A MECHANISM FOR THE DECOMPOSITION OF POTASSIUM FERRATE (VI) IN AQUEOUS SODIUM HYDROXIDE

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Major professor

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A MECHANISM FOR THE DECOMPOSITION
OF
POTASSIUM FERRATE(VI)
IN
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By

Orville N. Hinsvark

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ABSTRACT

A study was made on the decomposition of potassium ferrate(VI) in highly alkaline media. Polarographic techniques utilizing a rotating platinum microelectrode proved unsatisfactory in determining the oxidation states through which ferrate(VI) passes in its reduction. Alkaline solutions of potassium ferrate(VI) were found to obey Beer's Law at 500mμ ; and through spectrophotometric measurements, the kinetics of its decomposition could be determined. Utilization of these kinetic data was made in proposing a possible mechanism for ferrate(VI) decomposition. In order to explain the apparent unstable equilibrium, free hydroxyl radicals were suggested as one of the products which caused a reversal of the initial reaction by oxidation of the ferrite(III). The subsequent oxidation of the free radicals or their recombination product, H_2O_2, by ferrate(VI) was suggested as the primary explanation for the eventual completion of ferrate(VI) decomposition in aqueous alkaline media.

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INTRODUCTION

Iron in the higher oxidation states of plus four and six has been known for a long time. Bohnson[1] showed that the catalytic decomposition of hydrogen peroxide was due to the formation of ferric acid which subsequently reacted with the hydrogen peroxide to form oxygen and water. Bray and Gorin[2] have submitted some evidence to show the presence of low concentrations of ferryl ion, FeO^{+2}, in ferric-ferrous systems and in the catalytic decomposition of hydrogen peroxide with ferrous iron. Under certain limited conditions it is possible to form the perferrite ion, $FeO_3^{=}$, but this appears to be unstable with respect to decomposition into the plus three and six oxidation states.[5]

Solutions involving the ferrate ion are difficult to study because of their rapid decomposition unless the aqueous medium is highly alkaline. The slightly soluble barium ferrate(VI), $BaFeO_4$, appears to be the most stable of its salts. It can be suspended in dilute acetic acid with only slow de-

composition. In mineral acids, however, all ferrates decompose rapidly with the formation of iron in the plus three oxidation state. If the acid is nonoxidizable under these conditions, there is a rapid evolution of oxygen. In an aqueous solution the following reaction takes place:[6]

$$4K_2FeO_4 + 10H_2O \longrightarrow 8KOH + 4Fe(OH)_3 + 3O_2$$

In strongly alkaline media the stability of the ferrates is increased to such an extent that a study of the kinetics of its decomposition is possible.

The relative instability of the ferrates, coupled with the difficulties involved in obtaining them in the pure state, probably explains why the work pertaining to the study of this oxidation state has been limited. The latter detriment to this study has been overcome somewhat by a recently published paper[7] which describes a method for preparing potassium ferrate in a relatively pure state.

This study was made to ascertain the oxidation states through which potassium ferrate passes in its decomposition in an alkaline medium.

The report covering the work done in this study concerns itself with a possible mechanism for the decomposition of potassium ferrate and the experimental evidence used to substantiate the proposed mechanism.

EXPERIMENTAL WORK

Apparatus.

A Sargent Model XXI polarograph was used in an attempt to ascertain the steps through which potassium ferrate passes in its reduction. Since mercury is attacked by the potassium ferrate solution, a dropping mercury electrode could not be used; and a rotating platinum microelectrode was employed. The electrode was made, with slight modifications, according to specifications given by Lingane[4].

In the kinetic studies a Beckman D U spectrophotometer with corex cells was used. Unless otherwise stated, the temperature was maintained at 30° ± 0.2C by a constant temperature bath. The time was measured with a stopwatch, the readings made within ± 10 seconds.

Reagents.

The potassium ferrate was prepared according to Schreyer's[7] procedure; and its purity was ascertained using Schreyer's[8] chromic oxidation method. The purity of the different preparations analyzed by this method varied between 62.5 and 95.5% potassium ferrate, the impurities apparently being potassium hydroxide and ferric oxide.

Solutions.

The concentration of the potassium ferrate solutions was approximately one millimolar with respect to potassium ferrate

(VI). The sodium hydroxide solutions used as the solvent varied in concentration and were prepared by weighing C.P. grade sodium hydroxide and dissolving it in distilled water.

Experimental Procedures.

Polarographic Studies: These studies were made in the usual way. The solutions of potassium ferrate were introduced into the polarographic cell; and the diffusion current, caused by the reduction of the ferrate ion on a rotating platinum microelectrode, was recorded on a polarogram.

Colorimetric Studies: The aqueous sodium hydroxide solutions were prepared and brought to the desired temperature, 30°C, in a constant temperature bath. Weighed quantities of the analyzed potassium ferrate were added to the sodium hydroxide solution flasks, and the optical density of each resulting solution was measured at 500mμ, five minutes, ± 10 seconds, after dissolution of the potassium ferrate. Using these data, adherence to Beer's Law was observed.

Kinetic Studies Using A Beckman D U Spectrophotometer: The kinetic studies were performed in the following way:

(1) The aqueous sodium hydroxide solutions were prepared and placed in 100 ml volumetric flasks.

(2) The sodium hydroxide solution was then placed in the constant temperature bath and permitted to attain the desired temperature. In this work the temperature was usually 30° ± 0.2C.

(3) When the solvent had attained the desired temperature, a weighed quantity of potassium ferrate was introduced into the flask.

(4) The decomposition of the potassium ferrate was followed colorimetrically by withdrawing samples from this flask and introducing them directly into the absorption cell. When this was done, the optical density of the solution was measured at 500mμ. The optical density and the time of the reading were recorded.

(5) Since Beer's Law is obeyed and the optical density is proportional to the concentration, the optical density is used directly in the calculations and graphs. The curves obtained by plotting time versus optical density are found throughout the report. The data used in the plotting of these curves are found in the appendix.

EXPERIMENTAL RESULTS AND INTERPRETATIONS

The experimental results described in greater detail on the following pages show the data used in arriving at the conclusions found in the report.

The first portion of the work involved the use of the polarograph utilizing a rotating platinum microelectrode; while the second and major portion concerns itself with kinetic studies made with a Beckman D U spectrophotometer.

Polarographic Data.

If there is sufficient difference between the free energies of the oxidation states through which the ferrate passes in its reduction, these states should be recorded on a polarogram as a series of steps.

The electrode as described by Lingane could not be used since apparently the insulating wax on the shaft was not stable under the conditions employed. Leaks developed in the wax and the cell formed caused an enormous increase in the recorded current. An attempt was made to cover the shaft with glass tubing through which a platinum wire lead protruded. This design caused considerable stirring which apparently prevented the obtaining of reproducible diffusion currents. The polarograms obtained with varying potassium ferrate and sodium hydroxide concentrations had the same general shape, but no breaks were observed which would indicate a stable oxidation state between the known plus three and plus six levels.

While reproducible results could not be obtained from one run to the next, the diffusion current appeared to be proportional to the concentration of the ferrate in any given solution. This observation is substantiated by the data derived from kinetic runs on the decomposition of potassium ferrate in four normal sodium hydroxide. The temperature was maintained at 0°C in order to increase the stability. The applied emf was set at +.15V versus 0.1N NaOH, HgO electrode, and readings were taken at definite time intervals. This was continued until all the potassium ferrate had decomposed. In order to insure complete decomposition to obtain a base line, hot water was added to the bath until the color, characteristic of the ferrate ion, had disappeared. The polarographic cell and contents were then cooled to 0°C and the diffusion current measured. This diffusion current served as a reference line from which step height measurements were made. The step height at definite times was recorded; and when Log step height versus time was plotted, a straight line resulted. The result of this experiment is shown in Figure I. There is a great deal of dispersion of the points in the individual curves, but the slopes appear to agree closely with rate constants of 6.76×10^{-3} min.$^{-1}$ and 6.83×10^{-3} min.$^{-1}$. Midway through the rate run represented by curve 2, there was a sudden displacement of the diffusion current. This can probably be attributed to an inherent fault in the electrode, possibly a difference in the stirring. On the basis of the above observations, it is probable that if

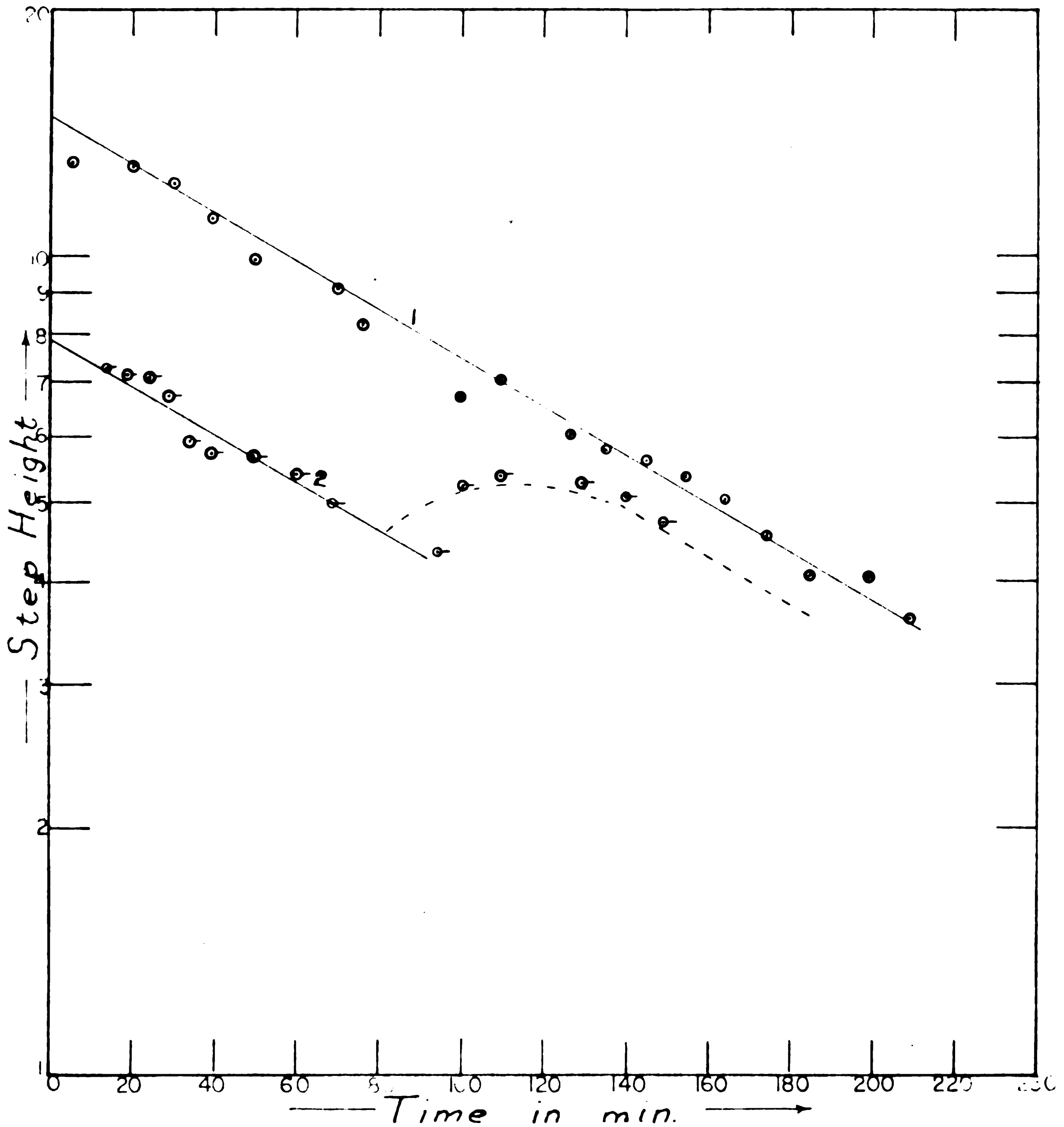

FIG.I: GRAPH SHOWING RATE OF DECOMPOSITION OF POTASSIUM FERRATE IN 4N NaOH AT 0°C. AS DETERMINED ON THE POLAROGRAPH.

stirring could be eliminated, the diffusion current would be proportional to the concentration; and reproducible results could be obtained.

