

A STUDY OF PROMOTER ACTION. THE OXIDATION
OF ANILINE SULFATE BY HOT SULFURIC ACID IN THE PRESENCE
OF COPPER AND MERCURY SULFATES

BY

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1. Introduction

Oxidation by hot sulfuric acid finds important application in the Kjeldahl method for the determination of nitrogen in organic compounds, and has until recently, been used to prepare phthalic acid from naphthalene. In both reactions mercury and copper sulfates act as catalyzers to promote destructive oxidation by sulfuric acid.

Kjeldahl published his method in 1883.¹ Since that time it has been the subject of many investigations which sought to prescribe empirical methods for the determination of nitrogen in various types of compounds.² The only study of the kinetics of the reaction, and a determination of the relation between catalytic effect and amount of catalyst present was that by Bredig and Brown.^{3,4} They determined the rate of oxidation of aniline sulfate, and of naphthalene, by hot sulfuric acid in the presence of metal sulfates.

An interesting result of their work was the discovery that when mercury and copper sulfates are used together as a catalyst, the catalytic effect is greater than can be accounted for on the assumption that each metal is acting independently. This enhanced catalytic activity, now called "promoter action", had previously been noted in a qualitative way by Arnold.⁵

Aside from its practical importance in the Kjeldahl method, this fact is of interest as a case of promoter action in homogeneous catalysis.

Bredig and Brown^{3,4} give only one set of data in which copper and mercury sulfates were used together as catalysts. Therefore it is impossible to state from their work: 1) the optimum concentration of mixed catalyst; 2) what relation exists between the composition of the mixed catalyst and the promoter effect; 3) the mechanism of the promoter action.

The purpose of this investigation was to extend the study of the catalytic effect of mixtures of copper and mercury sulfates in order that these points may be settled. The desirability of such measurements is mentioned by Rideal and Taylor.⁶

2. Previous Data

The results of the study by Bredig and Brown which are pertinent to this investigation are:

1. The reaction between sulfuric acid and aniline sulfate proceeds according to the equation:



2. The reaction obeys the first-order law.

3. The reaction is catalyzed by mercury and copper sulfates. Iron, nickel, and magnesium show only a slight catalytic effect; all other metals show no catalytic effect.

4. The effect of copper and mercury together is greater than the sum of their individual effects.

5. The catalytic effect of mercury is proportional to its concentration.⁷

6. The volume of gas formed is that required by the preceding equation, and is a true measure of the reaction rate. Mercury may be introduced as mercurous or mercuric oxide or sulfate without affecting the measured rate of oxidation.

7. The presence of a small amount of water does not affect the rate of oxidation.

3. Experimental Method

The method of studying the reaction rate was the same as that described by Bredig and Brown^{3,4}. It consisted in adding a weighed quantity of aniline sulfate to a volume of sulfuric acid at 275 degrees, and measuring at definite time intervals the volume of gas evolved.

MATERIALS USED. Mercuric oxide was prepared by adding a calculated amount of sodium hydroxide to a solution of C. P. mercuric chloride heated to 70 degrees. The precipitated red mercuric oxide was washed free of alkali and chlorides and dried at 100 degrees.⁸

