RATE OF REACTION BETWEEN ETHYLENE GLYCOL AND POTASSIUM PERMANGANATE IN THE PRESENCE OF SULFURIC ACID

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INTRODUCTION

Oxidation by potassium permanganate is intrinsically very interesting, as well as important in many reactions; particularly those of quantitative analysis. The equations which are commonly written to set forth its behavior as an oxidizing agent are so complicated as to be impossible from the kinetic point of view. Several studies of its rate of reduction have been made.

Schiloff (5) studied the rate of oxidation of formic acid, oxalic acid, and tartaric acid by this reagent in the presence of sulfuric acid. He found that heptavalent manganese is not reduced to divalent manganese in one step; but rather that there are some thirty three transition stages through which it may pass. He found it possible to represent the experimental results by means of reaction equations involving two variable quantities; B, which depends upon the influence of the reduction products which are present, and f, which depends upon that one of the thirty three possible intermediate transition substances which is present. In a particular case he finds that a small part of the heptavalent element is reduced to the divalent form, while the rest of it combines with the acid which is being oxidized. Then, under the influence of the divalent manganese, the part combined with the acid breaks down. This mechanism seems unnecessarily complicated; and, of course, it has not been possible to isolate these intermediate reduction products.

Launer (3) studied the rate of oxidation of oxalic acid by potassium permanganate in neutral solutions and in the presence Of sulfuric acid. He found that a variety of reactions may take place; but that the reaction between trivalent manganese ion and oxalic acid plays a very important part. An induction period in which formation of a little divalent manganese ion occurs precedes the more rapid reaction. Then reduction of heptavalent manganese by this ion comes about, both ions going to the trivalent state with the development of a pink color. Meanwhile a complex compound; $Mn(C_2O_4)_2^-$ forms, as well as a new ion, CO_2^- which comes from the oxalate ion. The course of the reaction is followed by the liberation of CO_2. When oxalate was present in excess the rate of the reaction could be expressed by the equation

$$\frac{d(P_{CO_2})}{dt} = k_1 \frac{Mn(C_2O_4)_2^-}{(C_2O_4^=)}$$

When the solution was deficient in oxalate ion it could be expressed by the equation:

$$\frac{d(P_{CO_2})}{dt} = k_2(Mn^{+++})(C_2O_4^=)$$

In view of these results he proposes the following as the chief reactions which take place;

$$MnO_4^- + 4Mn^{++} + 8H^+ = 5Mn^{+++} + 4H_2O$$
$$Mn^{+++} + 2C_2O_4^= = Mn(C_2O_4)_2^-$$
$$Mn^{+++} + CO_2^- = Mn^{++} + CO_2$$
$$Mn^{+++} + C_2O_4^= = Mn^{++} + CO_2 + CO_2^-$$

Later work by Launer and Yost showed that the reaction between the permanganate ion and the oxalate ion is very slow.

while that between tripositive manganese ion and oxalate ion proceeds at a measurable rate. They confirm the increase in rate which occurs when the divalent manganese ion is introduced. The action of the trivalent manganese ion may be suppressed by adding fluorides to the solution to form a complex compound with it; yet in their presence the reaction goes forward readily. For this reason they believe that the tetravalent manganese ion, which may also be present in the solutions, may play an important part. They propose the following as the chief reactions which take place:

$MnO_4^- + 4Mn^{++} + 8H^+ = 5Mn^{+++} + 4H_2O$ (rapid)

$Mn^{+++} + C_2O_4^= = Mn^{++} + CO_2 + CO_2^-$ (measurable)

$Mn^{++++} + C_2O_4^= = 2CO_2 + Mn^{++}$ (measurable)

$Mn^{+++} + 2C_2O_4^- = Mn(C_2O_4)_2^-$ (rapid)

$Mn(C_2O_4)_2^- + 4F^- = MnF_4^- + 2C_2O_4^=$

It seemed worth while to study the reduction of potassium permanganate by other, and perhaps milder, reducing agents. For this purpose ethylene glycol seemed to promise well. It is often determined in the quantitative way by this very oxidation, which makes the study more worth while. A search of the literature shows that this particular reaction has received very little attention. Since a Cenco Photelometer which could be used in the colorimetric determination of the permanganate ion was available, the experiments were so planned as to employ it.

The oxidation of ethylene glycol itself is known to proceed in steps. Among the possible products of its oxidation are glycollic aldehyde, glycollic acid, glyoxal, glyoxylic acid, oxalic acid and carbon dioxide. Water is, of course, a byproduct in each of these steps.

Hatcher and West (2) state that glycol is not oxidized to either oxalic acid or glyoxylic acid by potassium permanganate. It is not stated whether the solution was alkaline or acid.

The oxidation of glycol by alkaline potassium permanganate was studied by Evans and Adkins (1). The alkali present was potassium hydroxide. They believed that the oxidation first yields either glycollic aldehyde or glycollic acid; or perhaps that the aldehyde first forms and then is oxidized to the acid. Glycollic acid then oxidizes further to carbon dioxide and oxalic acid. The quantity of oxalate formed was found to be a linear function of the concentration of potassium hydroxide between the limits 0.5 and 3.0 grams of potassium hydroxide per liter.

Potassium permanganate is, of course, an excellent oxidizing agent in alkaline solution. Since the course of our investigation limited us to the study of solutions containing sulfuric acid this extensive literature is not reviewed.

Potassium dichromate is also used as oxidizing agent in the quantitative determination of ethylene glycol. In this case the reaction is carried to complete oxidation with large excess of the oxidizing agent, giving carbon dioxide and water. Riesenfeld and Hecht (7) studied this reaction from the point of view of photochemistry. Light was found to aid this oxidation, as it does in many other such organic reactions.

Plotnikov (6) found that potassium dichromate, and especially ammonium dichromate, in neutral solution quickly oxidize glycol. The solutions turn green, and contain alkali in excess. After the reaction they contain glycol aldehyde and glyoxal, as well as the chromium salts of glycollic acid, glyoxylic acid and oxalic acid. These investigations give but little which can aid in connection with our problem.

Uncertainties as to the nature of the reaction which glycol undergoes were, at least in part, eliminated by using it in large excess in all the experiments.

In view of the scanty references to such reactions as that which we had in mind, and of the unsatisfactory nature of the knowledge concerning them, we thought it advisable to limit the present research to a preliminary investigation which might, perhaps, serve as foundation for later and more extensive studies.

REAGENTS AND APPARATUS

Glycol.

The ethylene glycol used in this work was obtained from dynamite grade glycol. It was purified by distilling and the portion coming over between 197°C and 198°C (corrected) was collected. The glycol was then redistilled and the portion coming over at the constant boiling temperature of 197°C (corrected) was collected. The literature gives the boiling point as 197.2°C. When analyzed, the product showed a purity of 99.3%, the impurity probably being water that was taken up from the air. The glycol was stored in tightly stoppered flasks which were opened only to take out samples.

Water.

The water used in making up the stock solutions was ordinary distilled water.

Potassium Permanganate.

A solution of potassium permanganate was prepared from the reagent compound. Analysis showed it to be 0.09946 Normal.

Sulfuric Acid.

Sulfuric acid of C.P. quality was used. It was made up by diluting concentrated acid with three volumes of water. Standarization proved it to be 9.3760 Normal.

Potassium Iodide.

A solution of potassium iodide was prepared from the reagent compound. Its concentration was 0.1 Normal. The potassium iodide was stored in tightly stoppered bottles.

Sodium Thiosulfate

The sodium thiosulfate solution was prepared from the reagent compound. Analysis showed it to be 0.001 Normal.

Potassium Fluoride

A solution of 0.1950 molar potassium fluoride was prepared from the reagent compound.

Manganese Sulfate

The manganese sulfate was prepared from the reagent compound. The concentration was 0.0660 Molar.

Apparatus

Ordinary burettes, pipettes and flasks were used in this research. The photelometer was operated from a six volt storage battery, the battery being charged at the same time by a direct current generator. In order to keep the current steady, the battery was charged at a slower rate than it was discharged by the operation of the photelometer. The photelometer was calibrated by making up solutions of known concentrations of permanganate, and from the data obtained a graph was drawn plotting 100 minus the photelometer readings against the concentration. This graph was used in interpreting all readings. It gave directly molar concentrations in terms of 100 minus the photelometer readings. This graph is shown on page 32.

EXPERIMENTAL PART

Experiments were run at 25.0°C, 30.0°C, and 35.0°C to permit us to determine the effect of temperature upon the reaction rate. Since it was planned to follow the reaction by means of the photelometer precipitates could not be tolerated. Preliminary experiments showed that hydrated manganese oxides separated from the solutions after a few minutes if sulfuric acid was present in lower concentrations than about 0.40 molar. Above molar concentration of acid the reaction was too rapid to be followed satisfactorily at 35.0°C. This set the limits in acid concentrations. The upper limit in concentration of permanganate was set by the amount which could be satisfactorily determined by the photelometer. It was found, too, that within the above limits of acid concentration, when the permanganate was more concentrated than about 1/150 molar the solutions were likely to throw down a precipitate of hydrated manganese oxides. No solution more concentrated than 0.00099 molar was used. The upper limit of the concentration of glycol was set by the velocity of the reaction, since the rates increased rapidly with increasing concentration. The maximum concentration used was 0.024 molar.

The total volume of the solution in each reaction was 300 ml. The stock solutions were brought to constant temperature in the thermostat, and then such quantities of each were taken as would give the desired concentrations in the final solution. These were put into separate clean flasks and each of them was diluted with a known volume of water. They were then mixed, the glycol solution being added last, the flasks were stoppered, shaken and then placed in the thermostat. They were not opened thereafter except to take samples. For the photelometer 15 ml. samples were taken, transferred to the photelometer cell and the readings taken. In the cases (to be mentioned later) in which the analysis was carried out iodometrically 5 ml. samples were taken.

In analyzing our data it was found that straight lines were secured in every case when the logarithm to the base ten of the concentration was plotted against time. In some cases it was found that there were breaks in the curves so that two straight lines were found. It was noted, too, that at the time of the breaks the color of the solutions always turned from the purple of permanganate to pink, this change was also found by Launer and Launer and Yost. It seemed probable that, in these cases, the photelometer was not giving the true concentration of the oxidizing agent; and a few runs in which the concentration of the oxidizing agent was determined iodometrically showed this to be true. All experiments in which breaks had been found were repeated using the iodometric method, as were also a number of the others. We found that, so long as the color remained purple the two methods gave identical results, but the results were too low by the photelometric method when the color changed to pink. The photometric results are not reported for those cases where breaks were found, the results being those found by the iodometric method.

Our results fall into five groups. In the first, called Group I, the concentrations of potassium permanganate and sulfuric acid were maintained constant and the concentration of glycol was varied. The results of the various experiments are shown in Tables 1 to 14, inclusive. (In all these tables photelometric results are indicated by "100-Rdg." as the heading of the second column. Iodometric results are indicated by the heading "cc. $Na_2S_2O_3$".) The results are shown graphically in Figs. 1, 2 and 3.

In Group II the concentrations of potassium permanganate and of glycol were maintained constant and the concentration of sulfuric acid was varied. The results are given in Tables 15 to 28 inclusive. They are also shown graphically in Figs. 4, 5 and 6.

In Group III the concentrations of sulfuric acid and glycol were maintained constant and the concentration of permanganate was varied.. The results are given in Tables 29 to 40 inclusive. They are also shown graphically in Figs. 7 and 8.

In Group IV the concentrations of the sulfuric acid, glycol, and potassium permanganate were held constant, and the concentration of manganese sulfate varied. This was for the purpose of determining the results of added divalent manganese. The results are given in Tables 40 to 43 inclusive. They are shown graphically in Fig. 17.

In Group V the concentrations of the glycol, potassium permanganate, sulfuric and manganese sulfate are held constant and the concentration of potassium fluoride varied. The fluoride ion was added so as to study its effect upon the reactions in which manganese sulfate was added. The results are given in tables 43 to 46 inclusive. They are shown graphically in Fig. 17.

Reactions which were followed by the iodometric method are designated by # in table 47.

Experimental data are reported on the following pages.

DATA

Group I TABLE 1 25.0°C

0.00066 mols $KMnO_4$ per liter
0.675 mols H_2SO_4 per liter
0.0024 mols glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	36.0	0.000340
2	26.0	0.000195
3	18.5	0.000120
4	12.5	0.000070
5	8.5	0.000040
6	4.7	0.000020

TABLE 2 25.0°C

0.00066 mols $KMnO_4$ per liter
0.675 mols H_2SO_4 per liter
0.00180 mols glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	40.0	0.000430
2	32.4	0.000280
3	25.5	0.000190
4	20.0	0.000135
5	14.5	0.000085
6	10.5	0.000055
7	6.7	0.000030
8	5.0	0.000020
9	3.5	0.000015

TABLE 3 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	13.15	0.000525
2	9.30	0.000370
3	6.75	0.000270
4	5.10	0.000210
5	3.85	0.000155
6	3.20	0.000130
7	2.30	0.000093
8	1.70	0.000070
9	1.20	0.000050
10	0.80	0.000035
12	0.30	0.000015

TABLE 4 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_2 per liter
0.0060 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	14.30	0.000570
2	12.40	0.000495
4	9.50	0.000480
6	7.25	0.000290
8	5.70	0.000230
10	4.62	0.000186
12	3.90	0.000155
14	3.20	0.000130
16	2.70	0.000110
18	2.35	0.000095
20	2.04	0.000078
22	1.60	0.000065
24	1.30	0.000055

TABLE 5 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.00300 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	15.30	0.000610
2	14.00	0.000560
3	12.93	0.000517
4	12.00	0.000480
6	10.50	0.000420
8	9.65	0.000085
10	8.75	0.000398
12	7.93	0.000317
14	7.30	0.000290
16	6.60	0.000265
18	5.90	0.000235
20	5.40	0.000215
22	4.92	0.000198

TABLE 6 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.02400 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.00066
1	34.5	0.000315
2	21.7	0.000150
3	12.0	0.000065
4	6.5	0.000030
5	3.5	0.000015

TABLE 7 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols per liter
0.01800 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.00066
1	38.8	0.00040
2	28.5	0.000225
3	19.5	0.000130
4	12.5	0.000070
5	8.2	0.000040
6	4.5	0.000020

TABLE 8 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.50	0.00066
1	41.50	0.000465
2	34.50	0.000315
3	26.50	0.000200
4	21.20	0.000145
5	16.30	0.000100
6	13.00	0.000067
7	9.00	0.000045
8	6.50	0.000030
9	3.50	0.000019
10	2.50	0.0000150

TABLE 9 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.00600 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.00066
1	13.75	0.00055
2	11.50	0.00046
4	7.50	0.00030
6	5.35	0.000215
8	4.10	0.000165
10	3.10	0.000125
12	2.35	0.000095
14	1.70	0.000070
16	1.30	0.000055
18	0.95	0.000040

TABLE 10 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.00300 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.00066
1	14.50	0.00058
2	13.15	0.000525
4	10.50	0.000420
6	9.83	0.000353
8	7.80	0.000312
10	6.75	0.000270
12	6.00	0.000240
14	5.25	0.000210
16	4.65	0.000186
18	4.10	0.000165

TABLE 11 35.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.01800 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.00066
1	36.7	0.000355
2	21.2	0.000145
3	13.2	0.000075
4	6.5	0.000030
5	2.5	0.000010

TABLE 12 35.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	41.2	0.000460
2	28.5	0.000225
3	19.0	0.000125
4	13.2	0.000075
5	8.2	0.000040
6	5.5	0.000023
7	2.5	0.000010

TABLE 13 35.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.00600 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000880
1	12.50	0.000500
2	9.00	0.000360
3	6.90	0.000275
4	5.60	0.000225
5	4.60	0.000185
7	3.35	0.000135
9	2.45	0.000100
11	1.83	0.000075