Colorimetric Determination of Potassium Ferrate.

Since a solution of potassium ferrate is highly colored, it seemed quite logical to attempt a colorimetric analysis for the determination of ferrate concentration. This would afford a convenient and rapid method for following its decomposition in various media.

The absorbtion spectrum was determined to show the wave length at which a solution of potassium ferrate had maximum absorbancy, the results can be seen in Figure II. The scan was made by taking readings every 10$m\mu$ on solutions of potassium ferrate dissolved in 8N NaOH. The absorbtion spectrum obtained in this way showed that the solution absorbed strongly in the vicinity of 500$m\mu$. By making a scan with a solution of K_2FeO_4 which had essentially decomposed, the decomposition products, as indicated by curve 2, were shown not to interfere.

By setting the wave length at 500$m\mu$ and taking readings of the optical density, D, of the analyzed ferrate solutions, it is shown in Figure III that Beer's Law is obeyed over the range of concentrations used. Because of the instability of the solutions, it was necessary to make the readings at definite elapsed time intervals. If the elapsed time were five minutes ± 10 sec. as in Figure III, the extinction coefficient was found to be 5.15 l $g^{-1}cm^{-1}$. This was found to hold over

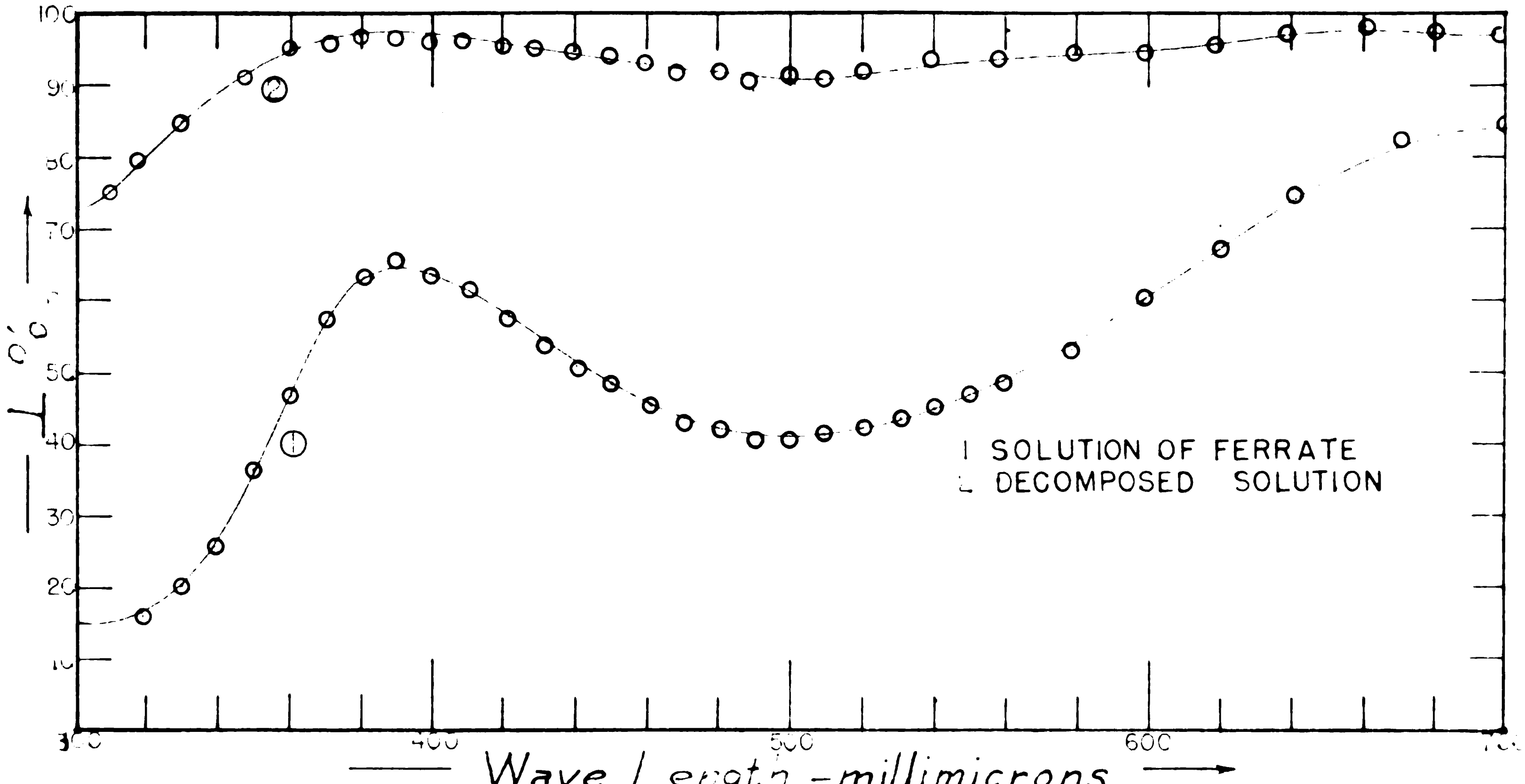

FIG. II: ABSORPTION SPECTRUM OF POTASSIUM FERRATE IN 8N NaOH.

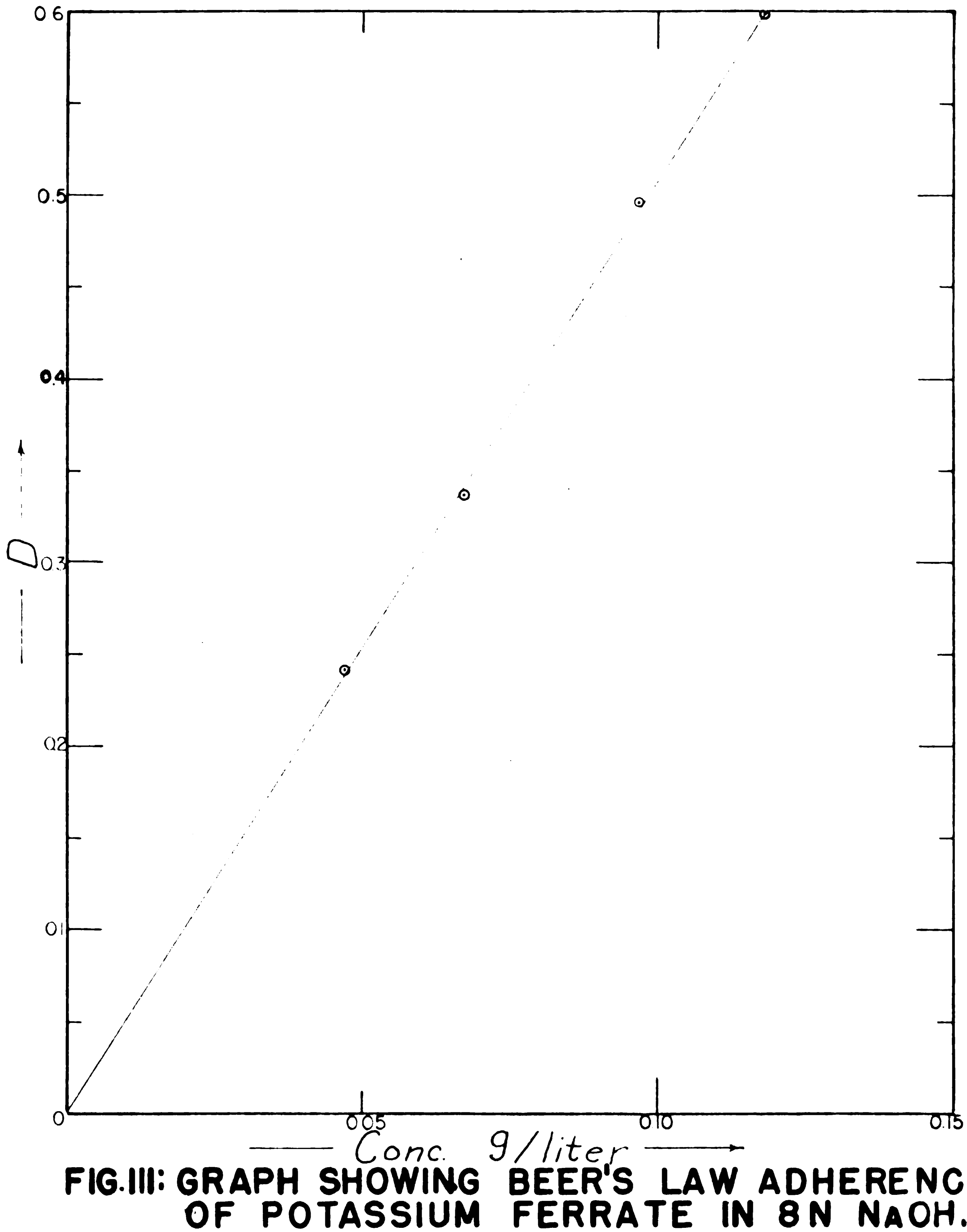

FIG. III: GRAPH SHOWING BEER'S LAW ADHERENCE OF POTASSIUM FERRATE IN 8N NaOH.

the concentration range from 0 to 0.125g K_2FeO_4/l. The potassium ferrate in this expression is expressed as pure potassium ferrate.

Kinetic Studies of Decomposition of Potassium Ferrate.

