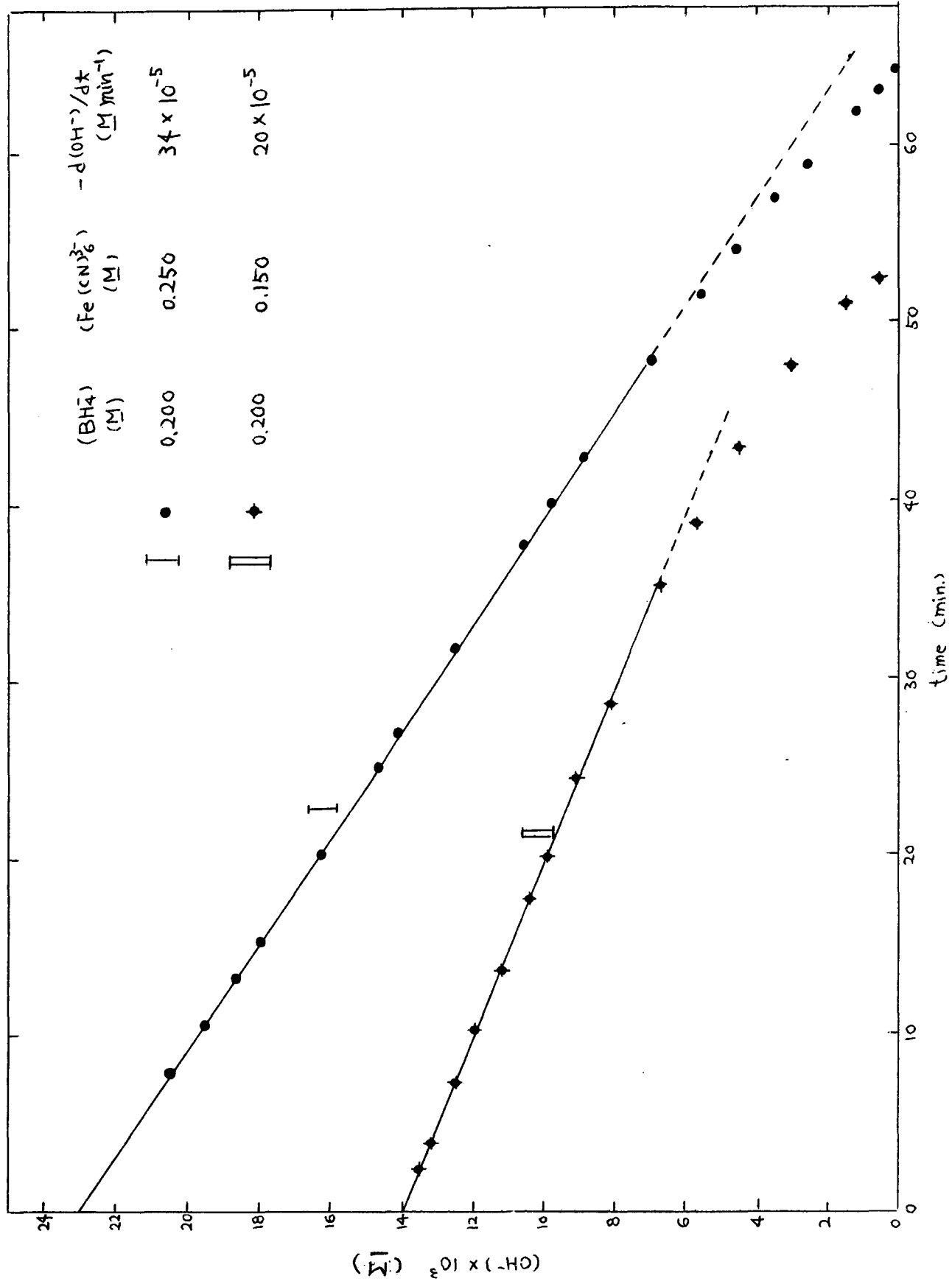
Fig. 2. (OH⁻) vs. time for reactions in glass beakers with stirring.

increased almost twice when ferricyanide was doubled. Neither of these observations could be explained by Freund's rate equation which suggested that $-d(OH^-)/dt = -d(Fe(CN)_6^{3-})/dt$ should be first order in hydrogen ion and zero order in ferricyanide.