TABLE 14 35.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.00300 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	13.75	0.000550
2	11.90	0.000475
3	10.50	0.000420
4	9.50	0.000380
5	8.65	0.000345
7	7.50	0.000300
9	6.40	0.000255
11	5.23	0.000210

Group II TABLE 15 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	34.4	0.000310
2	27.0	0.000205
3	20.0	0.000135
4	13.7	0.000080
5	10.0	0.000050
6	6.5	0.000030

TABLE 16 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.838 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	42.7	0.000500
2	33.7	0.000300
3	26.0	0.000195
4	20.5	0.000138
5	15.7	0.000095
6	11.5	0.000063
7	8.7	0.000044
8	6.5	0.000030

TABLE 17 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.0120 Mols Glycol per liter

Time in Min	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	13.15	0.000525
2	9.30	0.000370
3	6.75	0.000270
4	5.10	0.000210
5	3.85	0.000155
6	3.20	0.000130
7	2.30	0.000093
8	1.70	0.000070
9	1.20	0.000050
10	0.80	0.000035
12	0.30	0.000015

TABLE 18 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.0120 Mols Glycol per liter

Time in Min.	100- Rdg.	Conc.
0	48.5	0.000660
1	44.7	0.000550
2	41.2	0.000460
3	38.0	0.000385
4	35.5	0.000330
5	32.0	0.000275
6	28.5	0.000225
7	25.0	0.000185
8	21.7	0.000150
9	17.6	0.000121
10	16.2	0.000100
11	14.5	0.000085
12	12.5	0.000070
13	10.7	0.000057
14	9.7	0.000049
15	9.0	0.000042
16	8.2	0.000040

TABLE 19 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.019 Mols H_2SO_4 per liter
0.0120 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	15.00	0.000600
2	13.50	0.000540
4	11.52	0.000440
6	9.18	0.000365
8	7.25	0.000290
10	6.10	0.000244
12	5.30	0.000212
14	4.72	0.000190
16	4.45	0.000177
18	m4.05	0.000163
20	3.70	0.000150
22	3.35	0.000135
24	3.00	0.000120

TABLE 20 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.945 Mols H_2SO_4 per liter
0.0120 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	34,3	0.000310
2	22.2	0.000080
3	13.7	0.000040
4	8.2	0.000020
5	4.5	0.000010
6	2.5	0.000007
7	1.7	0.000005
8	1.5	0.000003

TABLE 21 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.848 Mols H_2SO_4 per liter
0.0120 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	39.0	0.000405
2	32.2	0.000277
3	24.0	0.000175
4	15.0	0.000090
5	9.0	0.000045
7	4.5	0.000020
9	2.5	0.000010

TABLE 22 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.0120 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	41.5	0.000465
2	34.5	0.000315
3	26.5	0.000200
4	21.2	0.000145
5	16.3	0.000100
6	9.0	0.000045
7	6.5	0.000030
8	3.5	0.000019
9	2.5	0.000015
10	1.7	0.000012

TABLE 23 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	13.00	0.000520
2	10.00	0.000400
3	7.70	0.000312
4	6.00	0.000240
5	4.60	0.000185
7	2.70	0.000110
9	1.60	0.000065
11	0.95	0.000040

TABLE 24 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.419 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	14.75	0.000585
2	12.90	0.000515
3	11.25	0.000450
4	10.00	0.000400
5	8.75	0.000350
7	6.90	0.000275
9	5.60	0.000225
11	4.50	0.000180
13	3.75	0.000150

TABLE 25 35.0°C

0.00066 Mols $KMnO_4$ per liter
0.838 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000550
1	30.5	0.000250
2	16.2	0.000100
3	8.2	0.000040
4	3.5	0.000015

TABLE 26 35.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	37.2	0.000365
2	26.5	0.000200
3	18.5	0.000120
4	12.5	0.000070
5	8.2	0.000040
6	5.8	0.000025

TABLE 27 35.0°C

0.00066 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	11.65	0.000465
2	8.75	0.000350
3	5.75	0.000230
4	3.75	0.000155
5	2.70	0.000110
6	2.00	0.000080
7	1.30	0.000055
8	0.95	0.000040
9	0.60	0.000025

TABLE 28 35.0°C

0.00066 Mols $KMnO_4$ per liter
0.419 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	13.50	0.000540
2	11.03	0.000440
3	8.90	0.000355
4	7.25	0.000290
5	5.90	0.000237
6	5.00	0.000200
7	4.20	0.000170
8	3.60	0.000145
9	3.10	0.000125
11	2.35	0.000095

Group III TABLE 29 25.0°C

0.000165 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	23.0	0.000165
1	20.3	0.000137
2	18.0	0.000115
3	15.8	0.000095
4	13.7	0.000080
5	12.2	0.000067
6	10.5	0.000055
7	9.3	0.000047
8	8.2	0.000040
9	7.5	0.000035
10	6.0	0.000027
11	5.0	0.000022
12	4.5	0.000020

TABLE 30 25.0°C

0.00033 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	35.5	0.000330
1	31.2	0.000262
2	28.0	0.000220
3	25.0	0.000185
4	22.5	0.000157
5	19.7	0.000132
6	17.5	0.000110
7	15.3	0.000092
8	13.3	0.000075
9	11.2	0.000060
10	10.0	0.000050
11	8.6	0.000042
12	7.5	0.000035

TABLE 31 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	48.5	0.000660
1	44.7	0.000550
2	41.2	0.000460
3	38.0	0.000385
4	35.5	0.000330
5	32.0	0.000275
6	28.5	0.000225
7	25.0	0.000185
8	21.7	0.000150
9	17.6	0.000121
10	16.2	0.000100
11	14.5	0.000085
12	12.5	0.000070
13	10.7	0.000057
14	9.7	0.000049
15	9.0	0.000042
16	8.2	0.000040

TABLE 32 25.0°C

0.00099 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	58.5	0.000990
1	53.5	0.000832
2	49.5	0.000690
3	45.8	0.000580
4	41.8	0.000475
5	38.7	0.000400
6	35.5	0.000330
7	32.3	0.000280
8	28.8	0.000230
9	26.0	0.000195
10	22.5	0.000160
12	17.5	0.000110
14	13.3	0.000075
16	10.5	0.000055

TABLE 33 30.0°C

0.000165 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	23.0	0.000165
1	19.0	0.000125
2	15.8	0.000095
3	13.2	0.000075
4	11.2	0.000060
5	8.5	0.000042
6	7.5	0.000035
7	5.7	0.000025
8	4.5	0.000020
9	3.5	0.000015
10	2.4	0.000010

TABLE 34 30.0°C

0.00033 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	35.5	0.000330
1	31.4	0.000265
2	26.5	0.000200
3	22.1	0.000155
4	18.5	0.000120
5	15.2	0.000092
6	13.2	0.000075
7	10.8	0.000057
8	9.0	0.000045
9	7.0	0.000033
10	5.7	0.000025

TABLE 35 30.0°C

0.00066 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	13.00	0.000520
2	10.00	0.000400
3	7.70	0.000312
4	6.00	0.000240
5	4.60	0.000185
6	3.70	0.000142
7	2.70	0.000110
9	1.60	0.000065
10	0.95	0.000040

TABLE 36 30.0°C

0.00099 Mols KMnO per liter
0.558 Mols $H_2SO^4_4$ per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	58.5	0.000990
1	52.5	0.000794
2	46.3	0.000595
3	42.0	0.000480
4	37.5	0.000370
5	33.0	0.000290
6	28.0	0.000220
7	23.0	0.000170
8	20.2	0.000135
9	17.5	0.000110
10	14.7	0.000086
11	12.2	0.000067
12	10.0	0.000050

TABLE 37 35.0° C

0.000165 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	23.0	0.000165
1	18.0	0.000115
2	13.8	0.000080
3	10.3	0.000053
4	8.2	0.000040
5	5.8	0.000025
6	4.3	0.000018

TABLE 38 35.0° C

0.00033 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	35.5	0.000330
1	29.2	0.000235
2	22.6	0.000160
3	17.0	0.000105
4	13.8	0.000080
5	10.5	0.000055
6	8.0	0.000038
7	6.4	0.000029
8	4.5	0.000020

TABLE 39 35.0° C

0.00066 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.01200 Mols Glycol per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	11.65	0.000465
2	8.75	0.000350
3	5.75	0.000230
4	3.75	0.000155
5	2.70	0.000110
6	2.00	0.000080
7	1.30	0.000055
9	0.60	0.000025

TABLE 40 35.0°C

0.00099 Mols $KMnO_4$ per liter
0.558 Mols H_2SO_4 per liter
0.0120 Mols Glycol per liter

Time in Min.	100-Rdg.	Conc.
0	58.5	0.000990
1	49.6	0.000692
2	45.6	0.000575
3	37.6	0.000375
4	28.9	0.000230
5	21.7	0.000150
6	17.5	0.000110
7	13.5	0.000076
8	10.5	0.000055

Group IV TABLE 41 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.0060 Mols Glycol per liter
0.0033 Mols $MnSO_4$ per liter

Time in Min	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	15.00	0.000599
2	13.45	0.000537
3	12.12	0.000484
4	11.50	0.000459
5	10.90	0.000435
6	10.32	0.000412
7	9.75	0.000389
8	9.20	0.000367

TABLE 42 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.575 Mols H_2SO_4 per liter
0.00600 Mols Glycol per liter
0.00660 Mols $MnSO_4$ per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	15.50	0.000619
2	14.40	0.000575
3	13.75	0.000549
4	13.15	0.000525
5	12.50	0.000500
6	11.95	0.000478

42 Continued

7	11.53	0.000460
8	11.00	0.000400

TABLE 43 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.0060 Mols Glycol per liter
0.000165 Mols $MnSO_4$ per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	13.40	0.000575
2	12.87	0.000513
3	11.30	0.000450
4	10.10	0.000403
5	9.23	0.000367
6	8.47	0.000338
7	7.82	0.000312
8	7.14	0.000285

Group V TABLE 44 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.0060 Mols Glycol per liter
0.0033 Mols $MnSO_4$ per liter
0.0065 Mols KF per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	14.75	0.000588
2	13.60	0.000522
3	11.57	0.000462
4	10.20	0.000407
5	9.53	0.000380
6	8.75	0.000350
7	8.00	0.000320
8	7.40	0.000295

TABLE 45 25.0°C

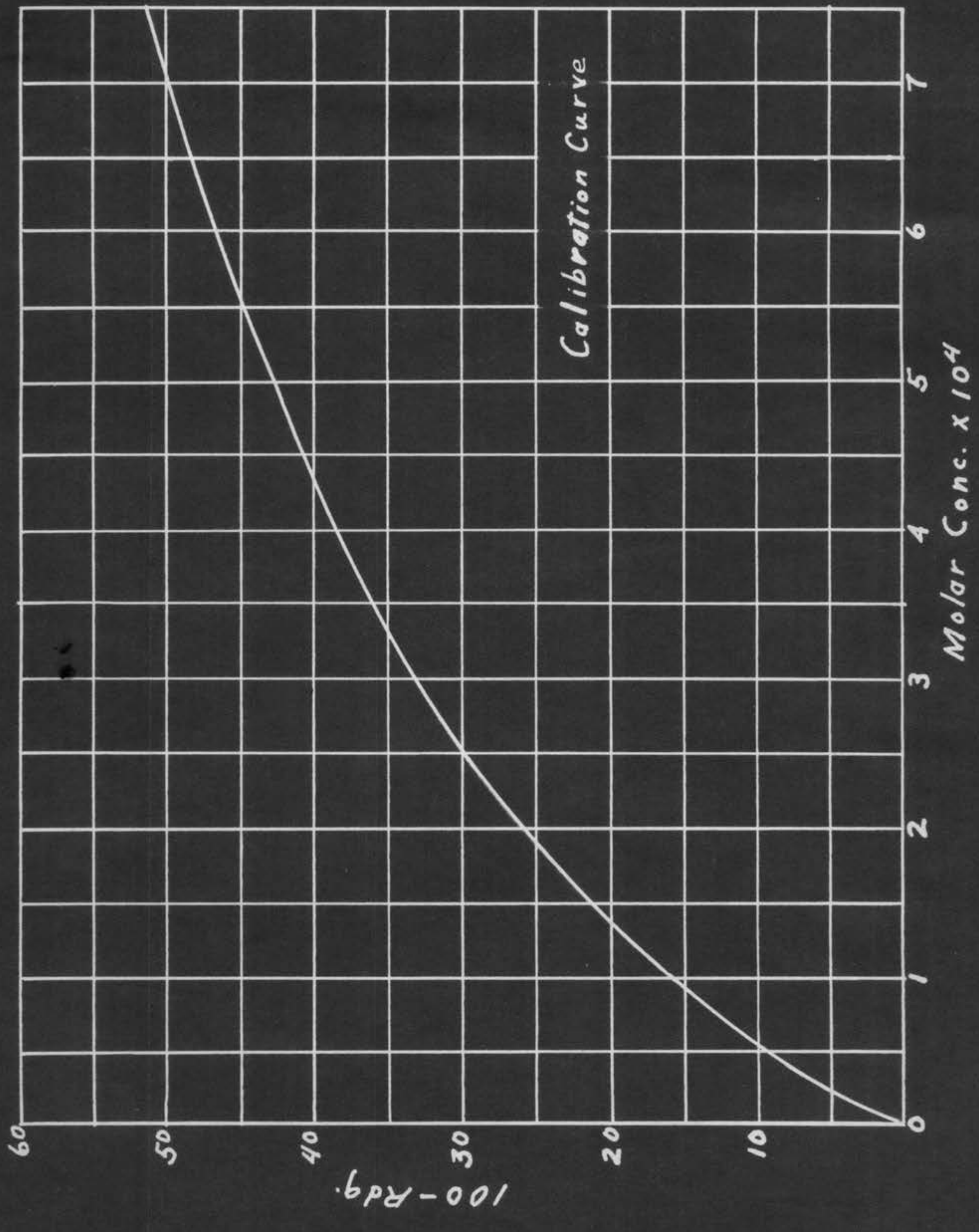
0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.0060 Mols Glycol per liter
0.0033 Mols $MnSO_4$ per liter
0.0130 Mols KF per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	14.40	0.000575
2	12.55	0.000501
3	11.12	0.000444
4	9.75	0.000389
5	8.45	0.000338
6	7.57	0.000302
7	6.90	0.000275
8	6.30	0.000251

TABLE 46 25.0°C

0.00066 Mols $KMnO_4$ per liter
0.675 Mols H_2SO_4 per liter
0.0060 Mols Glycol per liter
0.0033 Mols $MnSO_4$ per liter
0.0260 Mols KF per liter

Time in Min.	C.C. $Na_2S_2O_3$	Conc.
0	16.50	0.000660
1	14.60	0.000562
2	11.95	0.000478
3	10.21	0.000407
4	8.70	0.000346
5	7.40	0.000295
6	6.30	0.000251
7	5.35	0.000214
8	4.55	0.000182
9	4.05	0.000162
10	3.62	0.000146