As was stated previously, the purity of the prepared material analyzed by Schreyer's method varied between 62.5 and 95.5% potassium ferrate(VI).

Kinetic runs of the decomposition were made using the potassium ferrate samples of varying purity. The only difference in the experimental results was in the time required to attain the equilibrium condition. On the basis of these observations, it seems probable that the results should be applicable to the pure material and the impurity is of little significance in the reaction.

The shape of some typical decomposition curves plotting log D versus time is shown in Fig. IV. As can be seen, a straight line is observed over the first portion of the curve indicating a first order reaction. The slope then gradually decreases as competing reactions cause the reaction to become complex. The curve then finally graduates into another straight line function.

The shape of these curves suggests the existence of a first order reaction at the beginning, the rate of which is rapid, relative to the other reactions. Since the slope gradually decreases and graduates into another straight line whose slope is much less, it seems probable that the reaction

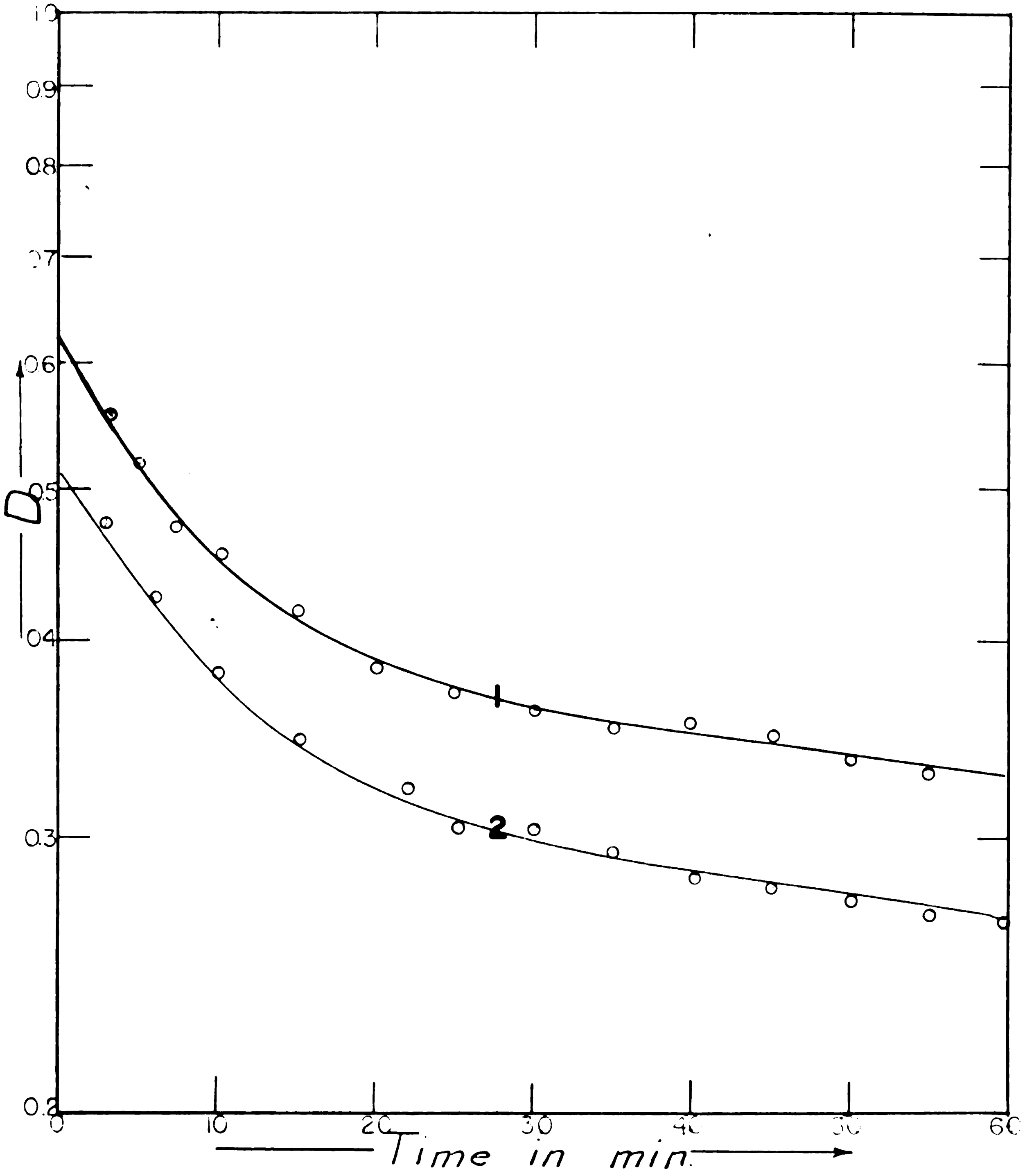

FIG. IV: GRAPH SHOWING TYPICAL RATE OF DECOMPOSITION CURVES OF POTASSIUM FERRATE IN 8N NaOH.

establishes an equilibrium with the relatively slow decomposition of one of the products.

Substantiation of Proposed Initial Equilibrium Reaction: In order to test the hypothesis concerning the unstable equilibrium reaction, kinetic runs were made varying the sodium hydroxide content of the potassium ferrate solutions. Sodium hydroxide concentrations from four to nine normal were used. (See Fig. V) The rates of reaction, found by taking the slope over the first straight line portion, were determined; and these rate constants were plotted against the normality of sodium hydroxide. Figure VI shows that the rate constant decreases in direct proportion to the normality of the NaOH. This suggests the existence of a relationship involving the concentration of hydroxyl ions to the first power.

TABLE #1

RELATIONSHIP OF k_1 TO NORMALITY OF NaOH SOLVENT

C_{OH^-}	k_1 X 10^2 min.
9N	2.92
8N	3.61
7N	6.07
6N	7.68
5N	8.65
4N	10.07

Grube and Gmelin[3] report the reaction:

$$2Na_2FeO_4 + 6e^- \rightleftharpoons Na_2Fe_2O_4 + ---$$

to be reversible at an iron anode in 40% NaOH at 50°C, hydrous ferric oxide being quite soluble in concentrated alkaline solutions.

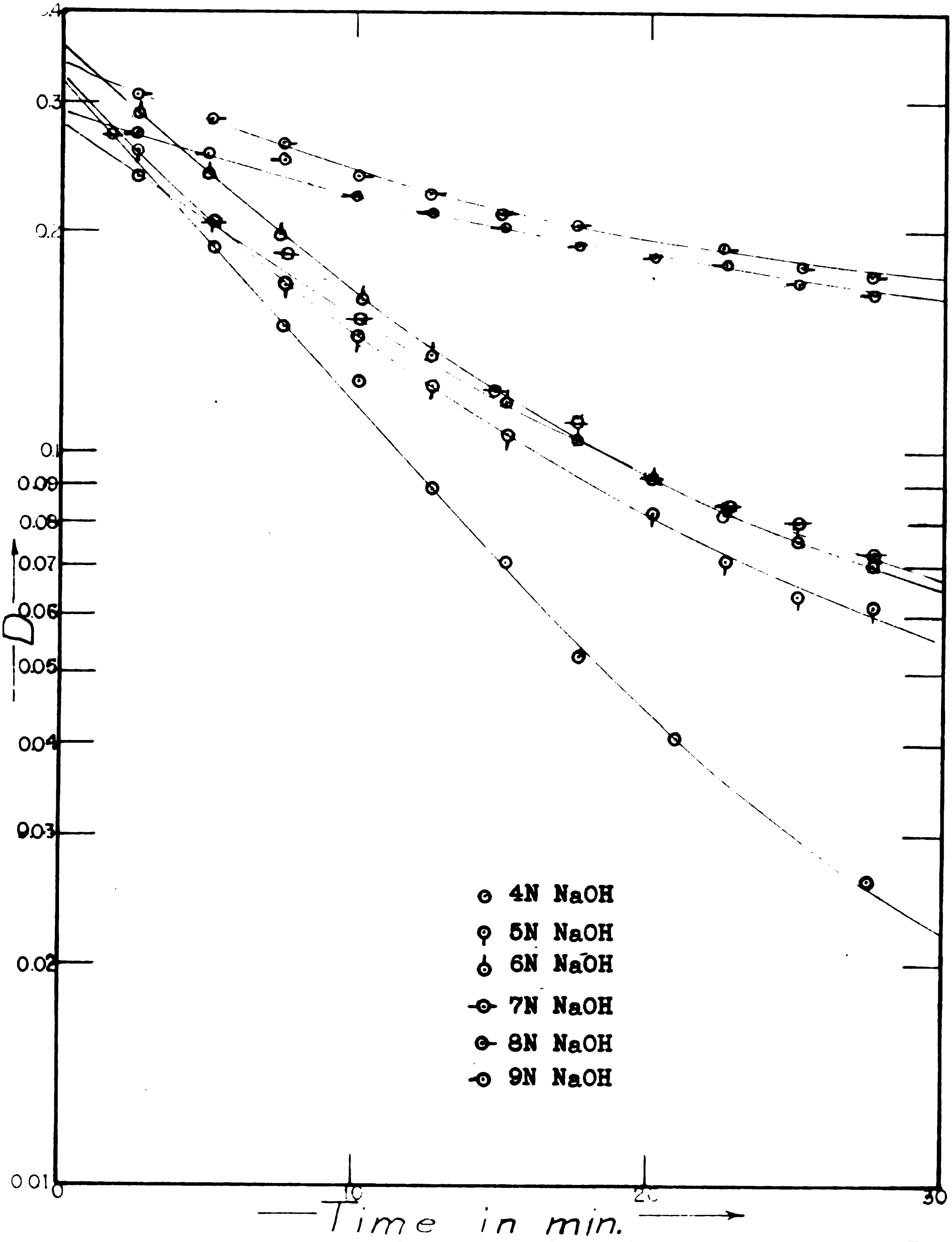

FIG.V: GRAPH SHOWING RATES OF DECOMPOSITION OF POTASSIUM FERRATE IN VARYING CONCENTRATIONS OF NAOH.