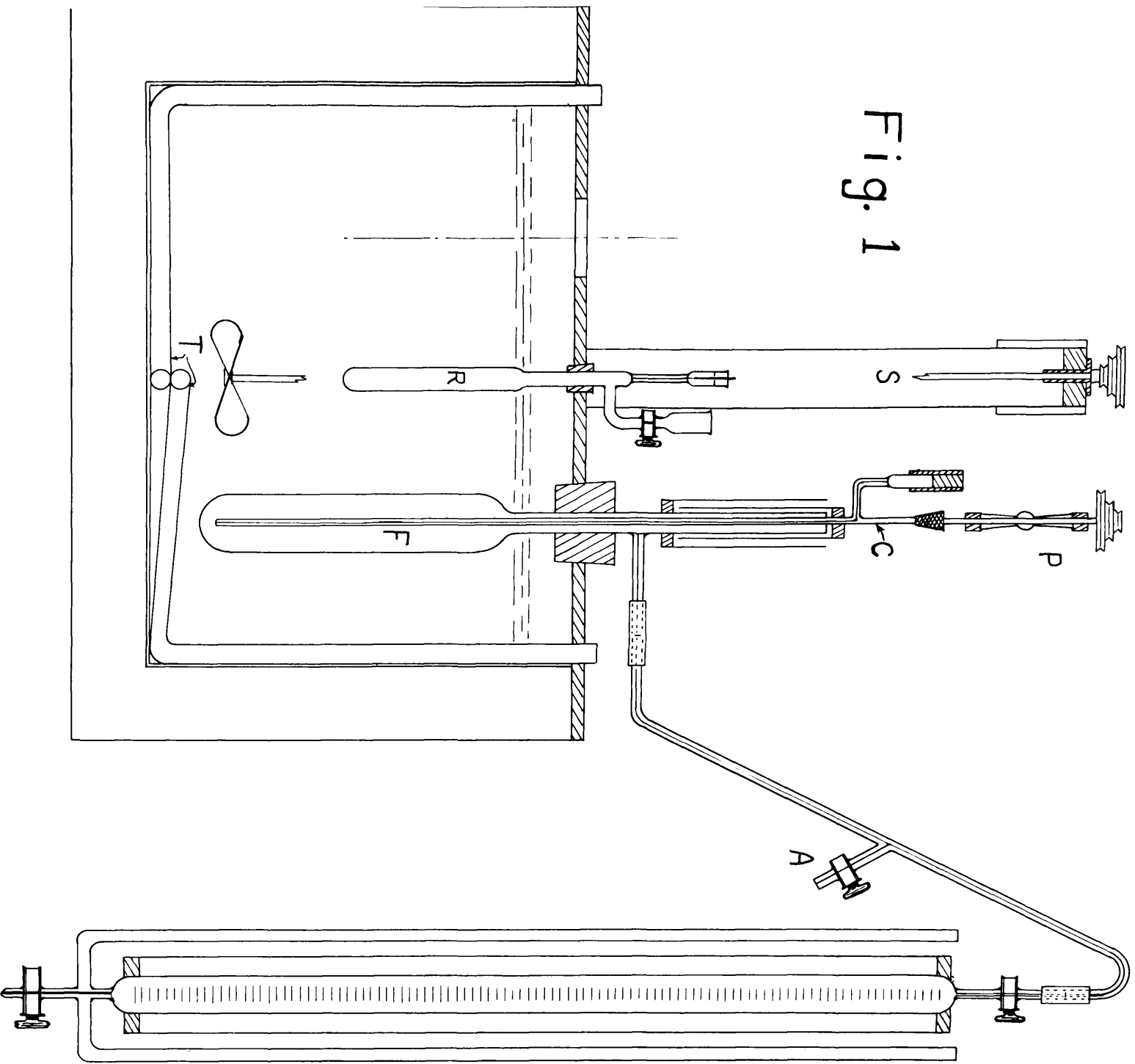
Copper sulfate used was the C. P. pentahydrate from a reliable source.

Sulfuric acid used was C. P. Reagent quality (specific gravity 1.83-1.84) and was free from any appreciable amount of heavy metals.

Aniline sulfate was the best grade furnished by the Eastman Kodak Company. Analysis by the Kjeldahl method gave 9.77% Nitrogen as compared to 9.86% for $(C_6H_5NH_2)_2 \cdot H_2SO_4$.

APPARATUS. The apparatus used was similar to that described by Bredig and Brown^{3,4}. One improvement was the use of an electric instead of a gas heater for the paraffin bath.

The apparatus is shown in the accompanying Figure 1.



The bath was made from a welded iron box fifteen inches square and twelve inches deep fitted with an asbestos covered lid held in place by anchor bolts. This iron box was placed in a wooden box and insulated from it on the bottom and sides by two inches of glass wool which served as an excellent insulator.

Ordinary paraffin (M.P. about 65 degrees) was used as the bath liquid. While it served the purpose well, paraffin is not the most desirable material for use above temperatures of 250 degrees. At 275 degrees, the wax distills slowly from the bath. For this reason paraffin must be added from time to time, and the thermostat must be placed so that the fumes may be exhausted from the room. At the higher temperature also, thermal decomposition sets in. One result of this is that the heating coil tubes become coated with carbon which finally results in their being broken.

The bath was heated by two coils of No. 24 nichrome wire; each coil containing 18 feet of wire with a resistance of about twenty-seven ohms. The source of current was at 110 volts. These coils were placed in two pyrex glass tubes, T, which were placed down the corners and diagonally across the bath.

One coil was used as a continuous heater and was sufficient to hold the bath near 275 degrees. The other was an intermittent heater and was operated through the mercury

regulator, R, shown in the diagram and through a relay not shown. Both coils were connected to the source of power through an auxiliary variable resistance (not shown) which permitted the bath to be adjusted to high, low and medium heat.

The bath liquid was stirred by the pulley and shaft arrangement, S. The stirrer ran at about 400 revolutions per minute.

Two-inch holes were drilled at the centers of the four quarters of the lid of the iron box. Through these holes the reaction flasks were inserted and held in the bath.

The reaction flasks, F, were made from 28 mm. i.d. Pyrex tubing and held about 75 cc. The flask was held in place in the bath by means of the large cork stopper which was put in place before the capillary side-arm was sealed on.

The reaction flask was fitted with a capillary tube, C, having a side-arm. This served both as a stirrer and as a means of introducing the sample of aniline sulfate solution. The side-arm of the capillary was closed by a glass-plugged tight-fitting piece of rubber tubing. The stirrer was rotated at 120 revolutions per minute by means of the pulley system, P, which was supported by a ring-stand

post bolted in the lid of the bath.