Furthermore, the lack of reproducibility mentioned before still remained, even though the ambiguity was greatly minimized by stirring of the solution. Therefore, we tried to study other possible effects which might be involved in this reaction.

c. Reaction with Exclusion of Air

Since this kinetic study was made by following the pH value of the solution, experimental error might be caused by the atmospheric carbon dioxide which dissolved into the solution if an open vessel was used. To test this, pure argon gas was blown over the top of the solution and the result thus obtained was compared with that of the reaction with solution directly contacted with air. Since argon gas is more dense than air, the solution could be isolated from air. As shown in Fig. 3, the rate of change of hydroxide ion was decreased for a small amount with exclusion of air by this method. A same result was obtained for an alkaline solution without any borohydride and ferricyanide in it. The $-d(OH^-)/dt$ due to air alone was of the order of 2×10^{-5} $\underline{M}$ min.$^{-1}$. However, since this value was small when compared to the observed total rate, this effect could be neglected for the first approximation.
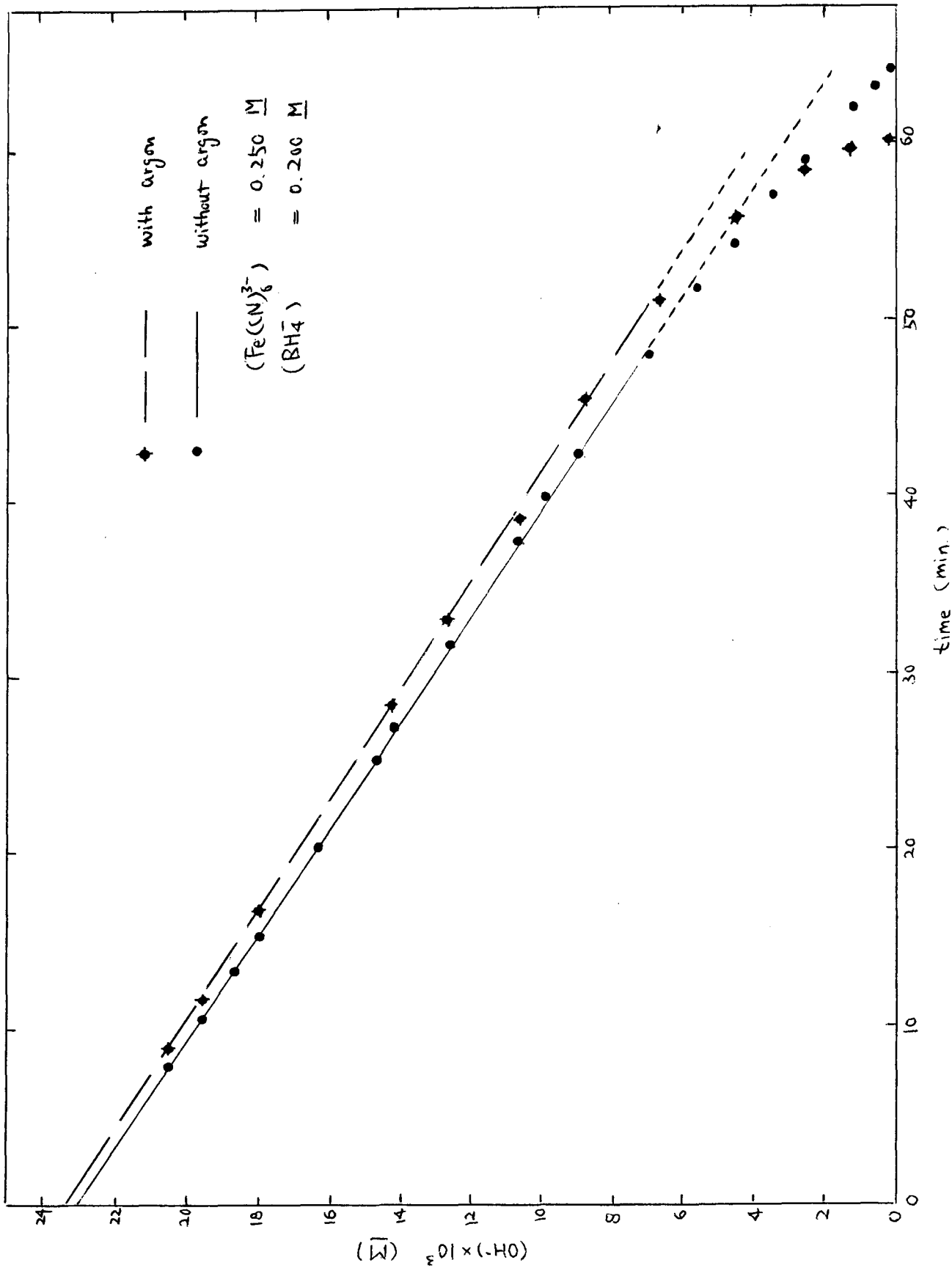
Fig. 3 (OH⁻) vs. time for reactions in glass beakers with and without Argon blowing over the top.

d. Surface Catalytic Effect

Surface catalysis was first noticed by observing that bubbles formed with a varied rate on the wall of the glass beaker during the reaction without stirring.   The situation was improved by using constant stirring of the solution.   The bubbles on the wall disappeared.   This might be connected to the difference of observations between reactions with and without stirring. However, it would be expected that surface catalysis still existed as long as a glass beaker was used.   Therefore, experiments in containers with paraffin (wax-coated) and polyethylene surfaces were performed.   Positive evidence was found that the reaction rates changed drastically for different types of surfaces.   A qualitative result was listed in Table 1 for comparison.