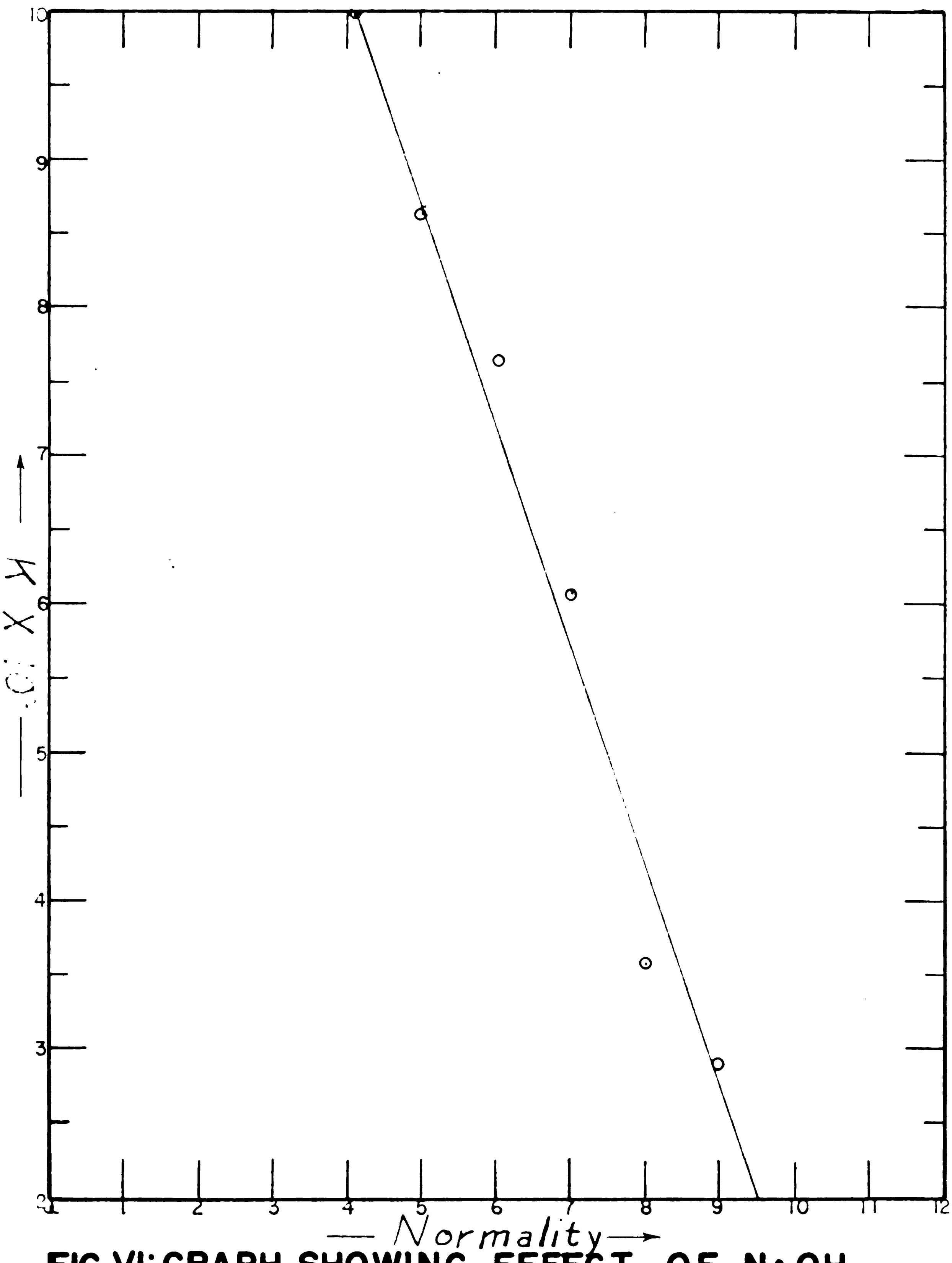

FIG. VI: GRAPH SHOWING EFFECT OF NaOH CONCENTRATIONS ON FIRST RATE CONSTANT.

The validity of this reaction was tested by saturating an 8N NaOH solution with $Fe_2O_3 \cdot xH_2O$, adding K_2FeO_4, and subsequently making a kinetics run on the ferrate decomposition. From the results of this run, shown by Figure VII, it can be seen that the initial rapid rate of decomposition, observed in ferrate solutions not containing the added $Fe_2O_3 \cdot xH_2O$, is not apparent. The result is essentially a straight line from the start. The slope of this straight line is the same as the second straight line portion of the normal decomposition curve.

The results obtained in these measurements apparently are not in full agreement with the reaction as written and proposed by Grube and Gmelin to take place at an iron anode.

It appears that the amphoteric species of $Fe_2O_3 \cdot xH_2O$ exists not in the form of $Fe_2O_4^{=}$, but rather as FeO_2^{-}. This conclusion is based upon the apparent first order reaction which occurs initially. If the dimer were formed immediately, the reaction should be more complex.

In order to further test this reaction, it would seem that if the ferrite ion concentration were reduced to such an extent that its concentration never became great enough to establish the unstable equilibrium condition, the reaction should continue to be first order with respect to the ferrate decomposition throughout the whole reaction.

The solubility of the ferrite would be expected to decrease with decreasing alkalinity and with decreasing temperature. Taking advantage of these suppositions, a rate run was

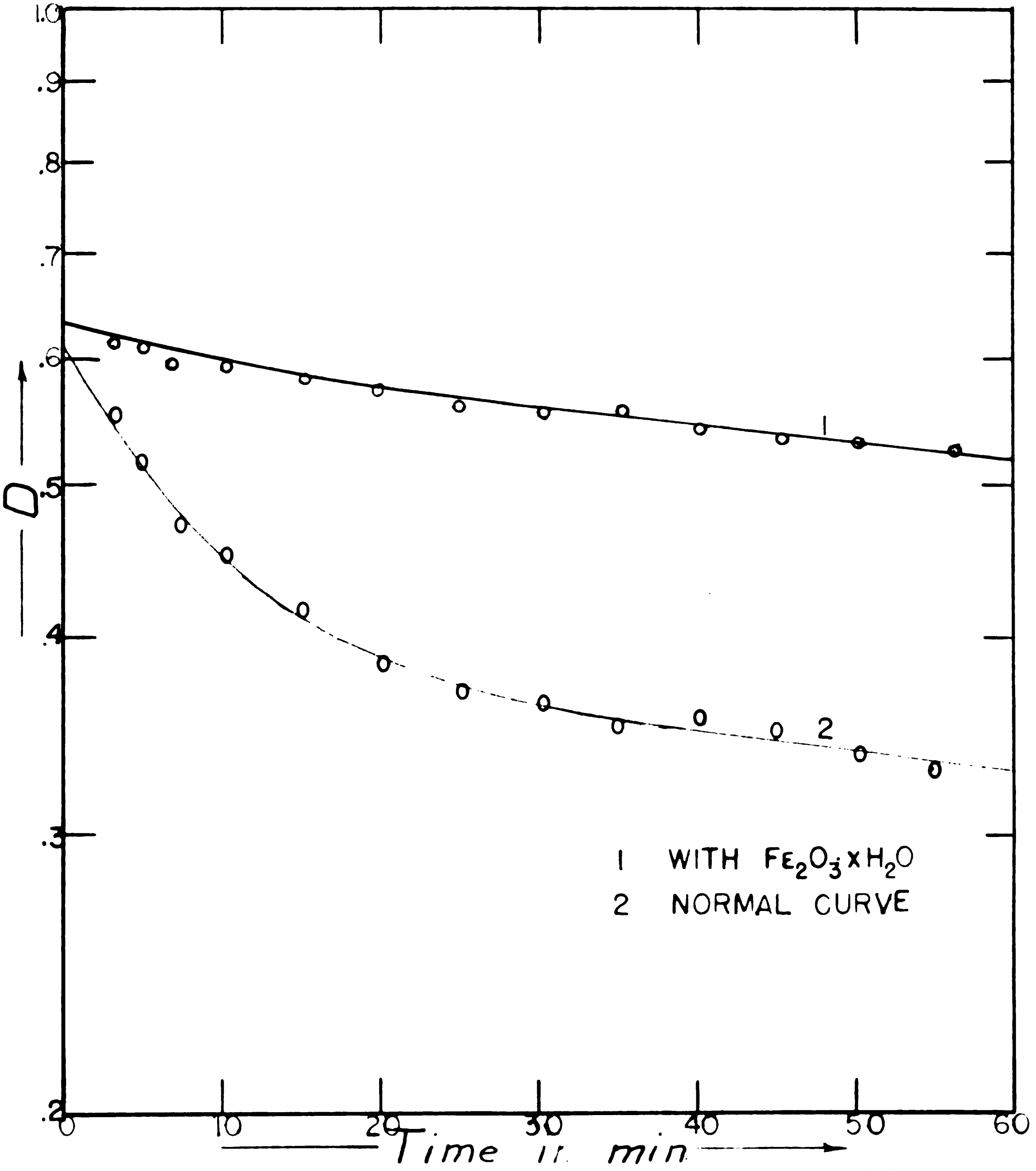

FIG. VII: GRAPH SHOWING RATE OF DECOMPOSITION OF POTASSIUM FERRATE IN 8N NaOH SATURATED WITH HYDROUS FERRIC OXIDE.

made at 0°C with the potassium ferrate dissolved in four normal sodium hydroxide. As can be seen in Figure VIII, a straight line is obtained when log D is plotted against time. There is considerable amount of dispersion observed in the points. This dispersion can be attributed to the moisture condensation which takes place on the windows of the cells. The measurements made in this run do not take into account the changes in the rate constants, both forward and reverse, with changes in temperature.

Since increasing hydroxyl ion concentration causes an increase in the stability of the ferrate solution, and since presumably only sodium hydroxide, water, ferrate, and ferrite are present, water must be the substance being oxidized by the $FeO_4^=$. This might be expected if the ferrate ion, $FeO_4^=$, exists as such in solution, the coulombic forces of repulsion would be prohibitive for collision and subsequent reaction to take place between the ferrate and hydroxyl ions.

The oxidation of water might be expected to occur in steps, eg.

$$FeO_4^= + 2H_2O \rightleftharpoons FeO_2^- + 3OH\cdot + OH^-$$

This reaction fits the data presented thus far and can probably be further substantiated by referring to the preparative method for K_2FeO_4.