Calibration Curve
Molar Conc. x 10⁴
0
1
2
3
4
5
6
7
100-Rdg.
0
10
20
30
40
50
60

Glycol Varied 25.0°C
Experimental Results

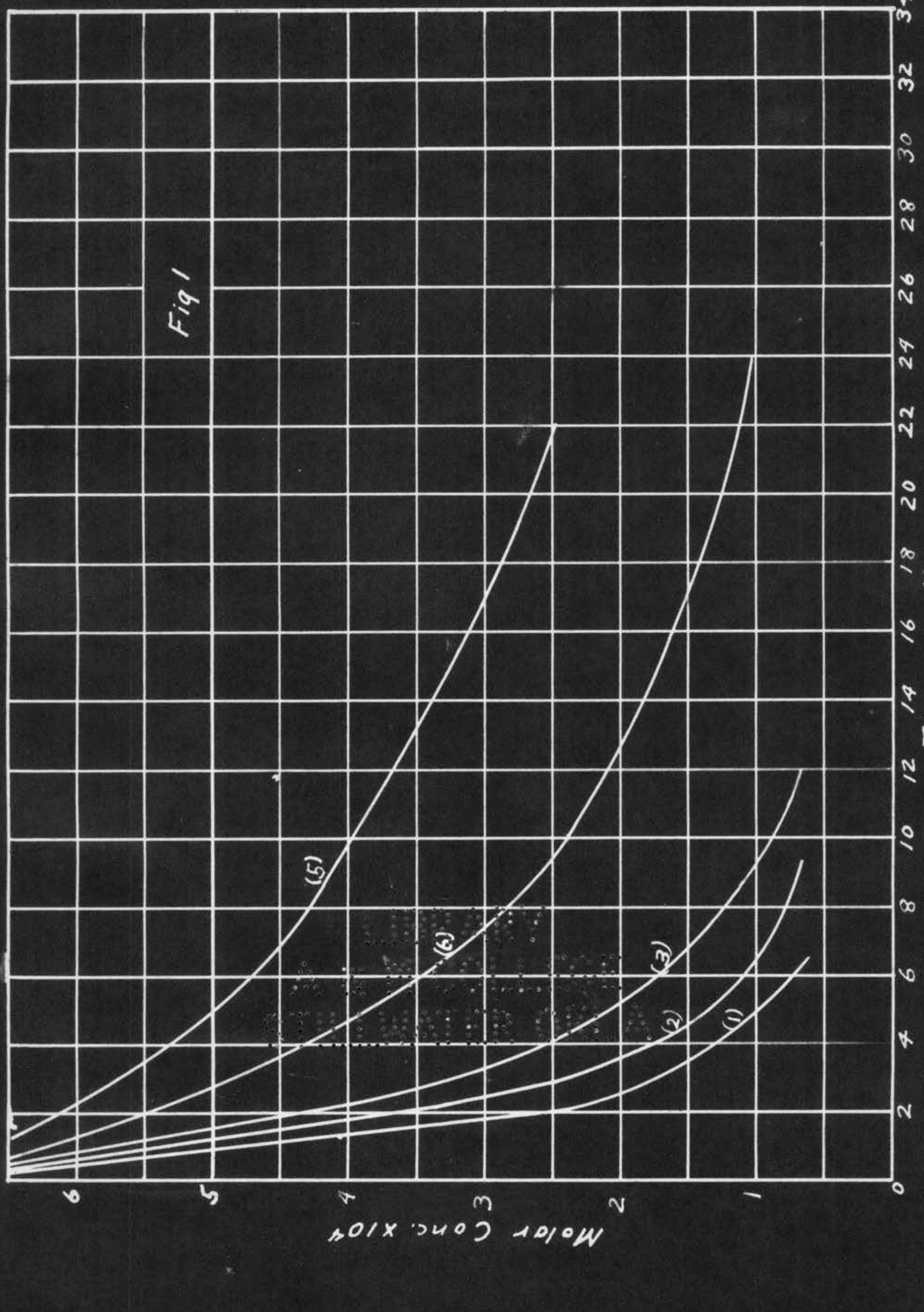


Fig 1

Glycol Varied 30.0°C
Experimental Results

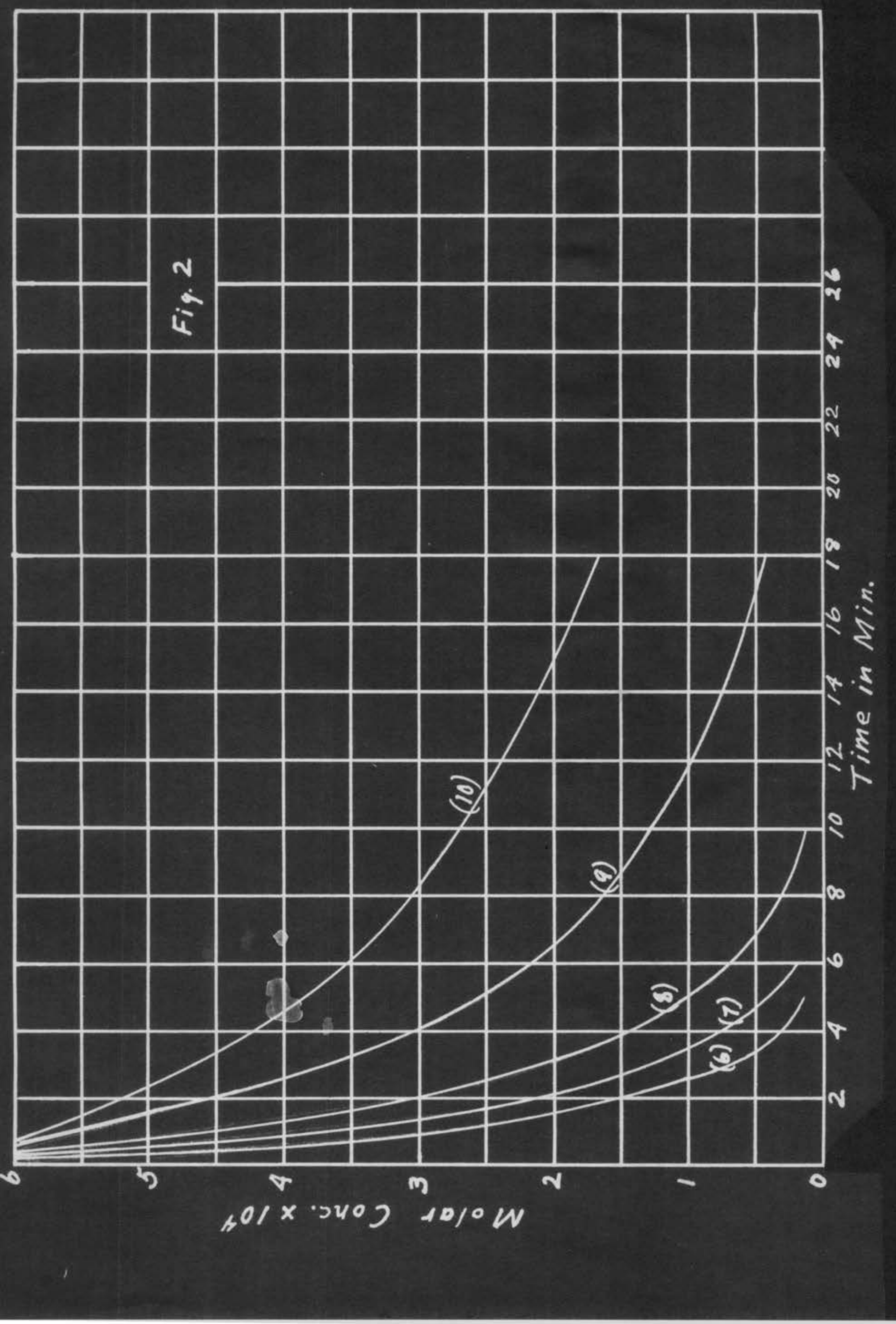
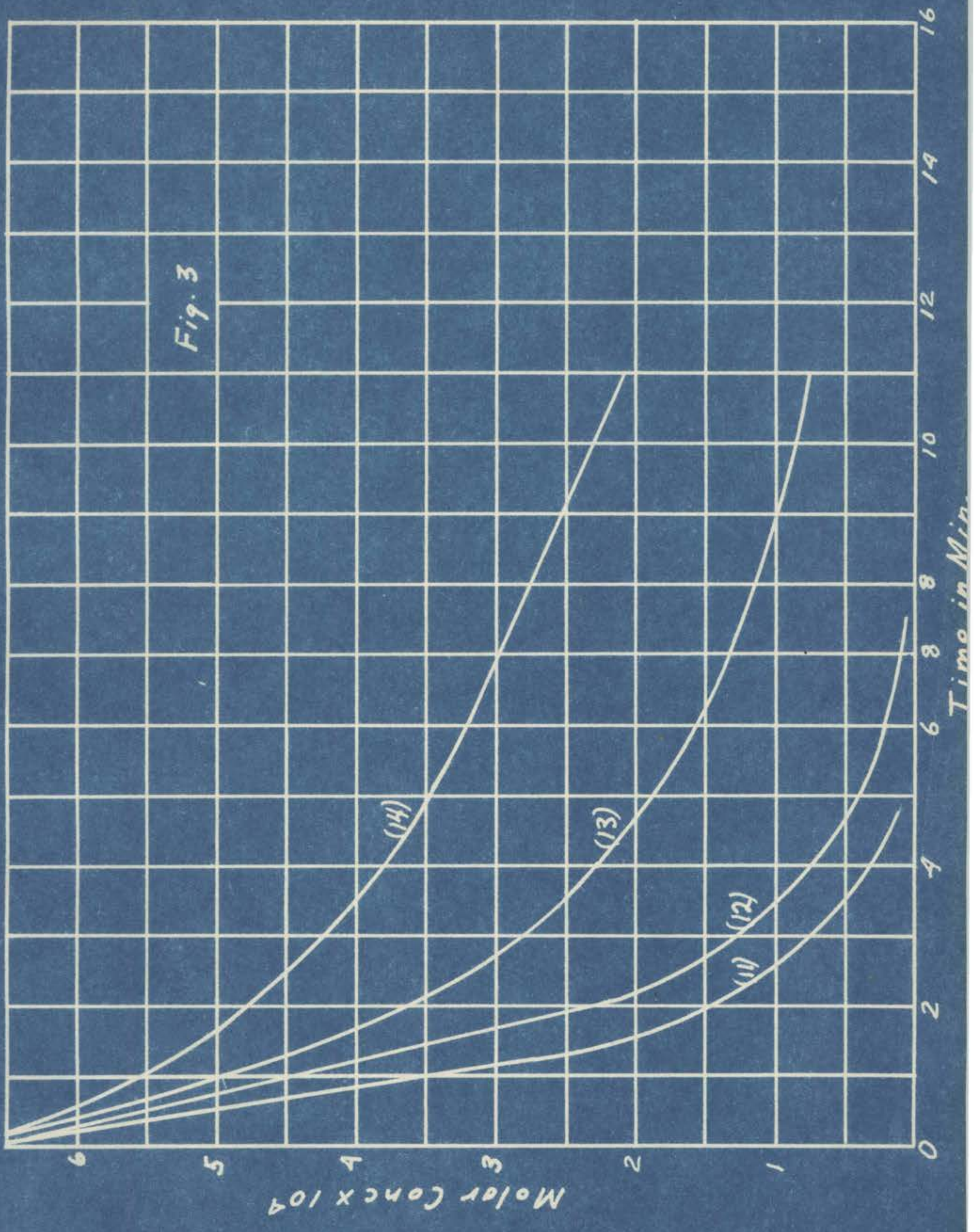


Fig. 2

Glycol Varied 35.0°C
Experimental Results



Acid Varied 25.0°C
Experimental Results

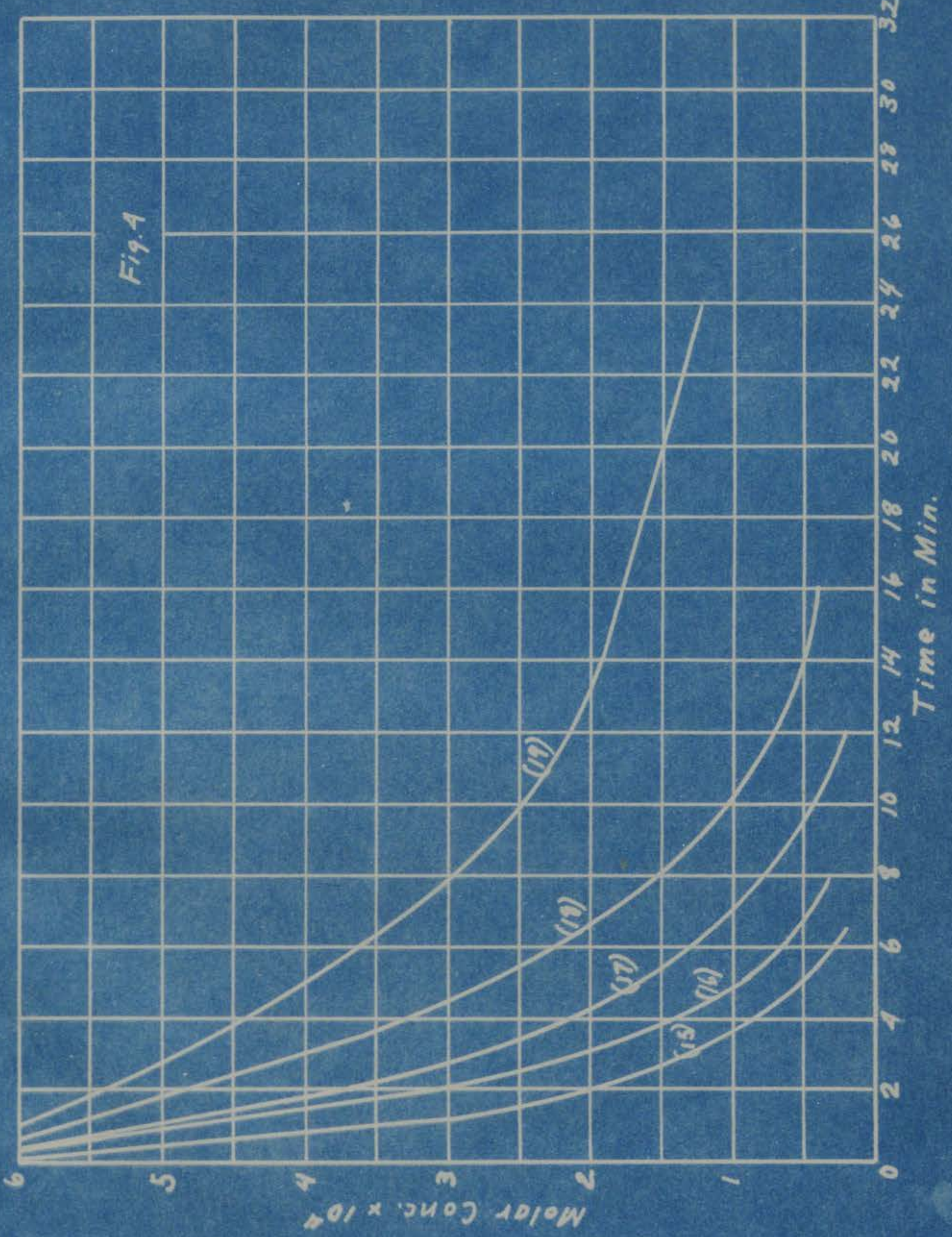


Fig. 4

Acid Varied 30.0°C
Experimental Results.