Table 1.   Rates of Disappearance of Hydroxide Ion with Solutions in Containers of Different Surfaces.
$(BH_4^-) = 0.1\underline{M}$; $(Fe(CN)_6^{3-}) = 0.25\underline{M}$
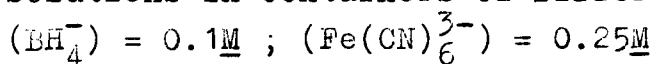
Types of Surfaces	$-d(OH^-)/dt$ $(\underline{M}\ min.^{-1})$
Glass	$\sim 13 \times 10^{-5}$
Polyethylene	$\sim 4 \times 10^{-5}$
Paraffin (Wax-Coated)	$\sim 1 \times 10^{-5}$

C. Reaction in Wax-Coated Beaker

As shown in Table 1, a wax-coated surface had the least cata-
lytic effect. A series of experiments was done for different
ferricyanide and borohydride ion concentrations in wax-coated
beakers. American Oil Parawax wax was used. Since the reaction
rates ranged from 1×10^{-5} to 12×10^{-5} $\underline{M}$ $min.^{-1}$ in this whole series,
the exclusion of air became more important. Therefore, argon
gas protection for the solutions was used for all runs. To
make sure that no reactions existed had contributions to the
$-d(OH^-)/dt$ term other than the true reaction between ferricyanide
and borohydride, several preliminary checks have been done.
Three kinds of solutions including (i) $(BH_4^-) = 0$, $(Fe(CN)_6^{3-}) = 0$,
$(OH^-) = 10^{-2}\underline{M}$; (ii) $(BH_4^-) = 0$, $(Fe(CN)_6^{3-}) = 0.3\underline{M}$, $(OH^-) = 10^{-2}\underline{M}$;
and (iii) $(BH_4^-) = 0.3\underline{M}$, $(Fe(CN)_6^{3-}) = 0$, $(OH^-) = 10^{-2}\underline{M}$ were
observed for two hours and no appreciable change in the hydroxide
ion concentration was found in either of the three cases. These
implied that (i) the wax surface had no active impurity; (ii) the
exclusion of air was complete; (iii) the ferricyanide was very
stable; and (iv) the hydrolysis of borohydride in this high pH
region had no contribution to the $-d(OH^-)/dt$ term.

This series included different runs with both ferricyanide
and borohydride from 0.1 to 0.5$\underline{M}$ and initial hydroxide ion from
1.4×10^{-2} to $2.4 \times 10^{-2}\underline{M}$.