Hypochlorite ions in a water solution can conceivably exist as $ClO\cdot H_2O^-$, or represented in a different way, $HOClOH^-$. This could react as follows:

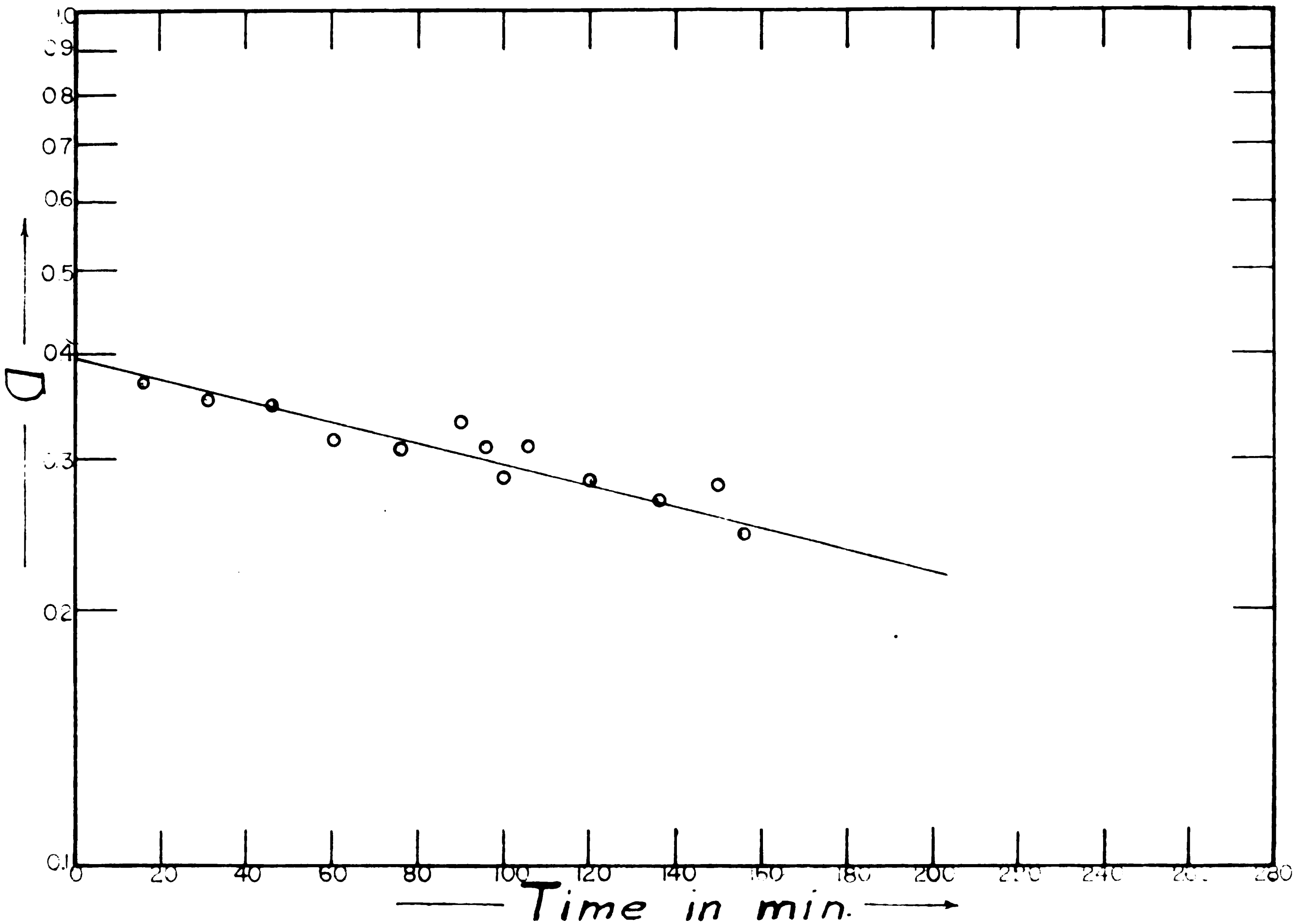

FIG.VIII: GRAPH SHOWING RATE OF DECOMPOSITION OF POTASSIUM FERRATE IN ·4N NaOH AT 0°C

(1) $3/2HOClOH^- \rightleftharpoons 3/2Cl^- + 3OH\cdot$

(2) $OH^- + 3OH\cdot + FeO_2^- \rightleftharpoons FeO_4^= + 2H_2O$

Reaction (2) shows a possible reversibility of the reaction for the formation of ferrate by a reaction with hydroxyl radicals and ferrite.

The free energy of formation of hydrogen peroxide by combination of two hydroxyl radicals is quite large*, estimated to be $\Delta F = -21$ kcal.[5] On this basis, it might be expected that the combination of hydroxyl radicals might be rapid and result in the following reactions:

$3OH\cdot \rightarrow 3/2H_2O_2$

$FeO_4^= + 2H_2O \rightleftharpoons FeO_2^- + 3/2H_2O_2 + OH^-$

This would indicate the existence of an equilibrium involving the production of ferrate through the oxidation of ferrite by hydrogen peroxide. This possible set of reactions is not substantiated by experimental observations. If the indicated equilibrium is established, the addition of hydrogen peroxide should stabilize the reaction mixture. The addition of hydrogen peroxide to the alkaline solution of potassium ferrate greatly increased the rate of decomposition of ferrate. The rapid evolution of oxygen prevented the possibility of following the decomposition colorimetrically. The rate, however, appeared to be immeasurable by this technique.

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* The values of the free energies involving free hydroxyl radicals must be considered as Latimer reports, "strictly tentative".

These observations are substantiated by Latimer. As Latimer reports, while the free energy of formation of hydrogen peroxide by combination of two hydroxyl radicals is relatively high, there is no experimental evidence to show that the reaction rate is rapid.

The increase in the rate of decomposition of potassium ferrate by hydrogen peroxide may not be expected since Bohnson showed that ferric acid is formed as an intermediate in the catalytic decomposition of hydrogen peroxide by plus three iron. While this happens in neutral solutions of hydrogen peroxide, the addition of hydrogen peroxide to a strongly alkaline solution of hydrous ferric oxide produced no ferrate, as would be evidenced by the appearance of the intense color characteristic of ferrate.

Free Hydroxyl Radical Reaction: On the basis of the above mentioned facts, it seems that while the combination of OH• may take place, the effect is relatively small. If the concentration of free hydroxyl radicals is high enough, one might expect the following reaction to take place:

$$3OH\cdot \rightarrow 3/4O_2 + 3/2H_2O$$

as a step preventing the reaction from attaining and maintaining a condition of a stable equilibrium. This would probably occur through combination of two hydroxyl radicals and the subsequent oxidation by a third free radical. This hypothesis is based upon the fact that the free energy of formation of atomic oxygen by interaction of two hydroxyl radicals is quite positive.

$$2OH\cdot \longrightarrow H_2O + O \qquad \Delta F = 8.3 \text{ kcal.}^5$$

Since the free energy change is positive, this particular reaction probably would not take place appreciably unless the concentration of free radicals were high or unless external energy were applied. Since the reaction between hydroxyl radicals apparently takes place to some extent, there must be combination first and subsequent oxidation.

In order to determine the extent recombination plays in the reaction, glass wool was added to the reaction vessel. Radical combination is reportedly a surface reaction; therefore, this reaction should be enhanced by the increased surface presented by the glass wool. The effect, an extension of the time required to attain equilibrium, is seen in Fig. IX.

This effect would be expected since the reversal of the proposed first reaction is dependent upon the reaction between ferrite and free hydroxyl radicals. One would expect, however, that if this were the main reaction preventing the attainment of a stable equilibrium condition, the effect would be more pronounced than that which was observed, possibly preventing attainment of the unstable equilibrium condition.

The above observations appear to substantiate the previous claim that the reaction:

$$3OH\cdot \longrightarrow 3/2H_2O + 3/4O_2$$

is not of great significance in the decomposition scheme of potassium ferrate(VI).

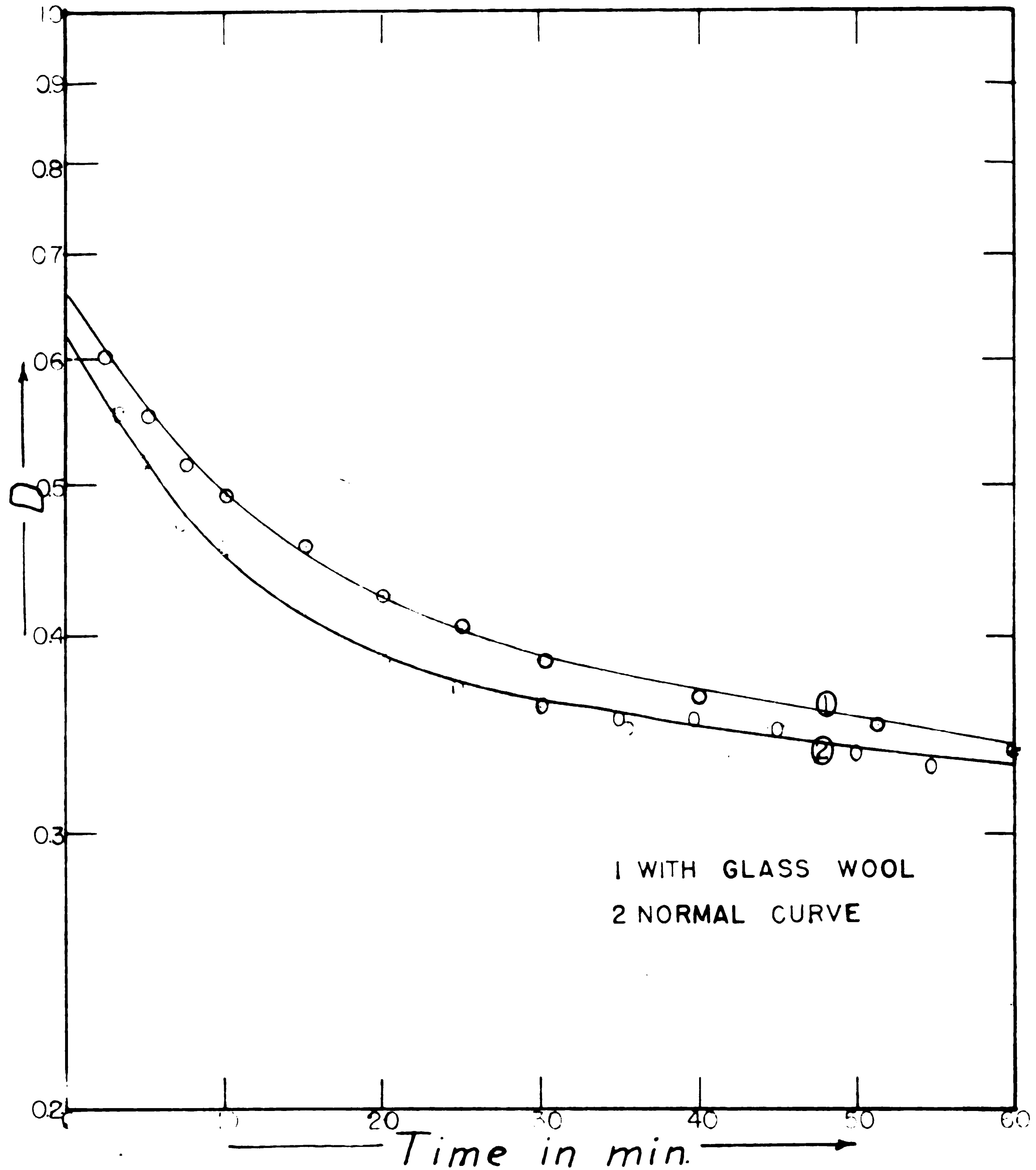

FIG. IX: GRAPH SHOWING RATE OF DECOMPOSITION OF POTASSIUM FERRATE IN 8N NaOH. GLASS WOOL ADDED TO REACTION MIXTURE.