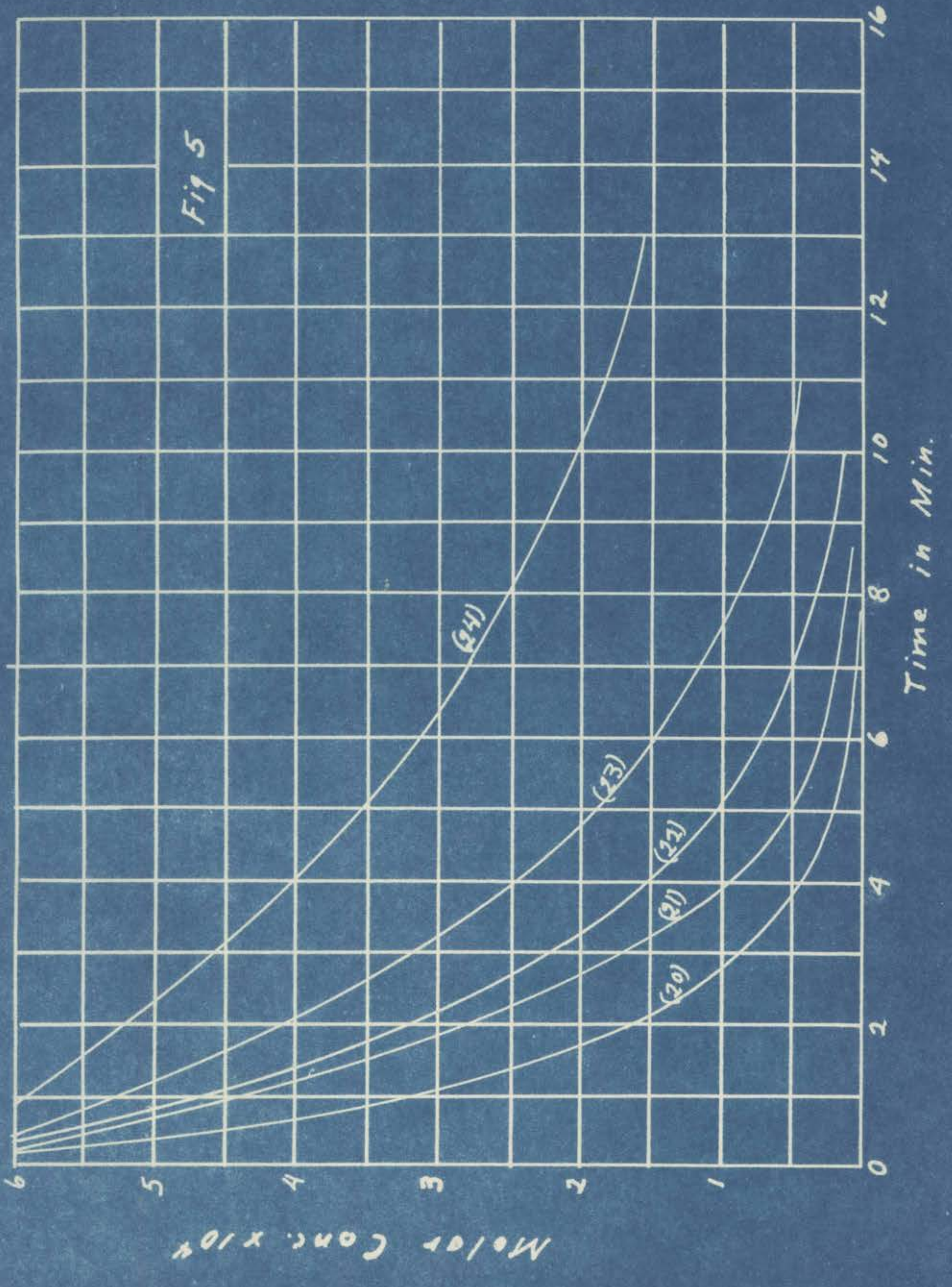


Fig 5

Sulfuric Acid Varied 35.0°C

Experimental Results.

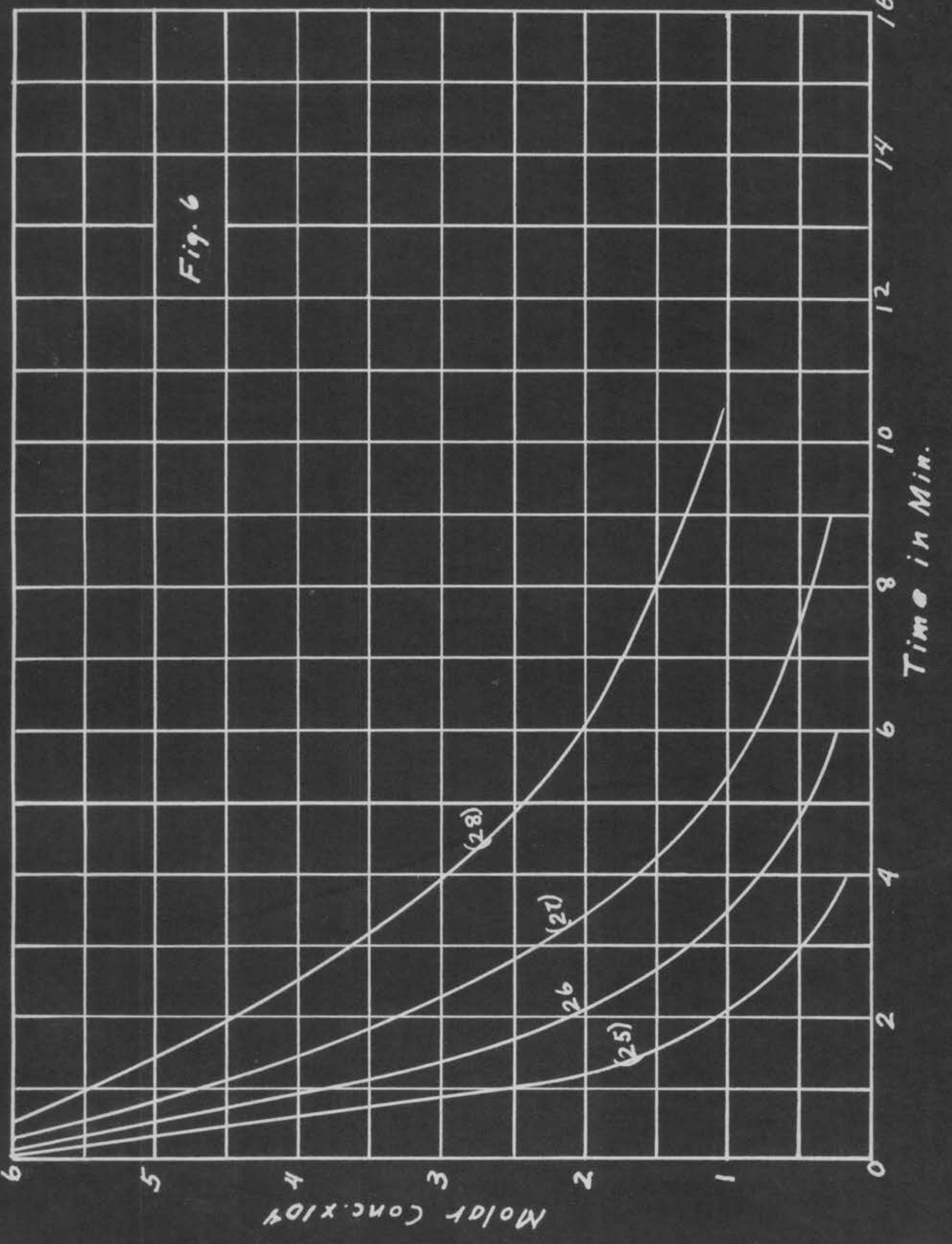
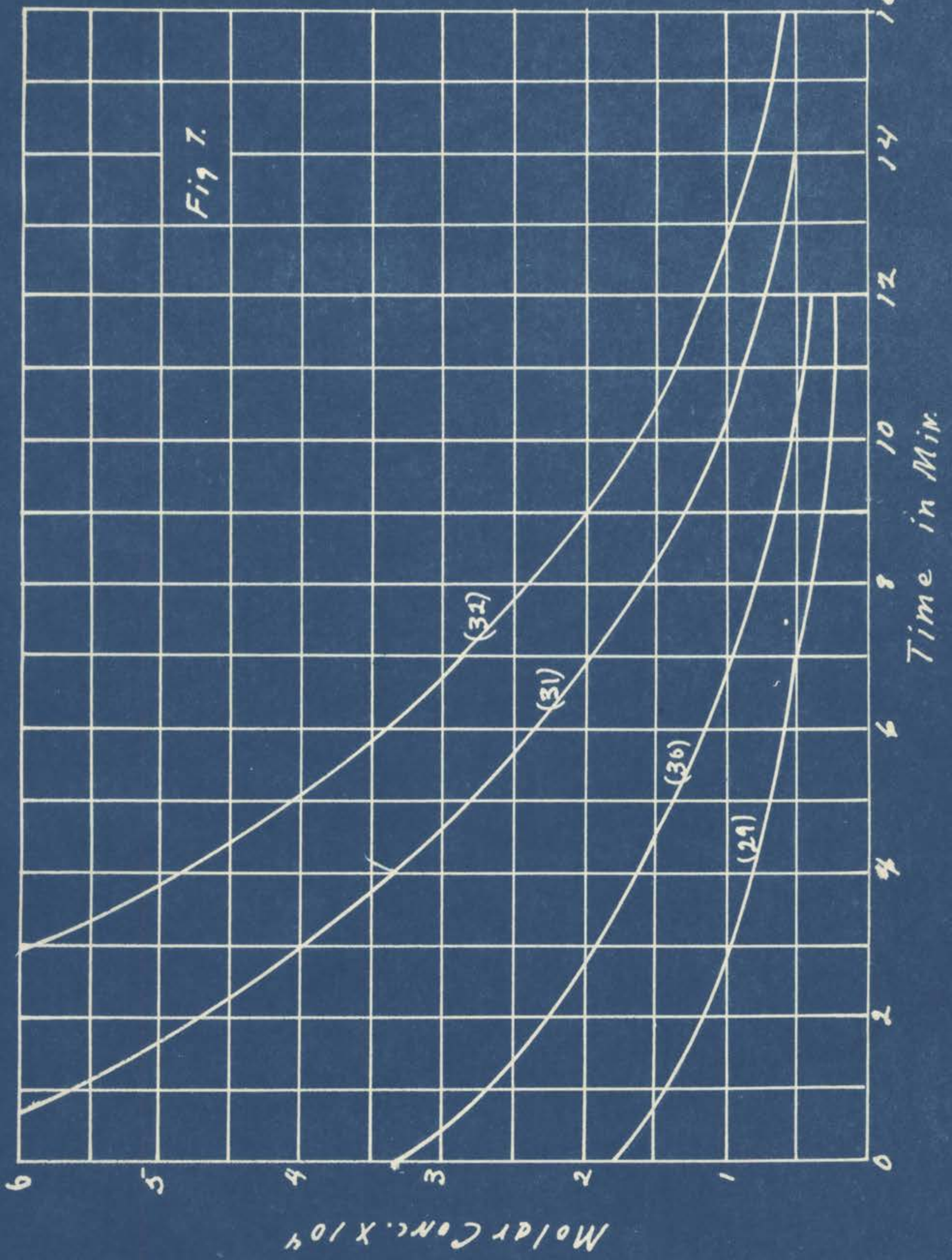


Fig. 6

Permanganate Varied 25.0°C.

Experimental Results.

Fig 7.