The typical (OH^-) vs. time plot for all runs as shown in Fig.4
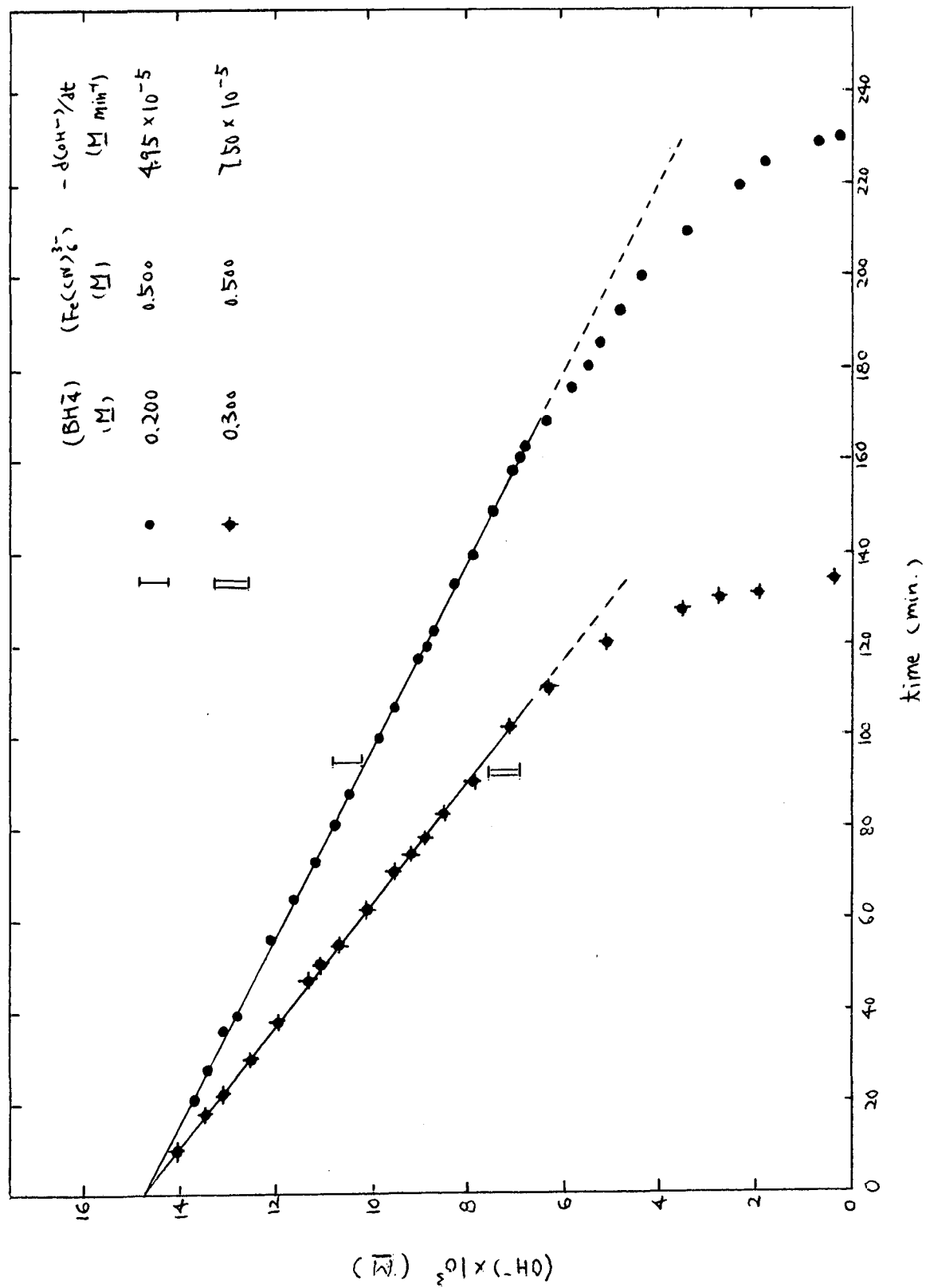showed the same tendency as seen before in glass beaker runs.

Fig. 4. (OH⁻) vs. time for reactions in wax-coated beakers.

It was linear in high (OH⁻) region and began to curve toward the time axis once a turning point, $(OH^-)_t$, was reached.

For the linear part, the slopes which gave the values of $-d(OH^-)/dt$ showed definitely first order dependence of the reaction rate on both ferricyanide and borohydride and zero order on hydroxide ion. This relation was obtained by comparing the lines with the equation,

$$- \frac{d(OH^-)}{dt} = 4.93 \times 10^{-4}(BH_4^-)(Fe(CN)_6^{3-}) \tag{7}$$

and the experimental results (Table 2) in Fig. 5 and Fig. 6. These slopes could be reproduced.

Table 2. Experimental Values of $-d(OH^-)/dt$ and $(OH^-)_t$.

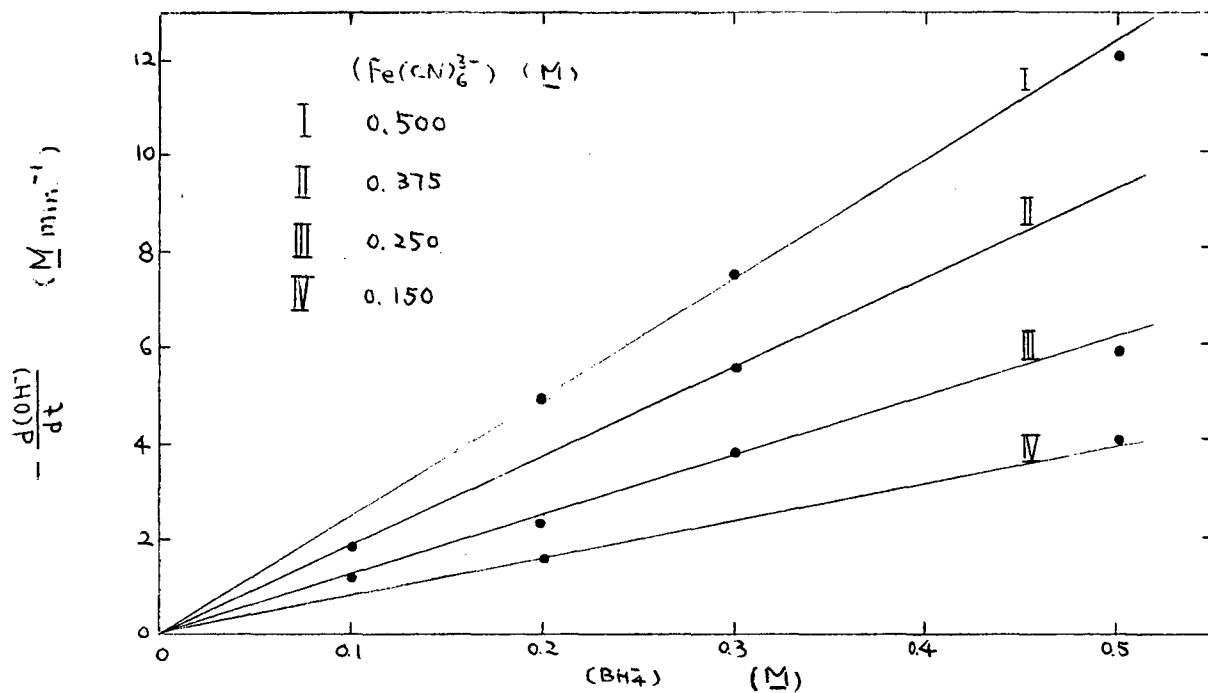| (BH_4^-) (M)	$(Fe(CN)_6^{3-})$ (M)	$-d(OH^-)/dt \times 10^5$ (M min.$^{-1}$)	$(OH^-)_t \times 10^3$ (M)
0.500	0.500	12.20	-§
0.500	0.250	5.90	7.0
0.500	0.150	3.85	5.3
0.500	0.100	2.75	-
0.300	0.500	7.50	6.2
0.300	0.375	5.60	-
0.300	0.250	3.80	7.0
0.200	0.500	4.95	6.2
0.200	0.250	2.25	-
0.200	0.150	1.55	-
0.100	0.375	1.85	-
0.100	0.250	1.20	-