Proposed Main Degradation Reaction: On the basis of the previously mentioned observations, there must be at least one more reaction which would be the major contributor to the instability of the equilibrium condition. The main degradation reaction proposed is as follows:

$$FeO_4^{=} + 3OH\cdot \longrightarrow 3/2O_2 + FeO_2^{-} + OH^{-} + H_2O$$

This supposition is supported by the fact that the decomposition is extremely light sensitive.

All of the previous reactions proceeded under essentially constant illumination from tungsten lamps; however, when the light was prevented from reaching the solution by using a blacked out bottle, there was a pronounced change in the observed results. This can be seen by referring to Figure X. The initial slope was essentially the same; but the uhstable equilibrium condition was attained much more rapidly; and the subsequent decomposition took place at a much slower rate.

According to Grotthusse's First Law of Photochemistry, "only the rays which are absorbed can produce a chemical change." Since tungsten lamps emit primarily visible and infra-red radiation and since only rays up to the relatively near infra-red region would be able to penetrate the reaction vessel, it would seem probable that the activation frequency must be in the visible region of the spectrum. In the reaction mixture, the only material which absorbs in the visible region is the potassium ferrate. This suggests that the reaction affected would be the reaction between the ferrate

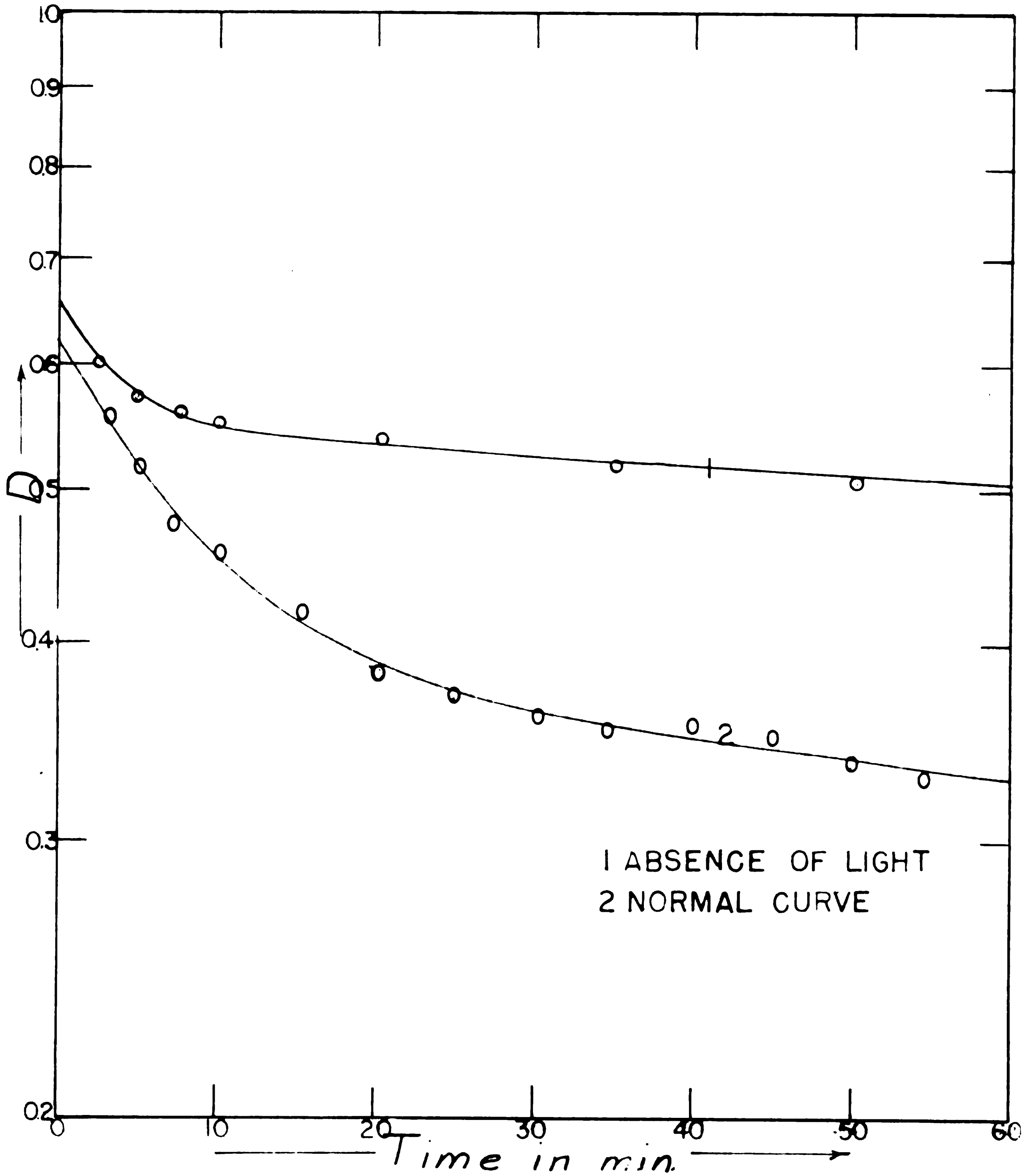

FIG:X: GRAPH SHOWING DECREASE IN POTASSIUM FERRATE CONCENTRATION IN 8N NaOH IN ABSENCE OF LIGHT ion and the hydroxyl radicals, and this would be the major contributor to the degradation process.

No attempt was made to ascertain the effect of different frequencies or to determine the quantum yield. Only the difference observable under the two sets of conditions were noted and studied.

DISCUSSION

The kinetic studies undergone in the experimental work indicate the following reactions to be the logical mechanism by which potassium ferrate decomposes in strongly alkaline media:

1) $FeO_4^{=} + 2H_2O \xrightarrow[k_1]{k_{-1}} FeO_2^{-} + 3OH\cdot + OH^{-}$

2) $FeO_4^{=} + 3OH\cdot \xrightarrow{k_2} FeO_2^{-} + 3/2O_2 + OH^{-} + H_2O$

3) $3OH\cdot \xrightarrow{k_3} 3/4O_2 + 3/2H_2O$

The rate expression for the proposed reaction would be developed as follows:

Placing: $[FeO_4^{=}] = x$ and since

$[OH^{-}]$constant, $[OH^{-}]\,k_{-1} = k'_{-1}$

$$\frac{dx}{dt} = -k_1x + k'_{-1}\,[FeO_2^{-}][OH\cdot]^3 - k_2x\,[OH\cdot]^3 - k_3[OH\cdot]^3$$

$$\frac{d[OH\cdot]}{dt} = k_1x - k'_{-1}\,[FeO_2^{-}][OH\cdot]^3 - k_2x[OH\cdot]^3 - k_3[OH\cdot]^3$$

a) steady state approximation:

$$\frac{d[OH\cdot]}{dt} = 0 = k_1x - k'_{-1}\,[FeO_2^{-}][OH\cdot]^3 - k_2x\,[OH\cdot]^3 - k_3[OH\cdot]^3$$

$$OH\cdot\ ^3 = \frac{k_1x}{k'_{-1}[FeO_2^{-}] + k_2x + K_3}$$

$$\frac{dx}{dt} = \frac{-2k_1x \quad k_2x + k_3}{k'_{-1}[FeO_2^{-}] + K_2x + k_3}$$

Placing a = initial concentration of x and integrating between the limits a x, this result is obtained:

$$\left\{\frac{k_{-1}a}{k_3} + 1\right\}\ln\left\{\frac{(k_3 + k_2a)\,x}{(k_3 + k_2x)\,a}\right\} + \left\{\frac{k'_{-1}}{k_2} - 1\right\} - \ln\left\{\frac{k_3 + k_2a}{k_3 + k_2x}\right\} = -2k_1t$$

The rate constants could not be determined individually; however, if the third reaction is neglected, the following differential equation can be obtained:

$$\frac{dx}{dt} = \frac{2k_1k_2x^2}{k'_{-1}[FeO_2^-] + k_2x}$$

If this is integrated between the limits a x, the following result is obtained:

$$\frac{k'_{-1}}{k_2}\left\{1 - \frac{a}{x}\right\} + \left\{\frac{k'_{-1}}{k_2} - 1\right\} \ln \frac{a}{x} = 2k_1t$$

As can be seen the rate constants k'_{-1} and k_2 are present as ratios in this expression. Since k_1 is known from initial slope of reaction curves, the ratio k'_{-1}/k_2 can be determined by taking the slope of the curve obtained by plotting $FeO_4^=$ versus time and placing this slope equal to dx/dt. (See Figure XI.) By using the differential equation and solving for the ratios, k_{-1}/k_2, a value can be obtained.

If the suppositions made in the report are correct, placing this value into the integrated expression, and plotting this expression, the resultant curve should correspond quite closely to the observed curve.

$2k_1 = 3.6 \times 10^{-2}$

$\frac{dx}{dt} = \text{slope} = 8.0 \times 10^{-4}$

$x = .328$

$a = .620$

$[FeO_2^-] = a - x = .292$

$k'_{-1}/k_2 = 10.8$

The result obtained by performing this operation can be seen in Figure XII.