Permanganate Varied 30.8°C

Experimental Results

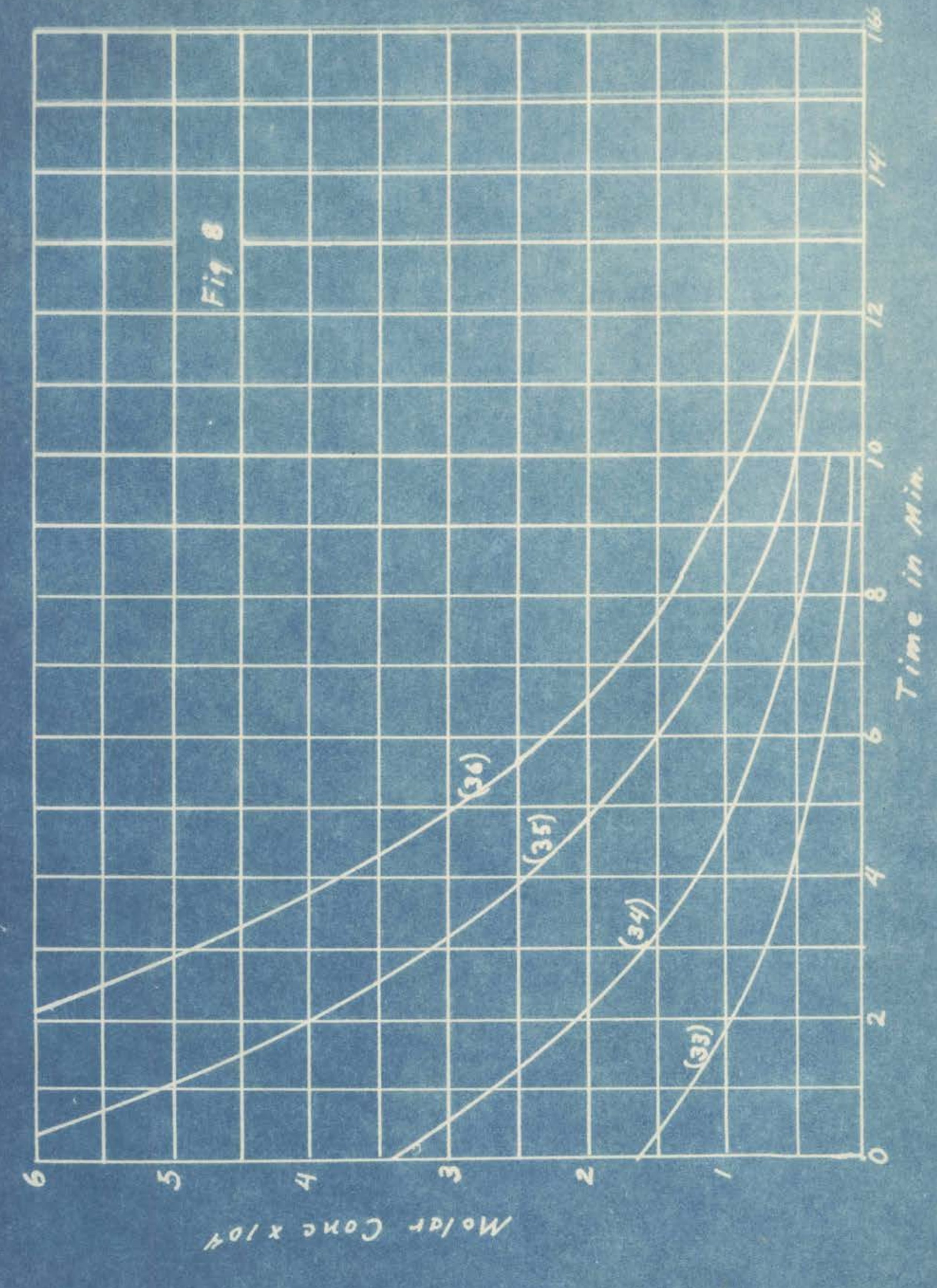


Fig 8

Permanganate Varied 35.0°C

Experimental Results

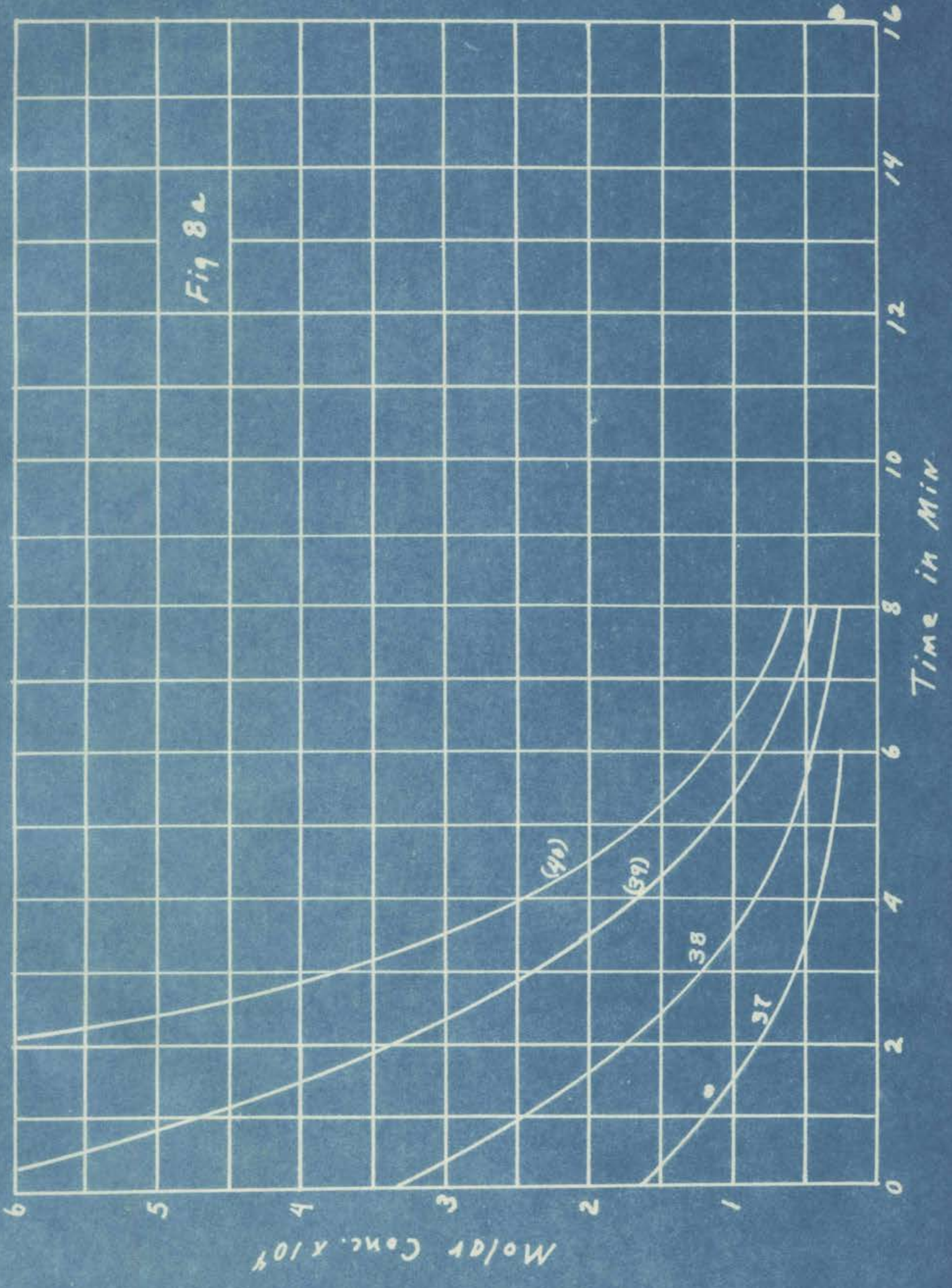


Fig 8a

Glycol Varied 25.0°C

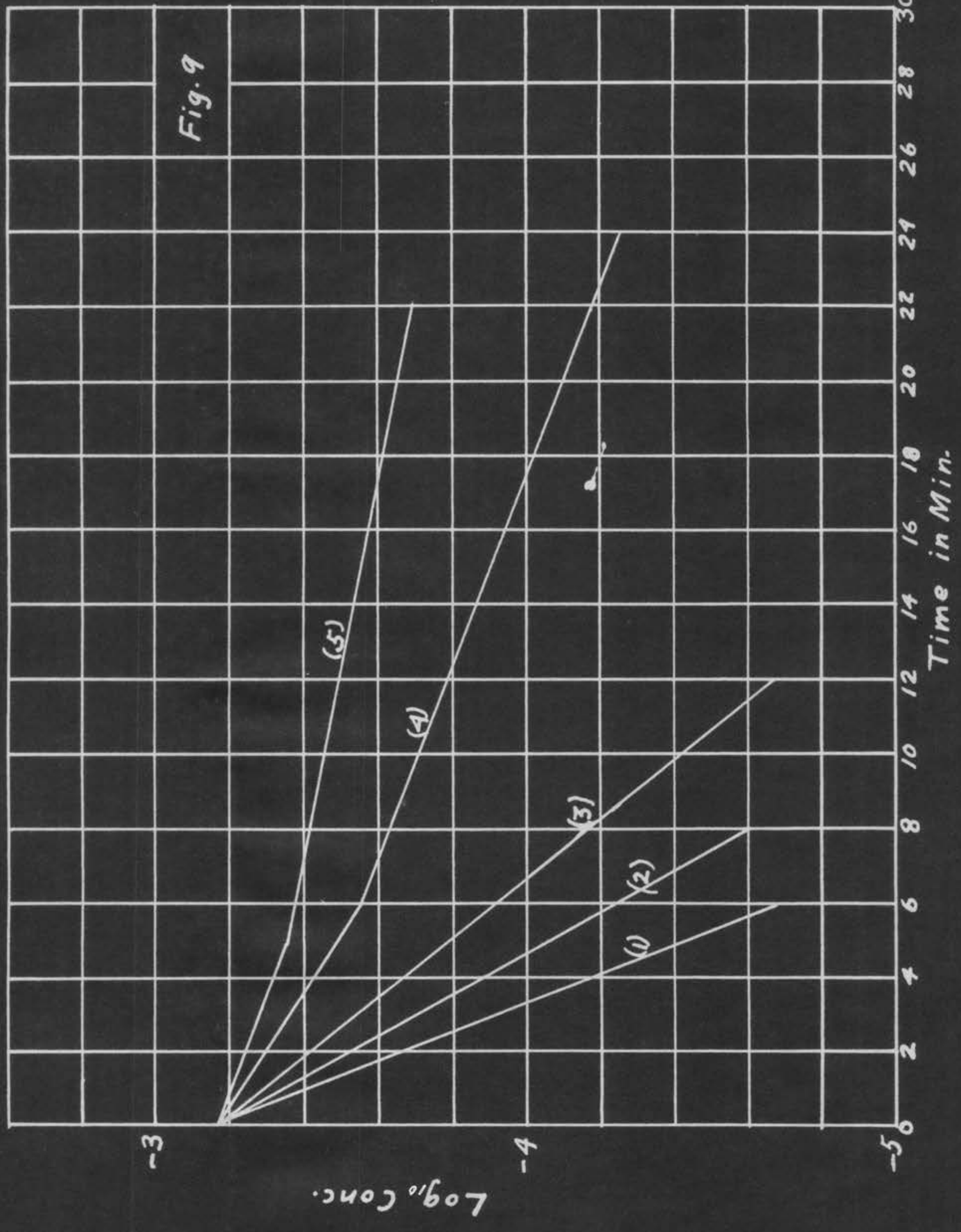


Fig. 9

Glycol Varied 30.0°C

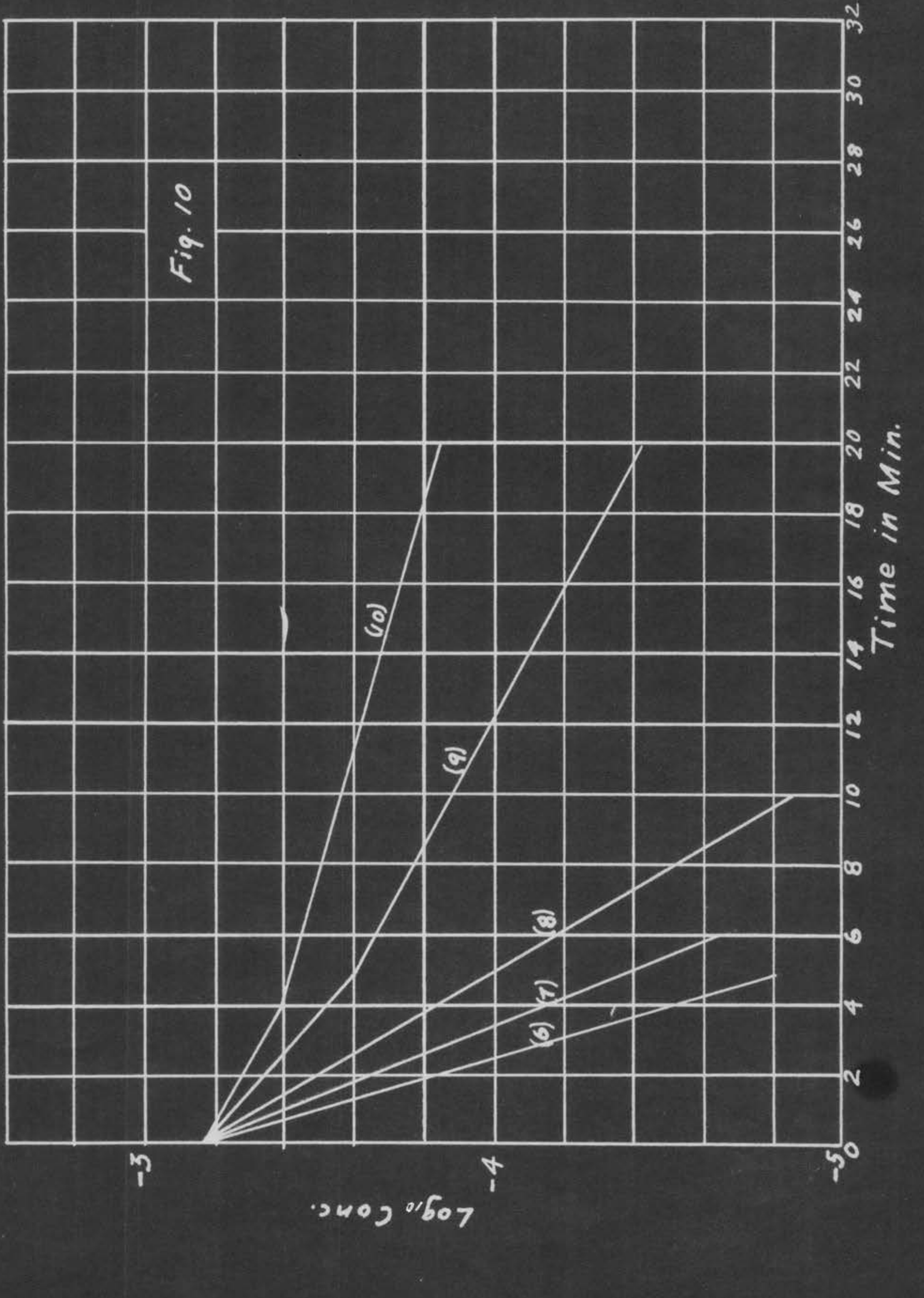


Fig. 10

Glycol Varied 35.0°C

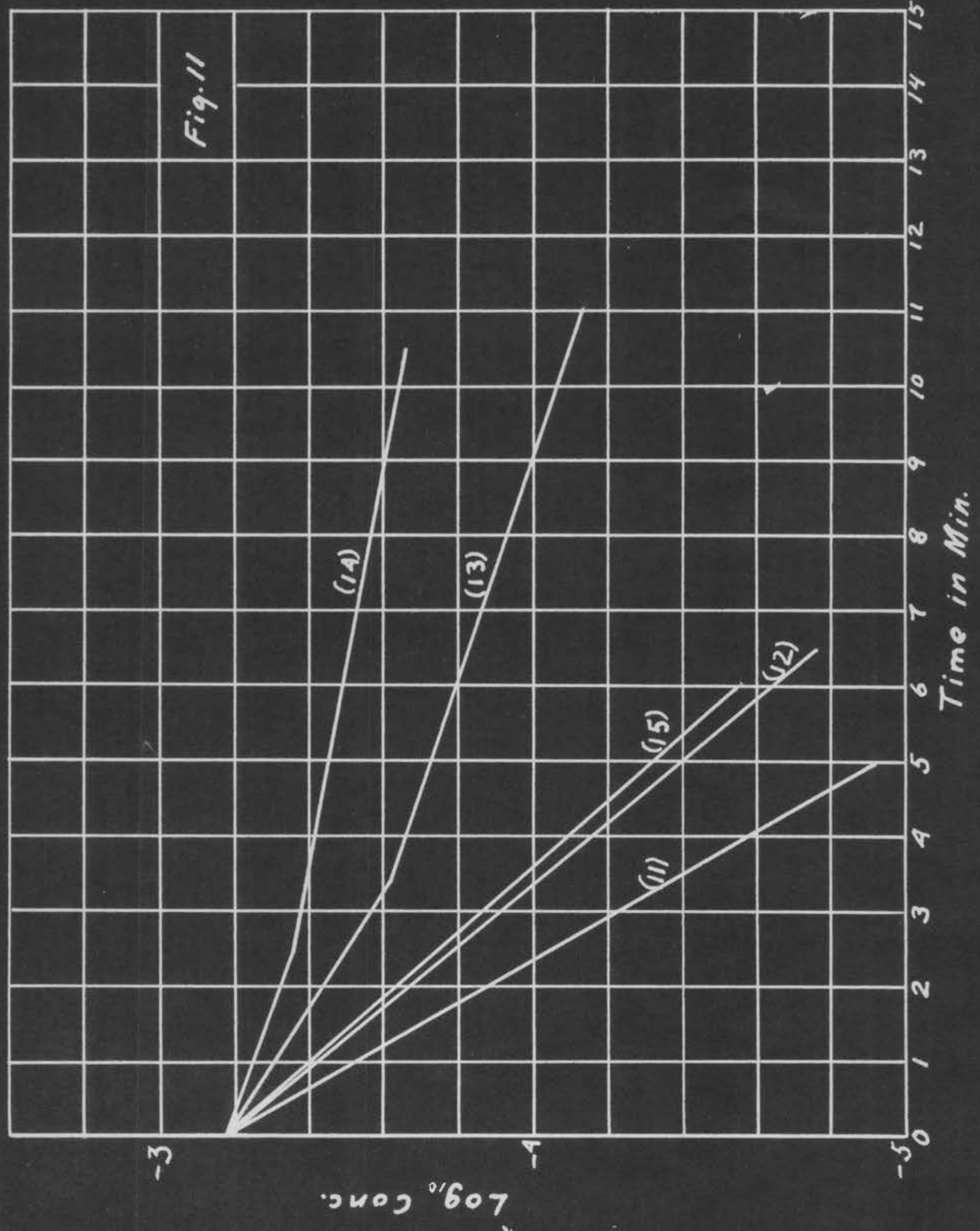


Fig. 11

Acid Varied 25.0°C.