§ $(OH^-)_t$'s were not determined in several runs.

Fig. 5. Rate of disappearance of hyroxide ion vs. borohydride Concentration. Each curve at a const. ferricyanide concentration.
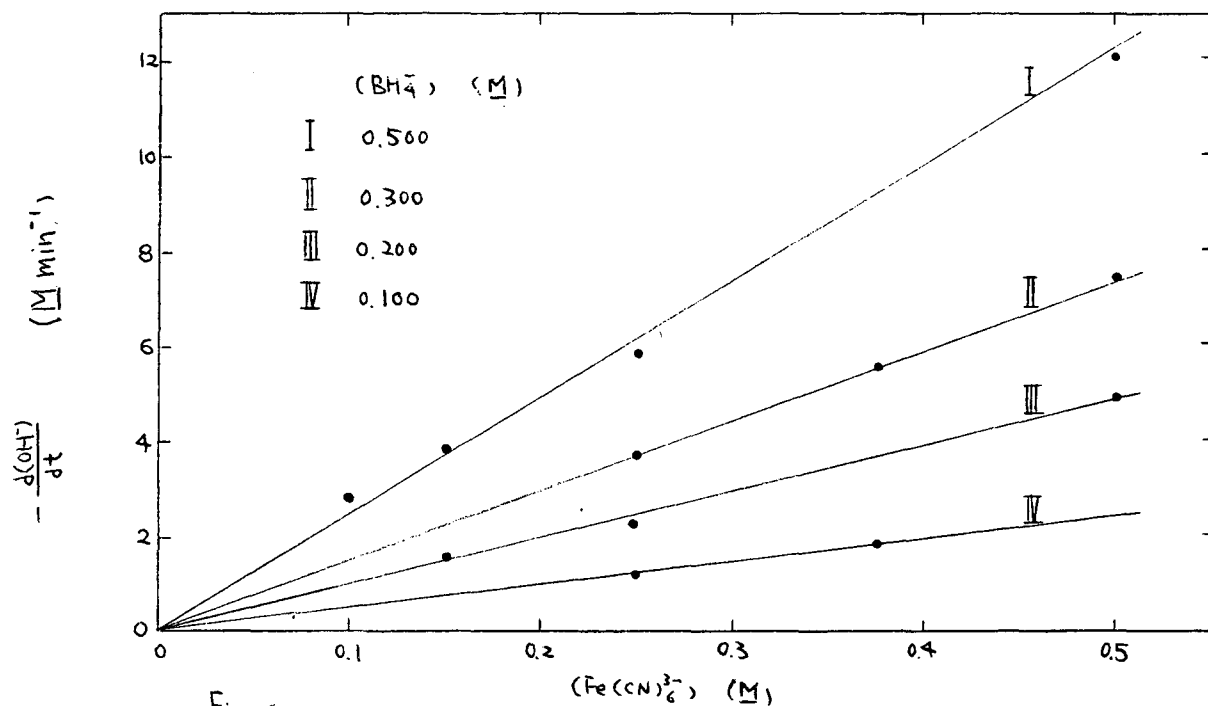

Fig. 6. Rate of disappearance of hydroxide ion vs. ferricyanide Concentration. Each curve at a const. borohydride concentration.