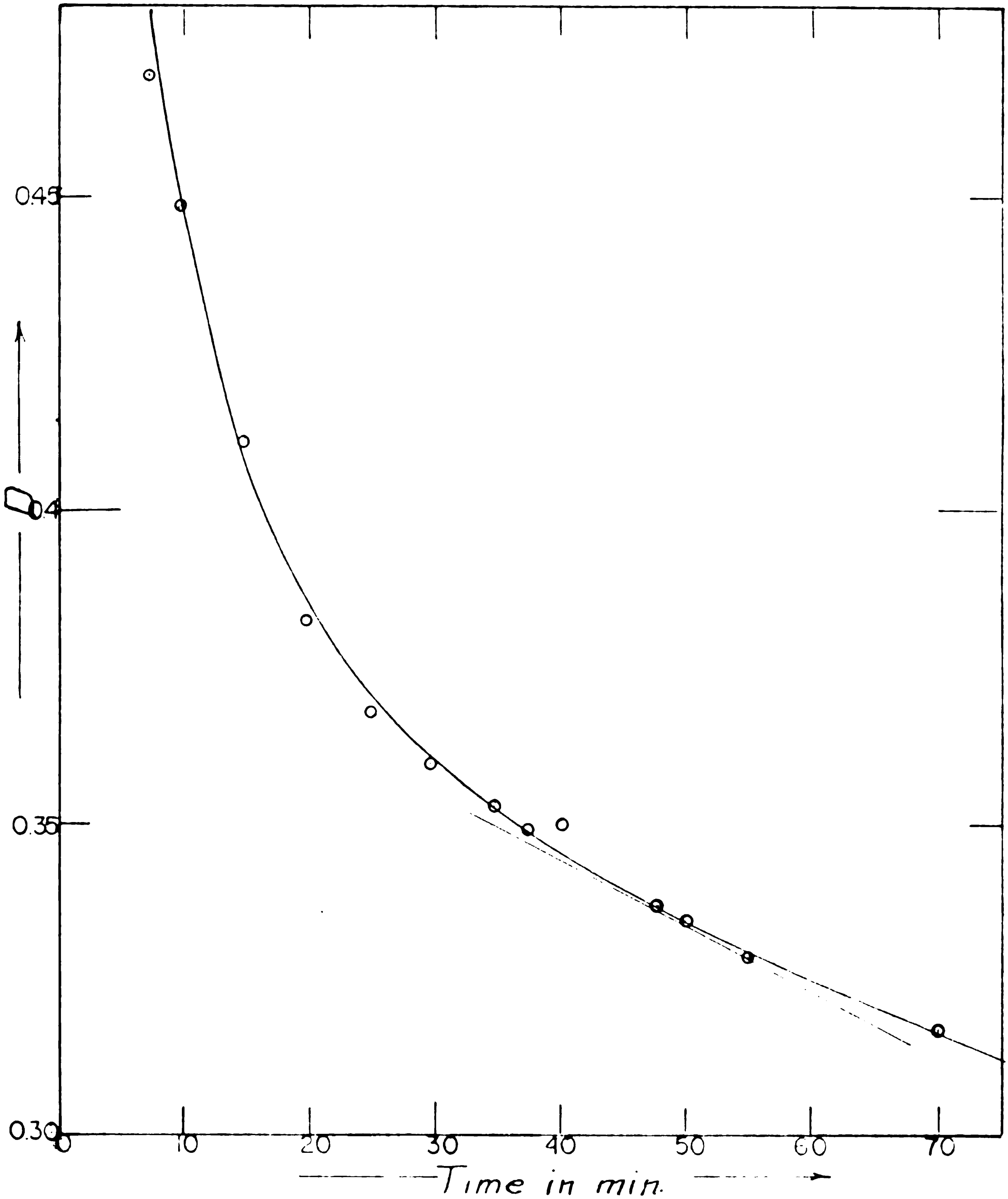

FIG. XI: GRAPH SHOWING RATE OF DECOMPOSITION OF POTASSIUM FERRATE IN 8N NaOH

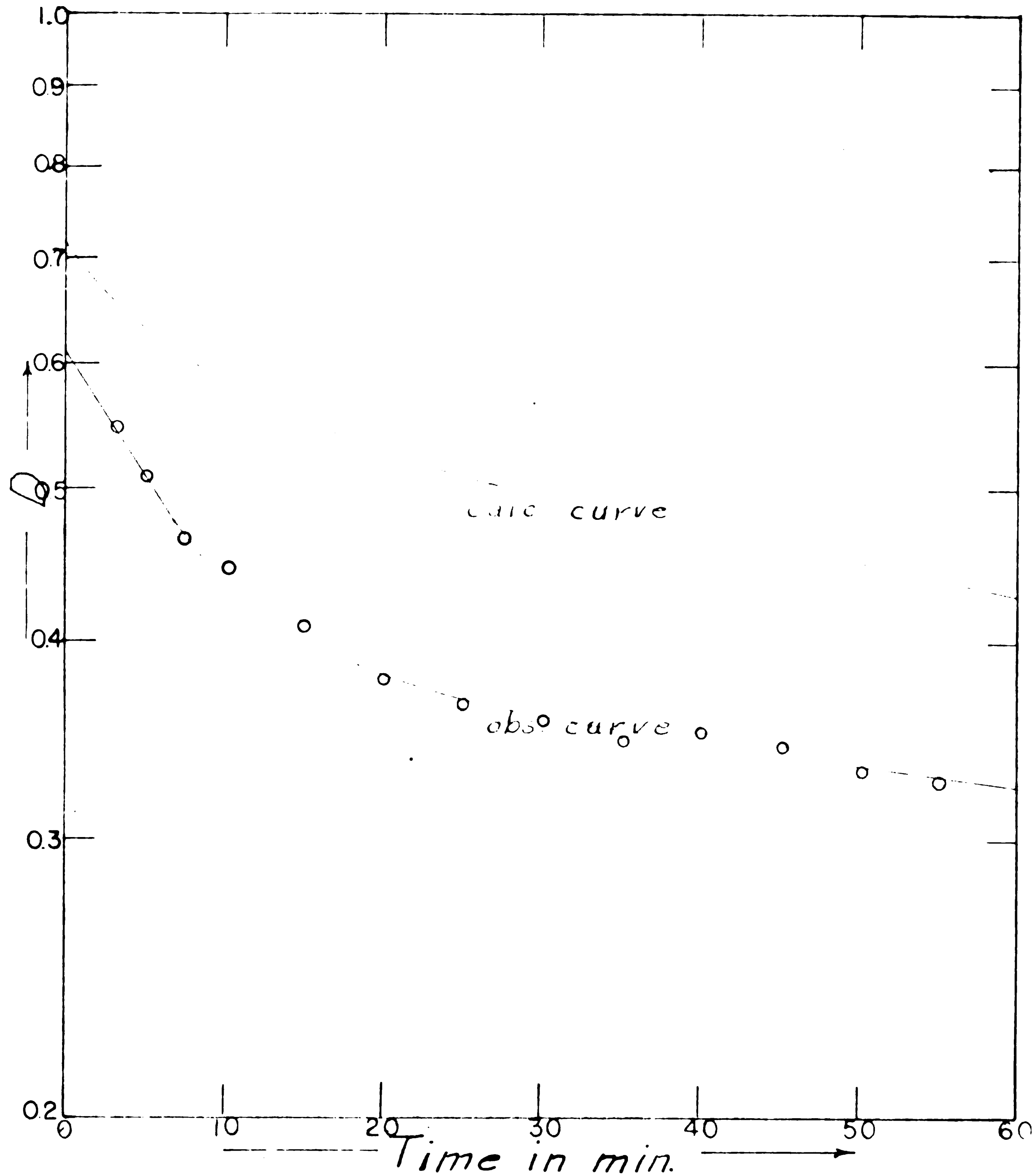

FIG.XII: GRAPH SHOWING RATE OF DECOMPOSITION OF POTASSIUM FERRATE IN 8N NaOH AS COMPARED WITH CALCULATED CURVE

Over the first segment of the graph, the calculated curve follows the observed curve closely. After this initial reaction rate is passed, however, the calculated curve deviates considerably, the slope being less than the observed curve. When this deviation is passed, the two curves again agree closely.

If the reactions proposed are accurate, this curve might be expected. In the first portion of the curve where the concentration of hydroxyl radicals is high, one would expect reaction (3) to exhibit its effect most strongly. As the concentration of hydroxyl radicals decreases and the ferrite concentration increases, one would expect this reaction to exhibit a lesser effect and finally might become negligable.

It is probable that the mass kinetics so employed in this work do not present the true picture of the over-all reaction, ie., the following (or somewhat analogous) reactions are probably present in the decomposition of $FeO_4^=$:

1' $FeO_4^= + 2e^- \longrightarrow FeO^{+2}$ or $FeO_3^=$

2' $FeO^{+2} + e^- \longrightarrow FeO_2^-$

Since plus four iron seems to be unstable with respect to decomposition into the plus three and plus six oxidation states, it seems that the reverse reaction of 1' could be immeasurably fast while the same would hold for the forward reaction of 2'. Essentially, the observed reaction would involve the plus three and plus six species.

This study uncovered no facts substantiating this supposition; however, by utilizing these reactions lower molecularities are permitted, increasing the probability of a reaction taking place.

CONCLUSIONS

In this study of potassium ferrate the following facts were observed:

1) Highly alkaline solutions of potassium ferrate do not appear to be applicable to polarographic studies.

2) Potassium ferrate solutions can be measured by colorimetrid methods; and at a wave length of $500 m\mu$, the solutions obey Beer's Law over the concentration ranges used in this work.

3) The kinetics of the reaction show the decomposition of potassium ferrate in alkaline media to be complex. The rate of this decomposition is definitely a function of the concentration of hydroxyl ions.

4) The decomposition is greatly accelerated by light.

On the basis of the observed data, the following mechanism was proposed to explain the decomposition of potassium ferrate in highly alkaline media at 30°C:

(1) $FeO_4^{=} + 2H_2O \rightleftharpoons FeO_2^{-} + 3OH\cdot + OH^{-}$

(2) $FeO_4^{=} + 3OH\cdot \longrightarrow FeO_2^{-} + 3/2O_2 + OH^{-} + H_2O$

(3) $3OH\cdot \longrightarrow 3/4O_2 + 3/2H_2O$

The kinetic data observed in the study seem to substantiate these reactions. The data indicate that reaction (2) is the main reaction taking place after the first equilibrium reaction has been established.

APPENDIX

TABLE 2

RATE OF DECOMPOSITION OF K_2FeO_4 IN 4N NaOH AS FOUND BY POLAROGRAPHIC AMPEROMETRIC TECHNIQUE

@ 0°C (0.0121g K_2FeO_4/25cc 4N NaOH)*

Time In Min. ±10 Sec.	Step Height Cm	Time In.Min. ±10 Sec.	Step Height Cm
5	12.90	100	6.65
10	12.90	105	6.65
20	12.85	111	7.10
30	12.15	125	6.05
35	10.90	135	5.80
40	11.05	145	5.60
45	10.85	155	5.42
50	9.700	165	5.15
55	9.700	175	4.60
70	9.100	185	4.15
75	8.050	195	4.00
		200	4.85

* Data used for plotting Curve 1 in Fig. I.

TABLE 3

RATE OF DECOMPOSITION OF K_2FeO_4 IN 4N NaOH AS FOUND BY POLAROGRAPHIC AMPEROMETRIC TECHNIQUE

@ 0°C (0.0096g K_2FeO_4/25cc 4N NaOH)*

Time In Min. ±10 Sec.	Step Height Cm	Time In Min. ±10 Sec.	Step Height Cm
15	7.20	120	4.90
20	7.10	130	5.20
25	7.00	140	5.00
30	6.65	150	4.65
35	5.85	160	5.00
40	5.65	175	4.40
50	5.60	180	4.03
60	5.45	190	3.25
70	4.95	200	4.10
95	4.35	210	3.65
100	5.15	220	3.10
110	5.30		

* Data used in plotting Curve 2 in Fig. I.