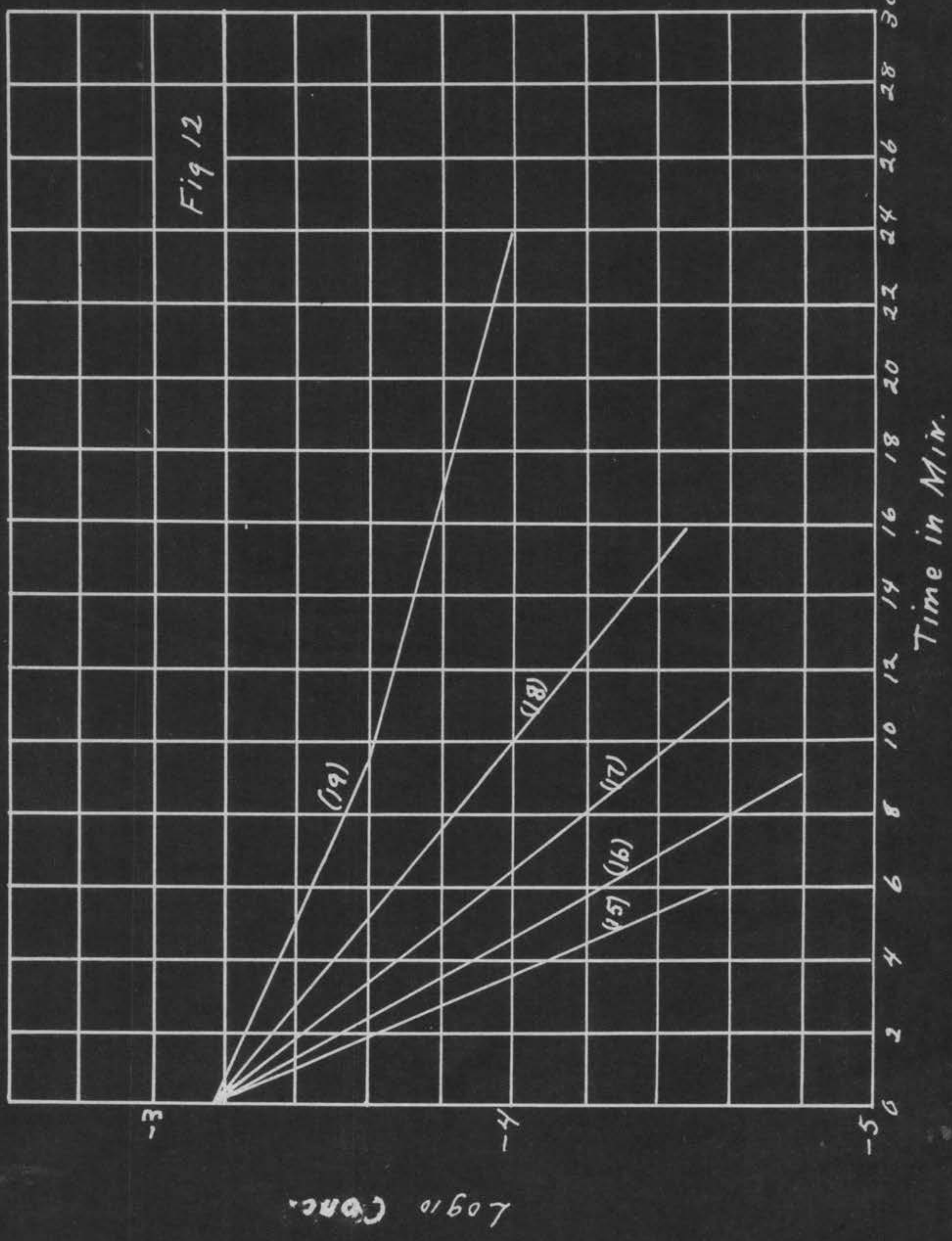


Fig 12

Acid Varied 30.0°C

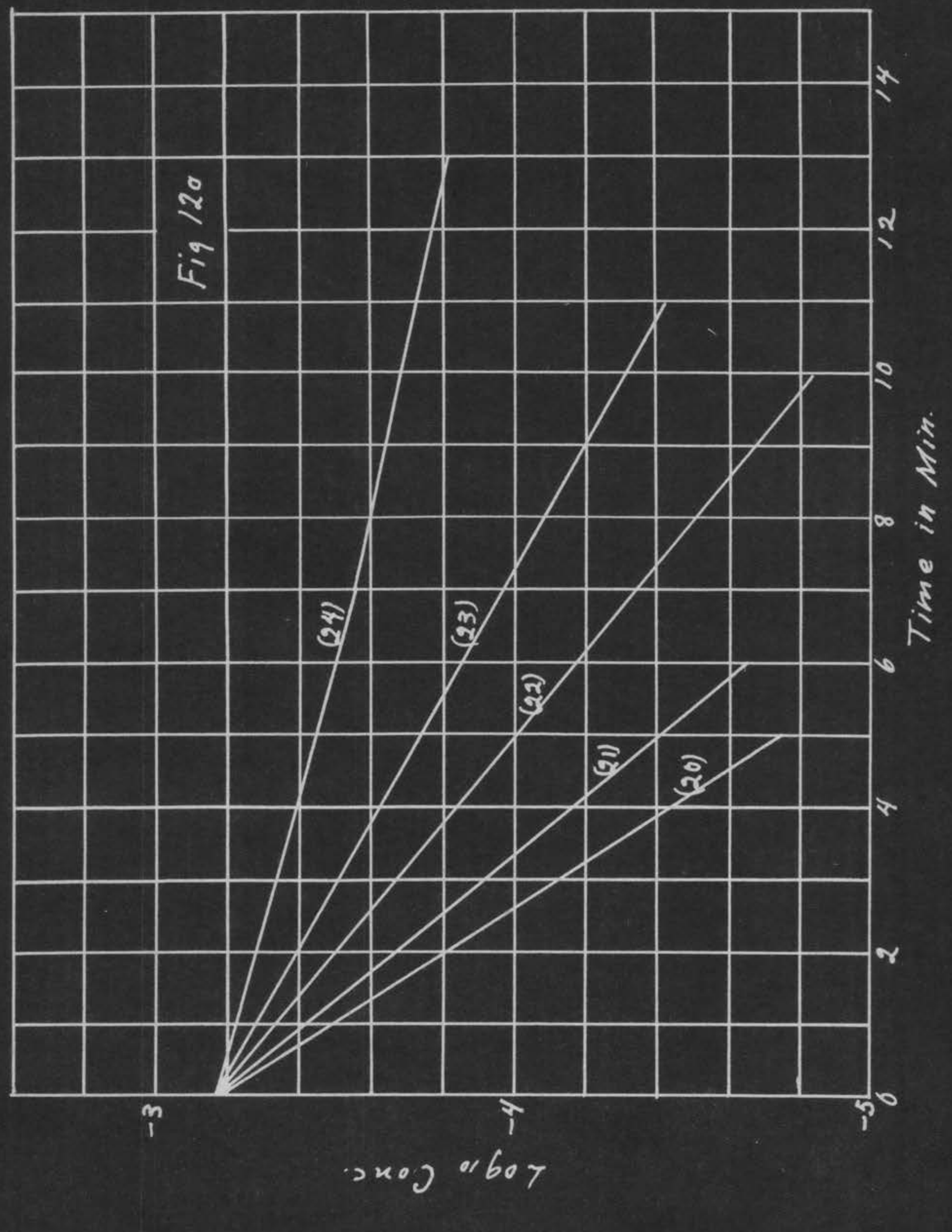


Fig 12a

Acid Varied 35.0°C

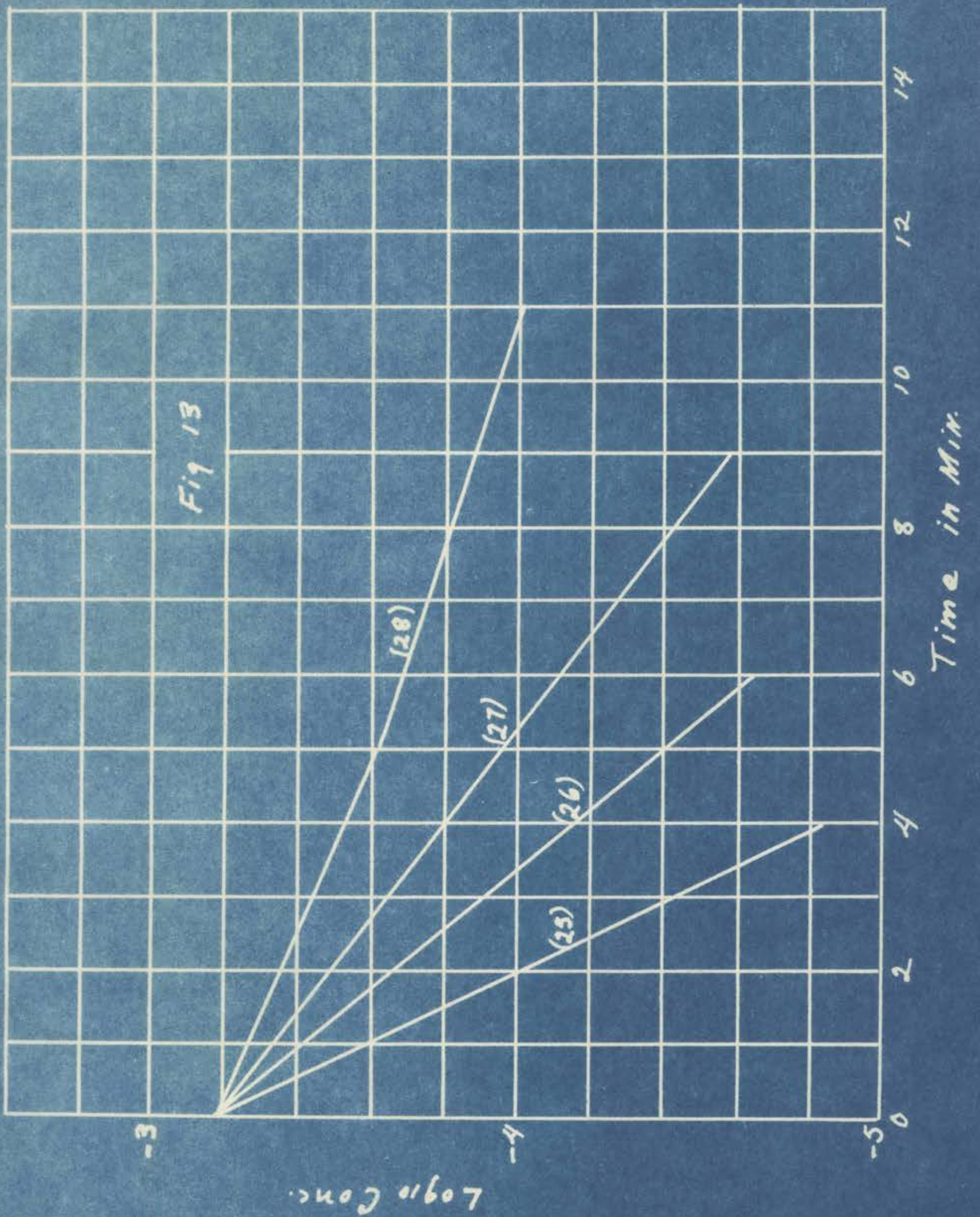


Fig 13

Permanganate Varied 25.0°C

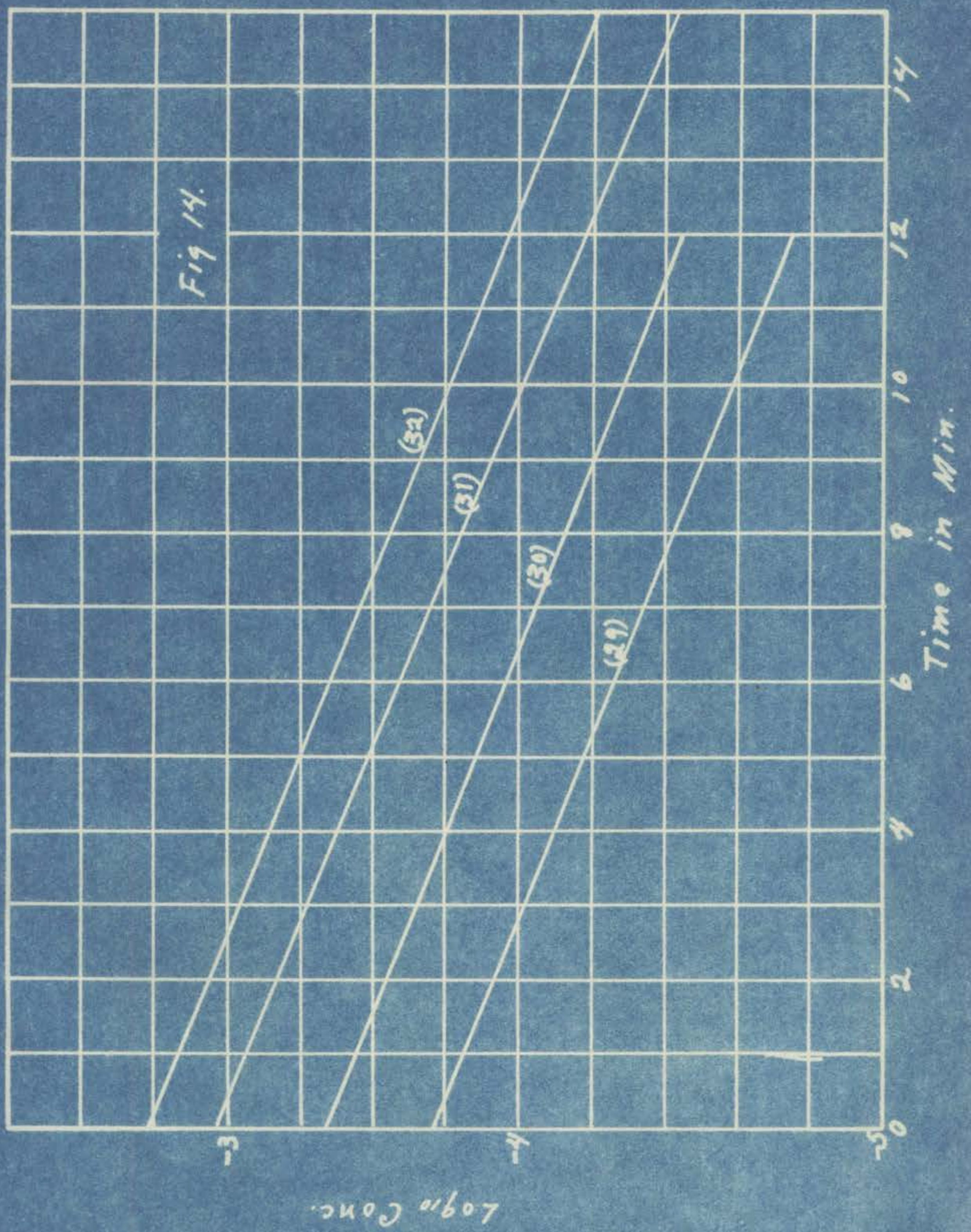


Fig 14.