For the lower curved end, however, the change of hydroxide ion concentration was not reproducible. It was thought that, for this part, the method of following the hydroxide ion concentration alone was not good enough for a kinetic study if a more complicated reaction was involved. Thus no further attempt has been made in this work to get exact information for this low hydroxide ion concentration region.

D. Surface Catalytic Effect in Low Concentration Region -- Check of Freund's Results

Since the surface catalytic effect was found to be important in this work, it should be worthwhile to check Freund's results for the reaction of ferricyanide with borohydride in low ferricyanide and borohydride concentration regions. In his experiments, solutions without stirring were contained in small glass cells used for absorption measurements. These cells had relatively large surface-volume ratios. A large surface catalytic effect, therefore, might be possible. To check this, results of two different runs with the same concentration were compared. One solution remained in the cell throughout the reaction (after Freund) and the other remained in a wax-coated beaker and was poured into the cell only when the absorption data were to be taken. The observation of no difference between the rates of the reaction under these two conditions implied that glass-surface catalytic effect was negligible in this low ferricyanide and borohydride concentration case.

Fig. 7 shows a typical result. However, two observations deviated from Freund's: (i) the rate constant differed from his value (Table 3); (ii) with initial ferricyanide ion concentration less than $10^{-4}\underline{M}$, the rate of disappearance of ferricyanide ion began to slow down at a concentration which increased with decreasing initial ferricyanide ion concentration (Fig. 8).

Table 3. Experimental Values of $-d(Fe(CN)_6^{3-})/dt$ and k. $(BH_4^-) = 3.5\times10^{-2}\underline{M}$, $(OH^-) = 10^{-2}\underline{M}$, $t = 23^{\circ}C$.

$(Fe(CN)_6^{3-})$ $(\underline{M})$	$-d(Fe(CN)_6^{3-})/dt\times10^6$ $(\underline{M}\ min.^{-1})$	$k\times10^{-8}$ $(\underline{M}^{-1}min.^{-1})$	
1×10^{-3}	7.7	2.2	This Work
1×10^{-4}	6.7	1.9	This Work
5×10^{-5}	6.4	1.8	This Work
$1.5\times10^{-4}-18\times10^{-4}$	11.2	3.2	Freund

Legend:
- Glass Surface
- Wax-Coated Surface

$(Fe(CN)_6^{3-})_{init.} = 10^{-3} \underline{M}$.
$(BH_4^-) = 3.5 \times 10^{-2} \underline{M}$.
$(OH^-) = 10^{-2} \underline{M}$.
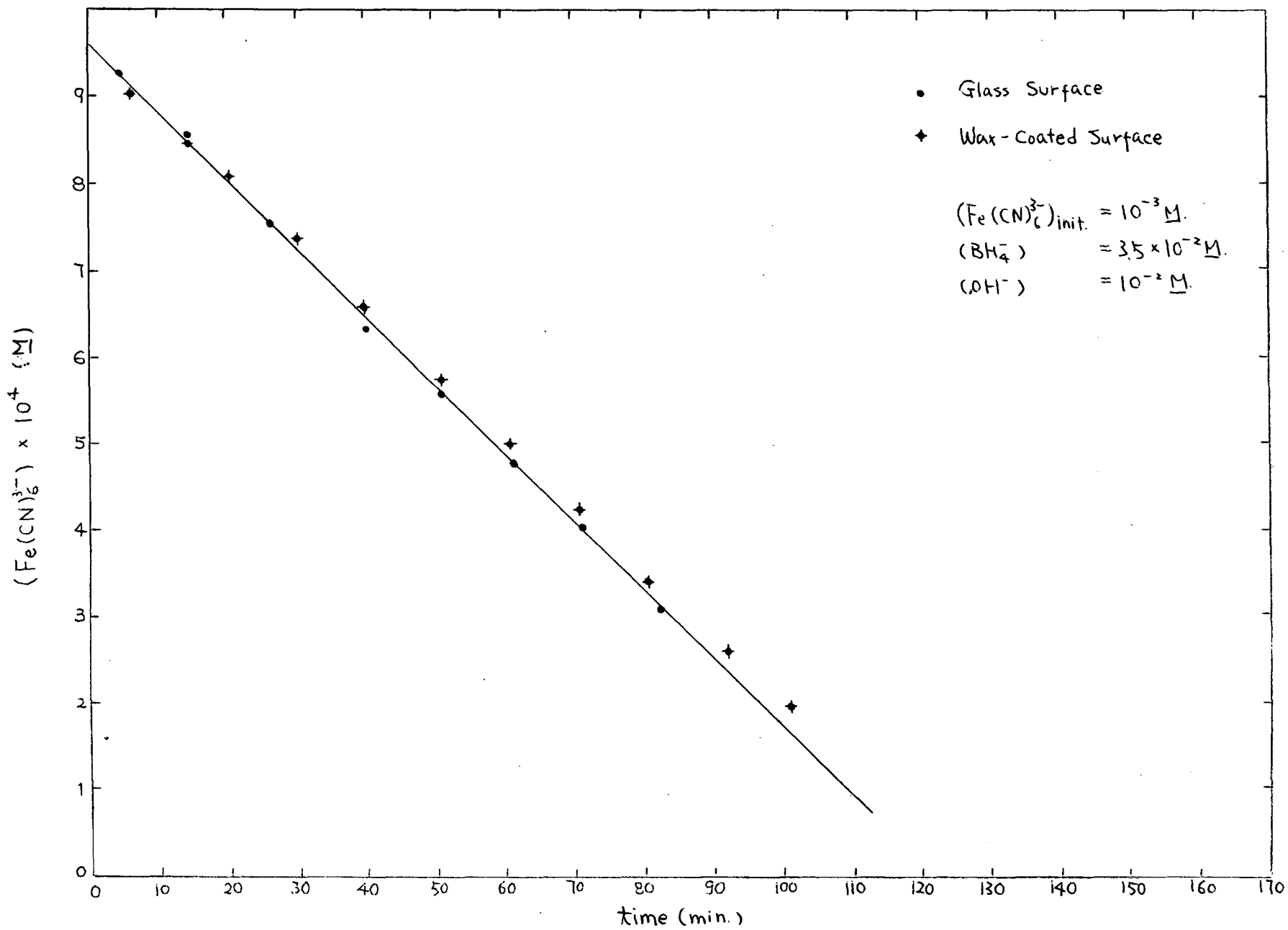
y-axis: $(Fe(CN)_6^{3-}) \times 10^4 \ (\underline{M})$