TABLE 4*

ABSORBTION DATA OF POTASSIUM FERRATE IN 8N NaOH MADE WITH A BECKMAN SPECTROPHOTOMETER

Wave Length In mμ	Slit Width, d, In mm	% Transmission T	Optical Density D
320	0.602	13.8	.725
330	0.440	19.2	.614
340	0.345	23.8	.540
350	0.280	35.9	.447
360	0.218	46.2	.335
370	0.203	57.0	.244
380	0.178	63.5	.197
390	0.157	65.2	.186
400	0.140	63.8	.190
410	0.125	60.5	.220
420	0.117	56.8	.246
430	0.104	52.9	.274
440	0.100	49.7	.304
450	0.094	47.0	.329
460	0.089	44.8	.350
470	0.084	42.7	.370
480	0.080	41.0	.387
490	0.075	40.0	.399
500	0.072	39.5	.402

TABLE 4 (continued)

λ	d	T	D
510	0.069	41.0	.387
520	0.068	42.0	.376
530	0.067	43.1	.365
540	0.068	44.3	.353
550	0.069	45.7	.340
560	0.071	47.1	.326
580	0.077	52.2	.290
600	0.100	58.5	.232
620	0.139	67.0	.174
640	0.180	74.5	.128
**600	0.190	59.6	.225
620	0.170	67.8	.170
640	0.152	75.7	.121
680	0.125	82.9	.083
700	0.118	81.7	.087
720	0.110	79.7	.100
740	0.108	77.9	.108
760	0.102	76.3	.117
780	0.099	76.1	.118
800	0.095	76.6	.116

* Data used in plotting Curvel in Fig. II.

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TABLE 5*

ABSORBTION DATA OF ESSENTIALLY DECOMPOSED POTASSIUM FERRATE SOLUTION- TO SHOW EFFECT OF DECOMPOSITION PRODUCTS

Wave Length In mμ	Slit Width, d, In mm	% Transmission T	Optical Density D
300	1.975	75.3	.124
310	1.010	74.0	.103
320	0.645	82.9	.083
330	0.470	85.6	.068
340	0.370	87.5	.058
350	0.295	90.0	.046
360	0.247	92.7	.032
370	0.215	95.1	.021
380	0.186	96.5	.015
390	0.162	96.5	.015
400	0.145	96.3	.016
410	0.132	95.6	.019
420	0.120	95.0	.023
430	0.111	94.3	.025
440	0.104	94.3	.025
450	0.096	93.7	.027
460	0.090	93.4	.029
470	0.086	92.6	.033

TABLE 5 (continued)

λ	d	T	D
480	0.081	92.5	.034
490	0.077	92.1	.035
500	0.074	92.2	.034
510	0.071	92.5	.033
520	0.069	92.9	.032
540	0.069	94.0	.027
560	0.072	94.2	.026
580	0.080	95.0	.022
600	0.101	95.5	.020
625	0.150	97.1	.012
**625	0.176	97.7	.010
650	0.145	98.7	.006
675	0.130	99.0	.005
700	0.118	99.0	.005
725	0.110	98.7	.006
750	0.104	98.4	.007
775	0.099	98.2	.008
800	0.095	98.7	.006

* Data used in plotting Curve 2 in Fig. II.

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TABLE 6*

DETERMINATION OF CONFORMITY OF POTASSIUM FERRATE SOLUTION IN 8N NaOH TO BEER'S LAW

Conc. Of $FeO_4^=$ In g/1	λ In mμ	d In mm	% T**	D**
0.075	500	.046	57.5	.241
0.109	500	.046	47.2	.335
0.154	500	.046	30.5	.498
0.186	500	.046	25.8	.596

* Data used in plotting Fig. III.

** Readings made after a five minute period had elapsed from time of mixing.

TABLE 7*

KINETIC RUNS OF THE DECOMPOSITION OF POTASSIUM FERRATE IN 8N NaOH MADE ON BECKMAN SPECTROPHOTOMETER AT 30°C.

Run #1 0.016g 62.5% K_2FeO_4/100cc 8N NaOH
d = 0.054 λ = 500 mμ

t Min	D	T	t	D	T
3.0	0.551	28.1	35.0	0.353	44.2
5.0	0.511	30.7	37.5	0.348	45.0
7.5	0.469	34.0	40.0	0.350	44.8
10.0	0.448	35.9	45.0	0.350	44.8
15.0	0.411	38.9	48.0	0.336	46.1
20.0	0.382	41.4	50.0	0.334	46.2
25.0	0.367	42.9	55.0	0.328	47.0
30.0	0.359	43.8	70.0	0.316	48.3

Run #2 0.0134g K_2FeO_4 (95.5%)/100cc 8N NaOH
d = 0.053 λ = 500 mμ

t	D	T	t	D	T
4.0	0.480	33.1	35.0	0.291	51.1
6.0	0.418	38.3	40.0	0.283	52.1
10.0	0.379	41.8	45.0	0.277	53.0
15.0	0.343	45.5	50.0	0.271	53.8
22.0	0.321	47.8	55.0	0.264	54.5
25.0	0.300	50.1	60.0	0.260	55.0
30.0	0.304	49.8	65.0	0.259	55.1
			70.0	0.251	56.1

* Data used in plotting Fig. IV.

TABLE 8*

KINETIC RUNS OF POTASSIUM FERRATE DECOMPOSITION MADE ON BECKMAN SPECTROPHOTOMETER WITH VARYING CONCENTRATIONS OF NaOH

Run #1 0.0110g 62.5% K_2FeO_4/100cc 4N NaOH

t Min.	T	D	t	T	D
2.0	56.8	0.246	15.0	84.9	0.071
5.0	63.8	0.197	17.5	87.0	0.061
7.5	70.7	0.151	20.0	88.5	0.053
10.0	74.8	0.126	27.5	94.0	0.027
12.5	81.5	0.090	30.0	90.5	0.043

Run #2 0.0100g 62.5% K_2FeO_4/100cc 5N NaOH

t	T	D	t	T	D
2.5	55.3	0.258	17.5	77.3	0.112
5.0	62.1	0.207	20.0	82.7	0.083
7.5	67.9	0.168	22.5	85.0	0.071
10.0	71.8	0.145	25.0	86.1	0.064
12.5	75.2	0.124	27.5	86.8	0.062
15.0	78.3	0.106	30.0	88.3	0.054

Run #3 0.0098g 62.5% K_2FeO_4/100cc 6N NaOH

t	T	D	t	T	D
2.5	51.3	0.290	17.5	79.0	0.103
5.0	57.2	0.242	20.0	80.9	0.093
7.5	68.2	0.167	22.5	81.4	0.084
10.0	69.0	0.161	25.0	83.8	0.077
12.5	73.0	0.137	27.5	85.0	0.071
15.0	76.3	0.117			

TABLE 8 (continued)

Run #4 0.0100g 62.5% K_2FeO_4/100cc 7N NaOH

t Min.	T	D	t	T	D
2.5	57.9	0.238	20.0	81.0	0.092
5.0	63.5	0.197	22.5	81.2	0.085
7.5	64.7	0.190	25.0	82.9	0.082
10.0	70.2	0.153	27.5	84.6	0.073
12.5	69.7	0.156	30.0	85.5	0.068
17.5	77.1	0.112	35.0	86.2	0.065

Run #5 0.0106g 62.5% K_2FeO_4/100cc 8N NaOH
@ 30°C., λ= 500mμ d = 0.053 mm

t	T	D	t	T	D
2.5	49.3	0.306	17.5	62.5	0.204
5.0	52.1	0.284	20.0	65.0	0.188
7.5	54.9	0.261	22.5	65.8	0.183
10.0	58.0	0.237	25.0	66.2	0.180
12.5	60.0	0.221	27.5	66.8	0.175
15.0	61.2	0.213	30.0	67.5	0.171

Run #6 0.0105g 62.5% K_2FeO_4/100cc 9N NaOH

t	T	D	t	T	D
2.5	53.5	0.273	17.5	64.0	0.194
5.0	55.2	0.258	20.0	65.0	0.188
7.5	55.8	0.253	22.5	64.1	0.193
10.0	59.0	0.229	25.0	67.8	0.170
12.5	60.9	0.216	27.5	68.2	0.165
15.0	62.8	0.203	30.0	68.7	0.162

* Data used in plotting Fig. V.

TABLE 9*

KINETIC RUNS OF THE DECOMPOSITION OF POTASSIUM FERRATE IN 8N NaOH SATURATED WITH $Fe_2O_3 \cdot xH_2O$

d = 0.054 λ = 500 mμ

t Min.	T	D	t	T	D
3.0	24.3	0.614	30.0	28.1	0.551
5.0	24.8	0.608	35.0	28.4	0.548
8.0	25.4	0.597	40.0	28.8	0.541
10.0	25.8	0.594	45.0	29.5	0.531
15.0	26.0	0.585	50.0	29.9	0.525
20.0	25.6	0.575	60.0	30.5	0.515
25.0	27.5	0.560	70.0	31.1	0.508

* Data used for plotting Fig. VII.

TABLE 10*

KINETIC RUNS OF THE DECOMPOSITION OF POTASSIUM FERRATE IN 4N NaOH AT 0°C.

0.0125g 62.5% K_2FeO_4/100cc 4N NaOH
d = 0.052 mm λ = 500 mμ

t Min.	T	D	t	T	D
15.0	42.5	0.370	95.0	48.7	0.313
20.0	42.5	0.370	100.0	51.5	0.289
25.0	42.9	0.368	105.0	48.5	0.317
30.0	44.2	0.354	120.0	50.2	0.300
60.0	48.3	0.316	135.0	51.9	0.270
65.0	48.3	0.316	150.0	52.5	0.288
75.0	49.1	0.308	155.0	55.2	0.258
90.0	46.2	0.335			

* Data used for plotting Fig. VIII.

TABLE 11*

KINETIC RUNS OF THE DECOMPOSITION OF POTASSIUM FERRATE IN 8N NaOH WITH GLASS WOOL ADDED TO REACTION VESSEL

0.0137g 92.5% K_2FeO_4/100cc 8N NaOH
d = 0.053 mm λ = 500 mμ

t Min.	T	D	t	T	D
3.0	23.5	0.630	30.0	41.0	0.387
5.0	28.0	0.553	40.0	42.9	0.362
7.5	30.9	0.512	51.0	44.5	0.352
10.0	32.3	0.490	60.0	45.8	0.340
15.0	35.1	0.455	70.0	46.2	0.335
20.0	37.8	0.425	80.0	47.1	0.326
25.0	39.4	0.405	95.0	48.0	0.319

* Data used for plotting Fig. IX.

TABLE 12*

KINETIC RUNS OF THE DECOMPOSITION OF POTASSIUM FERRATE IN 8N NaOH IN THE ABSENCE OF LIGHT

d = 0.019 mm λ = 500 mμ

t Min.	T	D	t	T	D
2.5	25.0	0.600	50.0	31.0	0.509
5.0	27.5	0.565	65.0	31.5	0.500
7.5	27.5	0.563	80.0	32.0	0.495
10.0	28.0	0.555	100.0	32.5	0.489
20.0	29.7	0.538	120.0	33.0	0.483
35.0	30.5	0.517	140.0	33.8	0.480

* Data used for plotting Fig. X.

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