Permanganate Varied 30.0°C

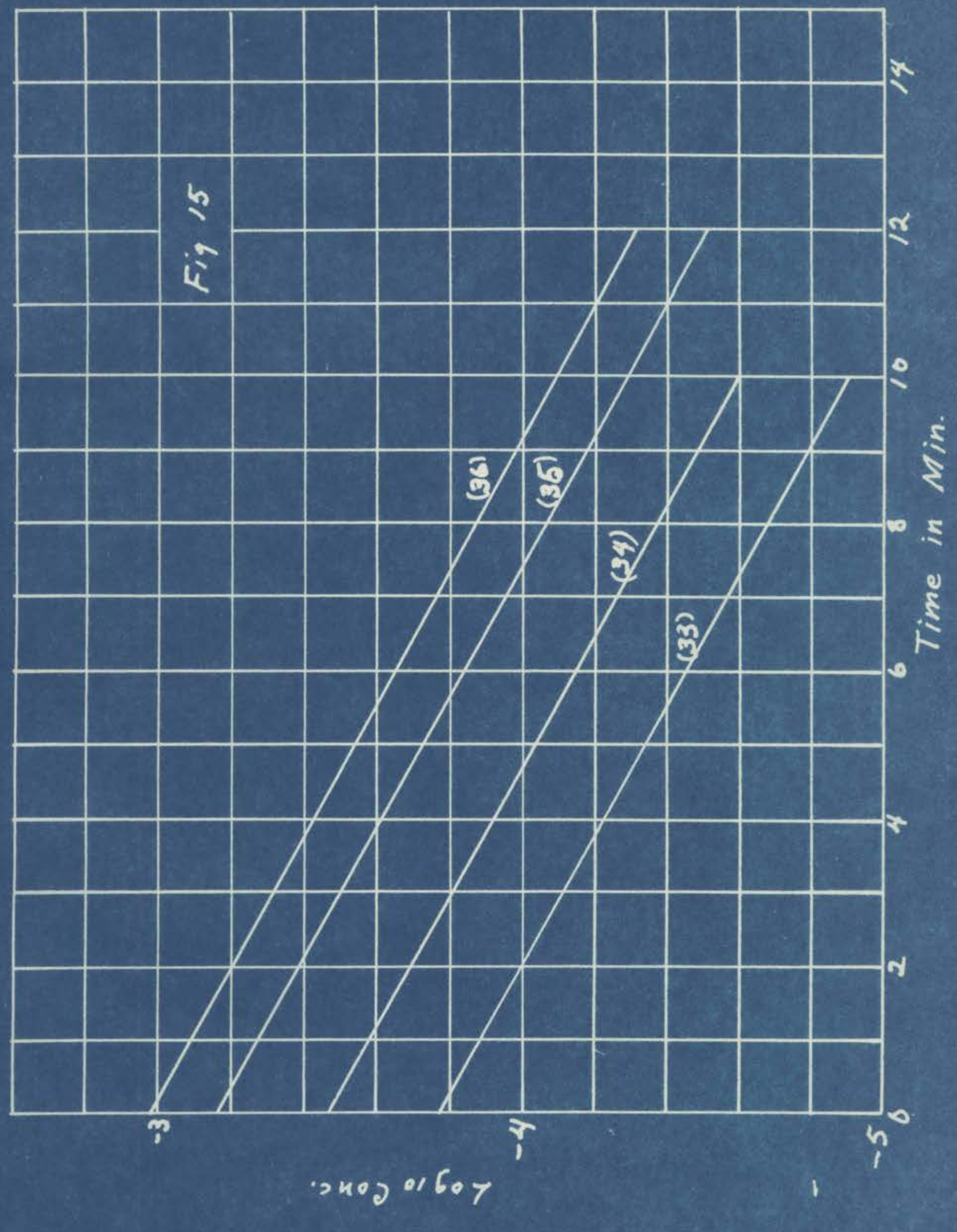


Fig 15

Permanganate Varied 35.0°C

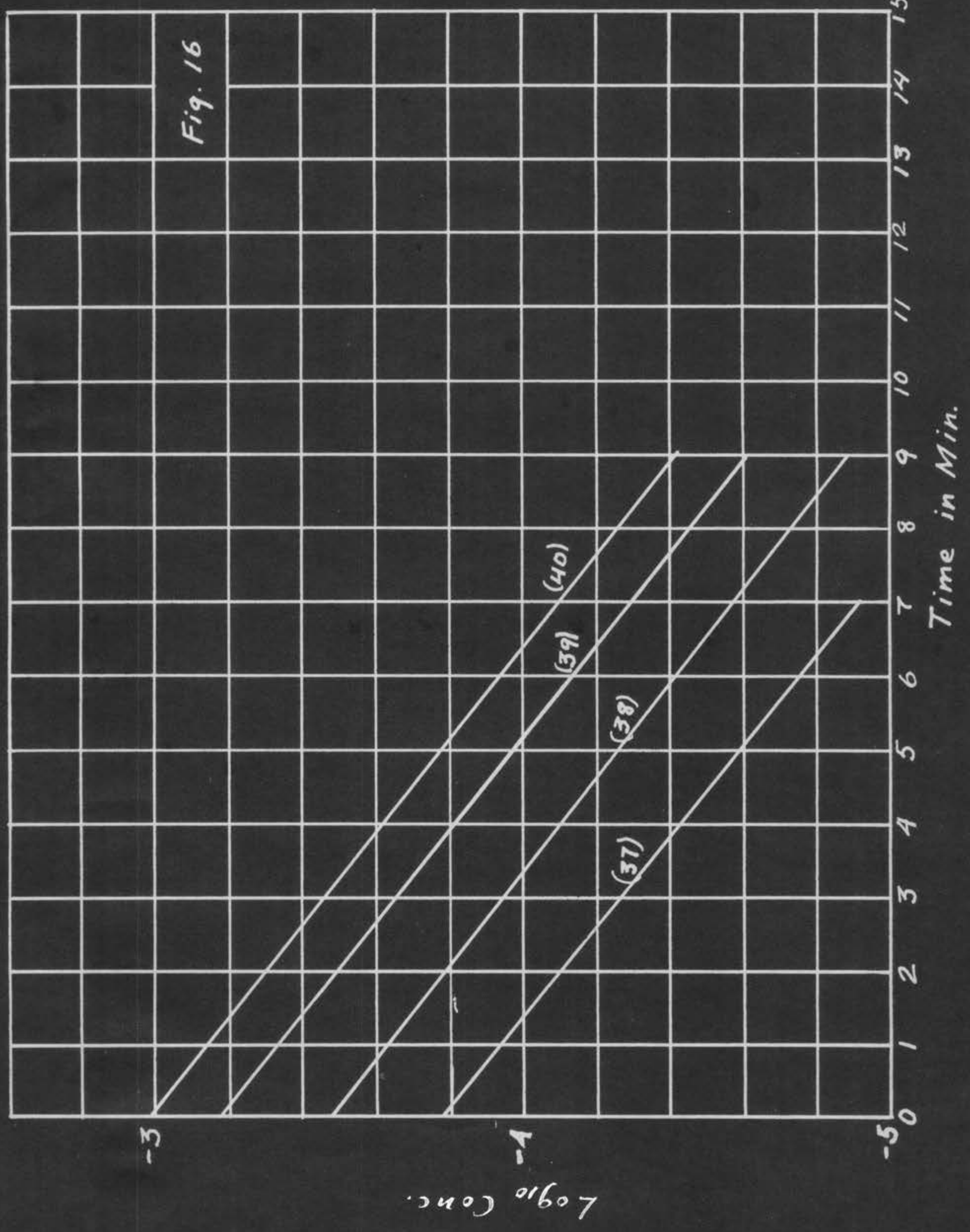


Fig. 16

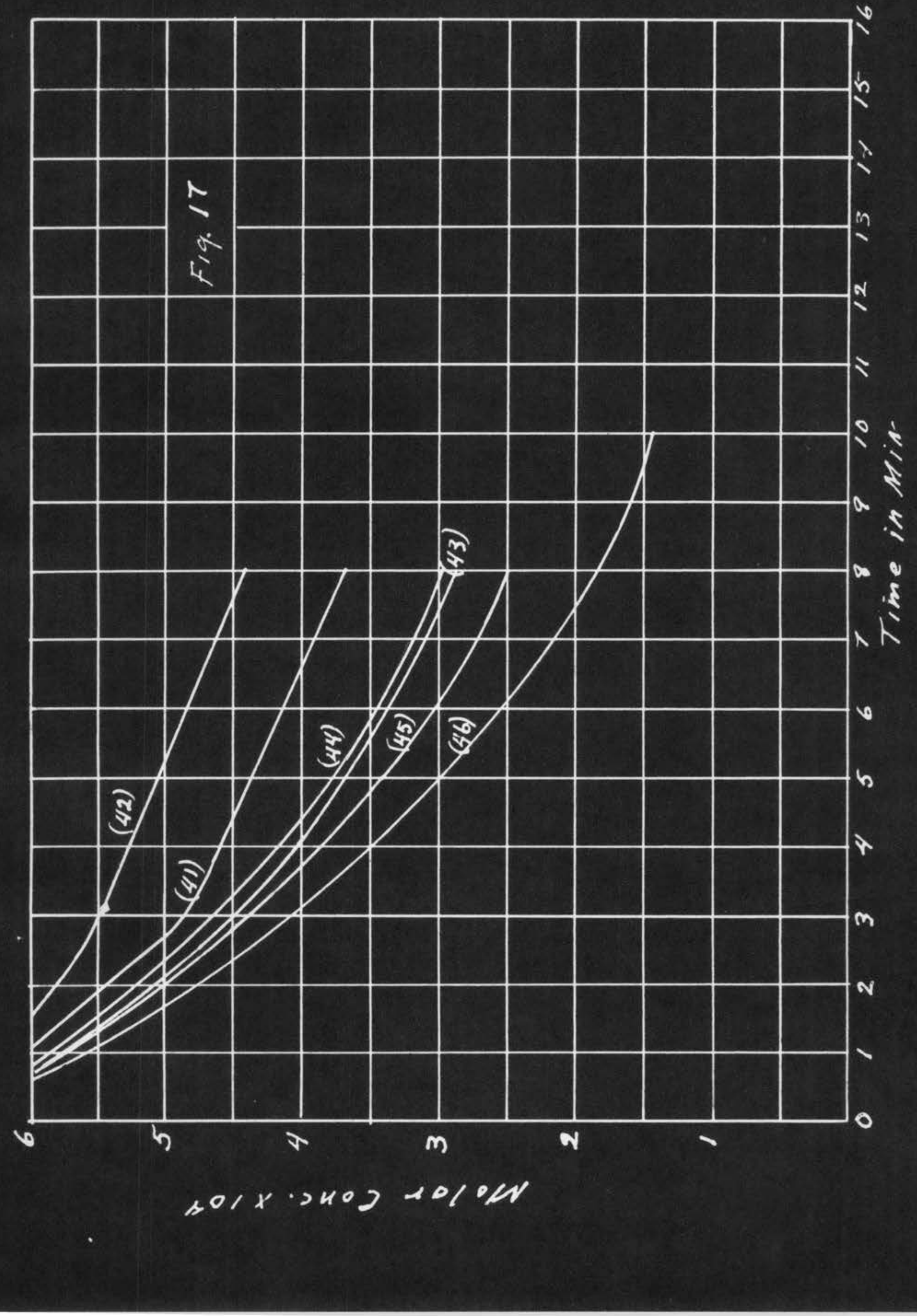


Fig. 17

Molar Conc. x 10⁴
6
5
4
3
2
1
Time in Min.
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
(42)
(41)
(44)
(43)
(45)
(46)

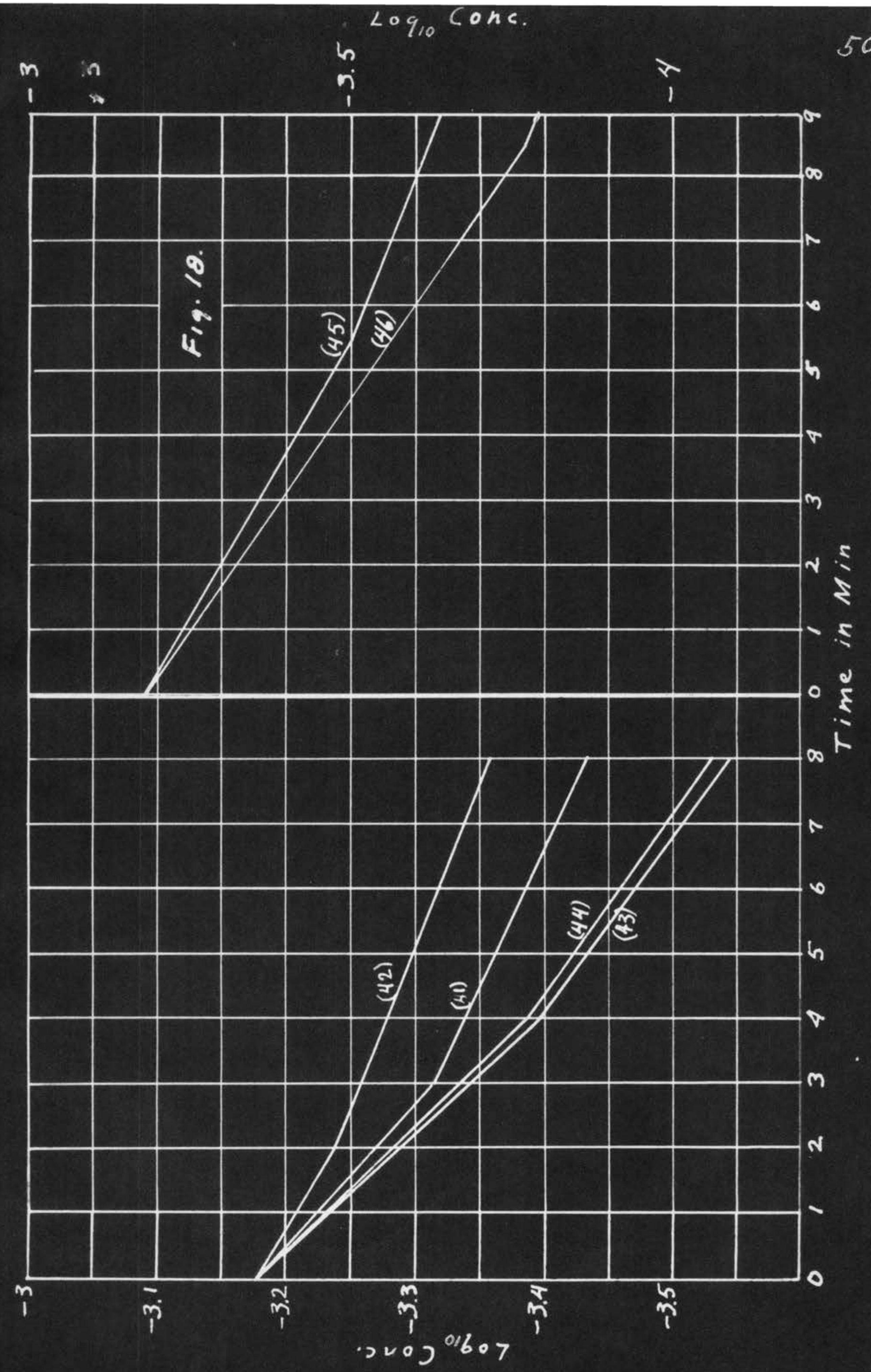


Fig. 18.

Log10 Conc.
-3
-3.5
-4
Log10 Conc.
-3
-3.1
-3.2
-3.3
-3.4
-3.5
Time in Min
0
1
2
3
4
5
6
7
8
0
1
2
3
4
5
6
7
8
9
(41)
(42)
(43)
(44)
(45)
(46)

TABLE 47

Group I 25.0°C

No.	$KMnO_4$	H_2SO_4	Glycol	Rate 1	Rate 2	Break
1	0.00066	0.675	0.0240	.00970	none	none
2	"	"	0.0180	.00670	none	none
#3	"	"	0.0120	.00468	none	none
#4	"	"	0.0060	.00237	.00150	6 min.
#5	"	"	0.0030	.00138	.00076	5 min.
30.0°C						
6	0.60066	0.675	0.0240	.01350	none	none
7	"	"	0.0120	.00930	none	none
8	"	"	0.0120	.00650	none	none
#9	"	"	0.0060	.00337	.00210	3 min.
#10	"	"	0.0030	.00194	.00106	4 min.
35.0°C						
11	0.00066	0.675	0.0180	.01350	none	none
12	"	"	0.0120	.00930	none	none
#13	"	"	0.0060	.00486	.00280	3½ min.
#14	"	"	0.0030	.00270	.00148	2½ min.
Group II 25.0°C						
15	0.00066	0.945	0.0120	.00890	none	none
16	"	0.837	0.0120	.00680	none	none
17	"	0.675	"	.00468	none	none
18	"	0.558	"	.00307	none	none
#19	"	0.419	"	.00173	.00096	9¼ min.
30.0°C						
20	0.00066	0.945	0.0120	.01230	none	none
21	"	0.838	"	.00946	none	none
22	"	0.675	"	.00650	none	none
#23	"	0.558	"	.00422	none	none
#24	"	0.419	"	.00241	.00135	7 min.
35.0°C						
25	0.00066	0.838	0.0120	.01380	none	none
26	"	0.675	0.0120	.00930	none	none
#27	"	0.558	"	.00595	none	none
#28	"	0.419	"	.00345	.00190	5 min.