x-axis: time (min.)

Fig 7. $(Fe(CN)_6^{3-})$ vs time for two reactions with same concentration but different surfaces of containers.

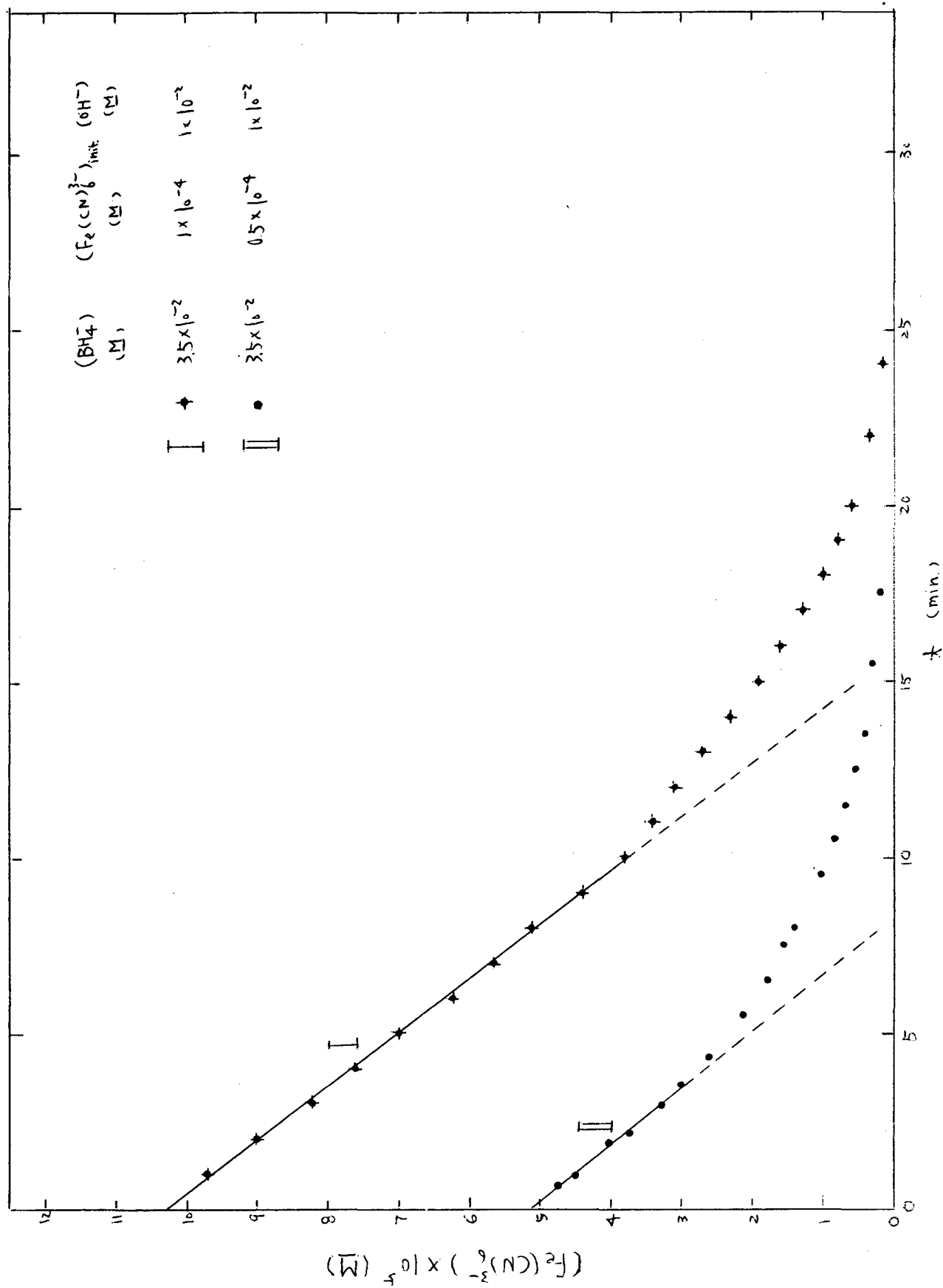Fig. 8. $(F_e(CN)_6^{3-})$ vs. time with excess (BH_4^-) and (OH^-).

III. RESULTS AND DISCUSSION

The discrepancy between Freund's rate equation and the preliminary observation in this laboratory for the reaction of ferricyanide with borohydride in alkaline aqueous solution with different concentration ranges has been affirmed. For the high ferricyanide and borohydride concentrations (both from 0.1 to 0.5$\underline{M}$) case, experimental data gave the rate of the reaction as

$$- \frac{d(OH^-)}{dt} = k'(BH_4^-)(Fe(CN)_6^{3-}) \tag{8}$$

at least for $(OH^-) > 7 \times 10^{-3}\underline{M}$. The rate constant k' was measured to be $4.93 \times 10^{-4} \underline{M}^{-1}\text{min.}^{-1}$. The rate of disappearance of hydroxide ion should be equal to the rate of disappearance of ferricyanide ion according to the over-all stoichiometry (Eq. (5)). However, Eq. (8) was completely different from Eq. (6) as reported by Freund ($k = 3.2 \times 10^8 \underline{M}^{-1}\text{min.}^{-1}$ at $t = 23^{\circ}C$). It would be easier to understand if

$$k'(BH_4^-)(Fe(CN)_6^{3-}) \gg k(BH_4^-)(H^+)$$
$$\text{for high } (Fe(CN)_6^{3-}) \tag{9}$$

and

$$k'(BH_4^-)(Fe(CN)_6^{3-}) \ll k(BH_4^-)(H^+)$$
$$\text{for low } (Fe(CN)_6^{3-}) \tag{10}$$

then the $k'(BH_4^-)(Fe(CN)_6^{3-})$ term would be negligible in Freund's result while the $k(BH_4^-)(H^+)$ term negligible in the result of this work. Unfortunately, even if relation (10) is true,

relation (9) does not hold. For example, with $(BH_4^-) = 0.2\underline{M}$, $(Fe(CN)_6^{3-}) = 0.25\underline{M}$, $(OH^-) = 10^{-2}\underline{M}$ or $(H^+) = 10^{-12}\underline{M}$, $k(BH_4^-)(H^+)$ was more than twice as large as $k'(BH_4^-)(Fe(CN)_6^{3-})$. There is still no satisfactory explanation for these different rate laws. The main problem is that, even another mechanism led to the $k'(BH_4^-)(Fe(CN)_6^{3-})$ term in the high concentration case, no one would expect the $k(BH_4^-)(H^+)$ term to vanish as long as its value is of the same order as the $k'(BH_4^-)(Fe(CN)_6^{3-})$ term.

The lower part of the hydroxide ion concentration vs. time plot is believed to arise from a more involved reaction. Below the turning point, which was at $(OH^-)_t = 5\times10^{-3}$ to $7\times10^{-3}\underline{M}$, the rate of disappearance of hydroxide ion became very fast and apparently depended on the concentration of hydroxide ion itself. However, it could not be reproduced. Other methods, which would be more effective than the pH measurement, should be used for further investigation.

The importance of surface catalysis in this reaction was an interesting discovery. This effect was positively proved to exist by the change of reaction rates in containers of different surfaces. It was found that wax-coated surface had the least catalytic effect. The reproducibility of results showed that surface catalysis was negligible for the reaction in a wax-coated beaker. Therefore, such beakers were used to obtain useful data. It would be instructive to point out here that the rate of reaction in a glass beaker was some ten times that

measured in a wax-coated one.   Again, on the other hand, this
glass-surface catalysis did not exist for low ferricyanide and
borohydride case.   Freund's result was thus checked to be
independent of the surface of the container.   However, a
different rate constant and a deviation from zero order dependence
of ferricyanide ion concentration of the rate law were observed.

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