No.	$KMnO_4$	H_2SO_4	Glycol	Rate 1	Rate 2	Break	$MnSO_4$	KF
			Group III		25.0°C			
29	0.000165	0.558	0.0120	.00290	none	none		
30	0.000330	"	"	.00300	none	none		
31	0.000660	"	"	.00307	none	none		
32	0.000990	"	"	.00288	none	none		
				30.0°C				
33	0.000165	0.558	0.0120	.00435	none	none		
34	0.000330	"	"	.00420	none	none		
35	0.000660	"	"	.00422	none	none		
36	0.000990	"	"	.00399	none	none		
				35.0°C				
37	0.000165	0.558	0.0120	.00610	none	none		
38	0.000330	"	"	.00614	none	none		
39	0.000660	"	"	.00614	none	none		
40	0.000990	"	"	.00615	none	none		
			Group IV		25.0°C			
#41	0.00066	0.675	0.0060	.00176	.000968	3 min.	.0033	0
#42	"	"	"	.00116	.00081	2 min.	.0066	0
#43	"	"	"	.00206	.00144	4 min.	.00165	0
			Group V		25.0°C			
#44	0.00066	0.675	0.0060	.00200	.00140	4 min.	.0033	.0065
#45	"	"	"	.00224	.00152	3½ min.	"	.0130
#46	"	"	"	.00272	.00190	3½ min.	"	.0260

TABLE 48

ENERGY OF ACTIVATION

This is shown on graph 19a page 58

Reaction No.	Energy of Activation
(a) 1 and 6	11810 calories
(b) 2, 7 and 11	12120 "
(c) 3, 7 and 12	12480 "
(e) 4, 9 and 13	13050 "
(g) 5, 10 and 14	12200 "
(b) 15 and 20	12860 "
(c) 16, 21 and 25	12480 "
(d) 17, 22 and 26	12030 "
(f) 18, 23 and 27	12550 "
(d) 19, 24 and 28	13520 "
(d) 29, 33 and 37	13020 "
(d) 30, 34 and 38	12630 "
(d) 31, 35 and 39	13790 "
(d) 32, 36 and 40	13790 "
Average	12795 "

DISCUSSION AND CONCLUSIONS.

In studies of kinetics reactions of the first order are found to be common, reactions of the second order numerous, reactions of the third order rare and reactions of higher orders are not found. Most reactions do not follow any of the simple formulas, and are not simple first or second or third order reactions. Frequently a reaction will follow one order of reaction at first and then will gradually change to a reaction of another order. Among the various complications are counter reactions, side reactions and consecutive reactions.

If the reaction is of the first order, the graph obtained when the $\log_{10}$ of the concentration is plotted against time is a straight line. It was found that when $\log_{10}$ of the concentration was plotted against time for these reactions that they were all of the first order. This may be seen to be true from Figs. 9, 10, 11, 12, 12a, 14, 15 and 16. However, it will be noticed that in some of the reactions there is a break in the straight line. This break indicates that there is a change in the reaction rate. These breaks were found to occur in reactions where the concentrations of the glycol and acid were lowest, the concentration of the glycol being 0.003 molar and 0.006 molar, respectively, and 0.4188 molar in the case of the acid. This break may possibly be due to the fact that glycol has undergone one stage in oxidation and that a new oxidation stage is setting in. It was noticed that in the neighborhood of these breaks there was a color change from purple to pink. It will be recalled that

Launer and Yost obtained a change in color such as this when they oxidized oxalic acid with potassium permanganate in the presence of sulfuric acid.

Referring to Table 47, it is seen that, in group I, which has to do with the variation of glycol while the concentrations of acid and permanganate were held constant, the rate of the reaction doubled when the temperature was increased from 25° to 35°. It was multiplied by 1.4 when the temperature was increased from 25° to 30°. The rate was also doubled when the concentration of the glycol was doubled.

In group II the concentration of the potassium permanganate and glycol was held constant and the concentration of sulfuric acid varied. When the concentration of the acid was doubled the reaction rate was quadrupled. When the temperature was increased from 25° to 30° C. the rate was multiplied by 1.4, and when the temperature was increased from 25° to 35° the rate was multiplied by 2.

Group III shows the results obtained when the concentrations of potassium permanganate were varied and the concentrations of the glycol and acid were held constant. It was found that the reaction rate was not influenced by the change in concentration of the permanganate. However, it was found that the temperature coefficient was the same as found in the cases where the concentrations of acid and of glycol, respectively, were varied.

These results seem to indicate that the reaction rate may be expressed by the equation:

$$\frac{dc}{dt} = K(\text{Glycol}) \quad (H_2SO_4)^2$$

The oxidizing agent, whatever it may be, is apparently present at all times in constant amount; for the rate is independent of its concentration.

Reaction rates may be found, if the reaction is of the first order, by plotting $\log_{10} C$ against time, taking the slope and multiplying by 2.303. They may also be found by substituting in the equation

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \qquad (1)$$

Both methods were used and the values agreed very closely.

According to present theories, it is necessary for molecules to become activated before they can react. If all molecules were equally active, it would be difficult to account for slow reactions. Reacting molecules must absorb definite quantities of energy to become active. The energy of activation is, then, the quantity of energy that must be absorbed before reaction can take place. The energies of activation were calculated from the reaction rates with the aid of equation

$$\log_{10} \frac{k_2}{k_1} = \frac{E\ (T_2 - T_1)}{2.303\ R\ \ T_2\ T_1} \qquad (2)$$

where k_2 and k_1 are the reaction rates at the temperatures

T_2 and T_1, E the energy of activation, and R the gas constant.

Figure 19a shows the straight line plots of the same slope when $\log_{10}$ K, the reaction rate, was plotted against 1/T where T is the absolute temperature. The slopes of these curves when multiplied by 2.303 also give the energy of activation. The average value by both methods is 12795calories. This seems to show that all reactions studied were of the same essential nature.

Figure 19b shows essentially the same thing as does Figure 19a. In Figure 19b the slopes of the lines are the same as in Figure 19a. This shows that the energy of activation of the reaction going forward after the occurrence of the break is the same as before the break. Calculation by equation 2 also shows this to be true.

Set IV shows the effect of adding $MnSO_4$ to the reaction mixture. When this was done, the reaction rate decreased when compared to corresponding reactions when the $MnSO_4$ was absent. This seems to show that the trivalent Mn ion is not active in this particular reaction, for addition of Mn^{++} should promote its formation. When a solution of KF was added to a mixture containing glycol, permanganate, acid, and $MnSO_4$ corresponding to the above reaction, the rate was increased though still not to that which was found in the absence of both salts. The addition of KF to the reaction seems to undo to some extent the effect of added $MnSO_4$. Further experiments are necessary before these data can be interpreted. These effects are shown graphically in Figures 17 and 18 as well as in the tabulated results.

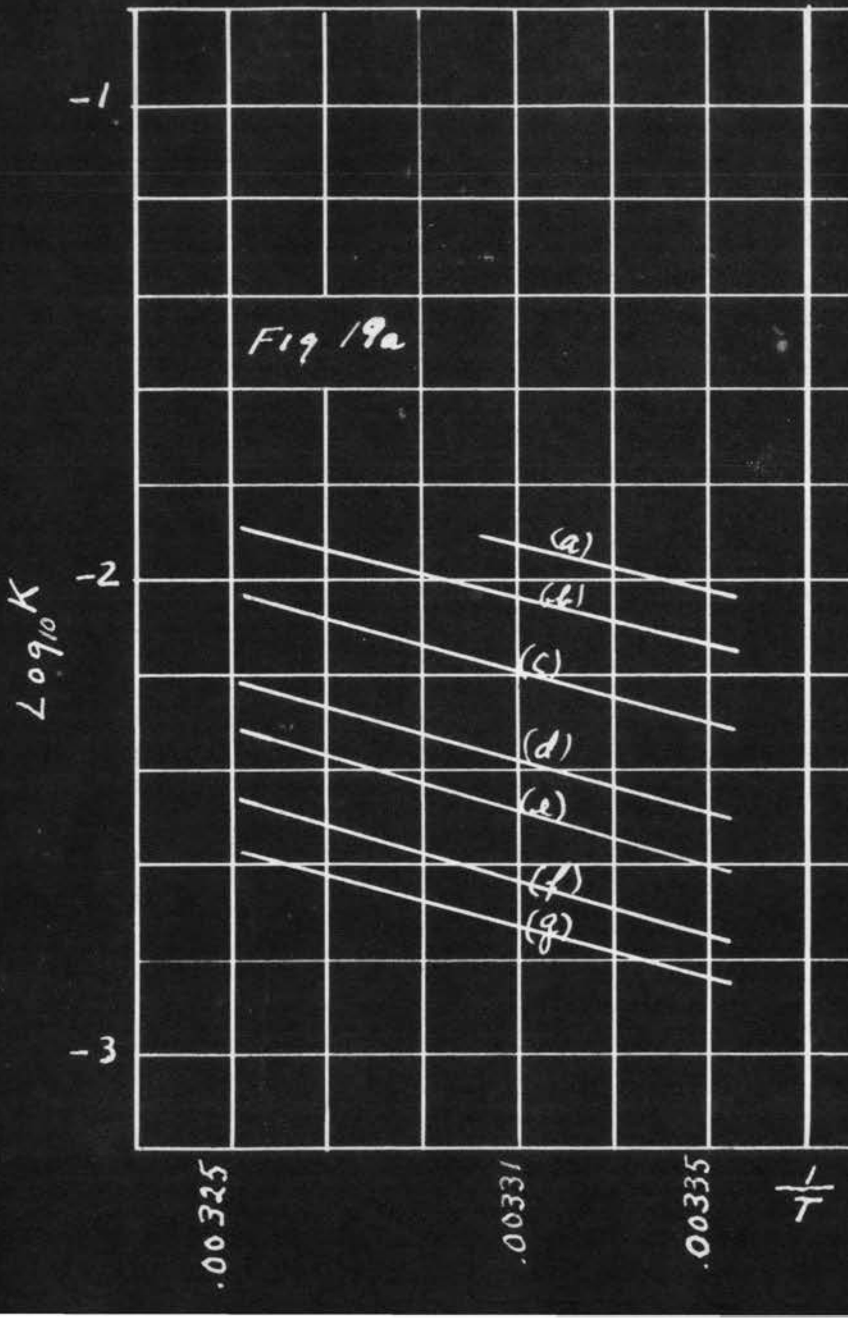


Fig 19a

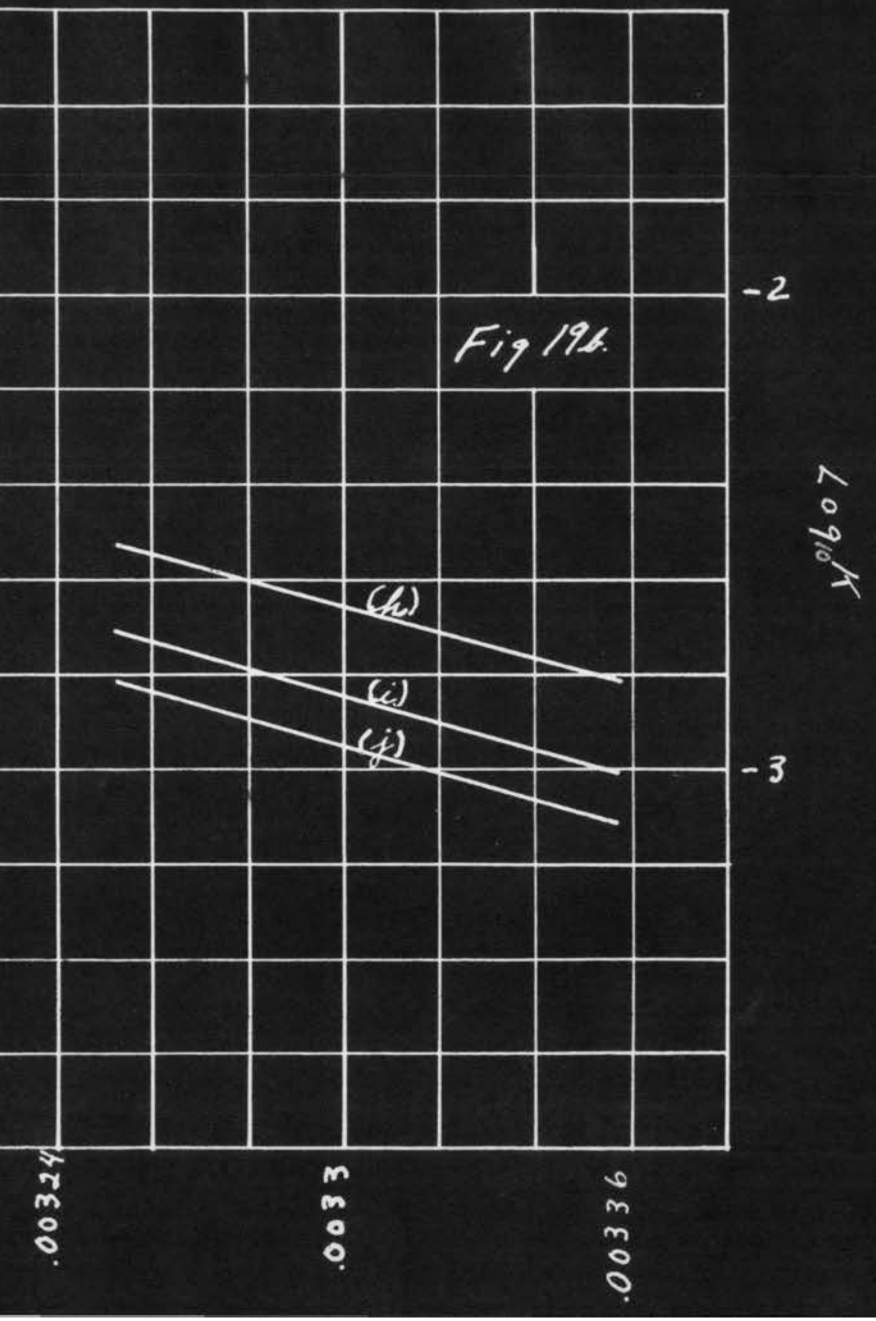


Fig 19b

SUMMARY

It has been found that the reaction between glycol and potassium permanganate in the presence of sulfuric acid is a first order reaction. The reaction rates were calculated and it was found that when the concentration of the glycol is doubled, the reaction rate is doubled. When the concentration of the acid is doubled, the rate is quadrupled. The rate is independent of the concentration of potassium permanganate. This seems to indicate that the rate of the reaction is expressible by the differential equation

$$\frac{dc}{dt} = K(\text{Glycol})\,(H_2SO_4)^2$$

It was found that when there is a 10^0 C rise in temperature, the rate is doubled. In some of the reactions where the concentration of the glycol or acid was the lowest, the reaction went forward at one rate but changed to a slower rate only 0.6 times as fast. The energy of activation was calculated and found to be 12,795 ± 452 calories. This seems to indicate that essentially the same reaction occurs in all the cases studied. Addition of $MnSO_4$ decreases the rate of oxidation, contrary to what would be expected if Mn^{+++} is the oxidizing agent. Addition of KF in the presence of $MnSO_4$ causes an increase in the rate of reaction, though it is still slower than in the absence of these salts. Our experiments are too few to permit the drawing of any conclusions as to the actual mechanism of the reaction.

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I, William A. Weaverling, was born at Cambridge, Kansas, August 11, 1912, and I attended the grade schools and graduated from the Burden, Kansas, High School in May 1930. I entered the Central Missouri State Teachers College, Warrensburg, Mo., in September 1930, and graduated May 1934, receiving the Degree of Bachelor of Arts in Mathematics, and the Degree of Bachelor of Science in Physics.

I taught Mathematics and Physics in the Creighton, Missouri, High School from September 1934 to May 1937.

I entered the Graduate School of Oklahoma Agricultural and Mechanical College in June 1937. The requirements for the Degree of Master of Science will be completed in May 1938.