The flasks were closed with an ordinary mercury seal.

The gas collecting burettes were the ordinary water-jacketed type reading to 0.20 cc. The gas was collected over mercury which was allowed to run from the burette as the volume increased. As an aid in reading the burette and in adjusting the mercury level to one atmosphere, it was fitted with the two side-arms as shown.

The gas burette was connected to the reaction flask by capillary tubing. The stop-cock, A, was used in introducing the sample whenever a slight suction was required to start the flow down the capillary tube into the flask.

The bath temperature was measured with a 360 degree thermometer which had an error of -1.5 degrees at 275 degrees for which it was corrected. The temperature regulation of the bath was unusually good, and was constant within \pm 0.10 degree.

METHOD OF PROCEDURE. Quantities of the catalyst (mercuric oxide or copper sulfate pentahydrate) were weighed out and introduced into the reaction flask through a long-stem funnel. Fifty cubic centimeters of sulfuric acid were then introduced through the funnel; this served to rinse the catalyst into the flask. The stirrer and mercury seal were then put in place and the flask fitted into the bath. The

mixture was stirred for one hour. This was sufficient time for the catalyst to dissolve and for the mixture to come to temperature.

The stirrer was then stopped for a short time while the sample was introduced. This was done by adding a weighed amount of a standard solution of aniline sulfate in sulfuric acid from a weight burette to the well of the side-arm of the capillary stirrer; the stop-cock, A, being closed. The stop-cock, A, was then opened, and the solution allowed to run into the reaction mixture. Sometimes a very slight suction applied at A, was required to start the flow down the tube. The sample was followed immediately by 1-1.5 cc. of concentrated sulfuric acid to rinse the solution into the flask. The stirrer was started, stop-cock, A, was closed, and, the initial time noted. After some practice, the successive steps in this operation could be done very quickly. Great care had to be exercised to prevent air from being drawn into the system when the sample was introduced.

The system was kept constantly at one atmosphere pressure by allowing mercury to run from the burette as the gas collected. The side-arms of the burette were very convenient in this operation.

4. The Data and Calculations

The data recorded in this investigation were:

1) the weight of standard aniline sulfate solution introduced into the reaction mixture; 2) the volume of gas at 0, 5, 10, 15, 25, 45, 90, (minutes for mixed catalysts) 120, 150, 180, (minutes for single catalysts), 240, 360 minutes for zero catalyst concentration; 3) the temperature and pressure of the collected gas.

The standard aniline sulfate solution in sulfuric acid was an approximately 8 percent solution by weight. The weight of aniline sulfate introduced varied from 0.0500-0.0900 grams. For comparison, the data from each determination was calculated by direct proportion to the volume of gas which would have been given off by 0.0500 grams of the salt. This calculation is valid since Bredig and Brown showed that the volume of gas which results is directly proportional to the amount of aniline sulfate present. All volumes were corrected to standard conditions. The data so treated is found in the tables below under the column giving the number of the determination.

For an individual experiment these determinations were averaged and recorded as "average". These average values were then plotted on a large scale and the best smooth curve was drawn through the points. In a few cases this curve

did not pass through the origin, but had an intercept on the volume axis of from one to two cubic centimeters. In such cases the curves were corrected to pass through the origin.

From this corrected curve in each experiment, the volumes at the recorded times were read, and the values obtained are recorded as "Corrected from Curve". These values are taken as the best averages of the volume readings recorded in each experiment. The curve had to be corrected through the origin in some instances to correct for any small volume of air which may have been drawn into the reaction flask with the sample of aniline sulfate.

The equation for the reaction given above shows that twenty-nine molecules are involved. Hence, it is of interest to calculate the reaction velocity constant and to determine the order of the reaction. The reaction mixture contained three molecular species, but only the aniline sulfate changed in concentration as the reaction proceeded. The sulfuric acid was present in large excess and changed but little in concentration; the metal salts act as true catalysts and are not used up in the reaction.

In view of these facts, the equations for the reaction velocity having terms representing the concentration of sulfuric acid, (b), and of metal salt, (c), all reduce to the expression for the mono-molecular rate, with these

concentration terms embodied in the calculated constant.⁹

Thus,

$$(K''b) = K' = \frac{1}{t} \ln \frac{a}{(a-x)}, \text{ and}$$

$$(K'''b) = K'' = \frac{1}{t} \ln \frac{a}{(a-x)}$$

If the reaction is mono-, di-, or tri-molecular with respect to aniline sulfate, then the following expressions will hold:⁹

$$K' = \frac{1}{t} \ln \frac{a}{(a-x)}$$

$$K'' = \frac{1}{t} \frac{x}{a(a-x)}$$

$$K''' = \frac{1}{t} \frac{1}{2} \frac{1}{(a-x)^2} - \frac{1}{a^2}$$

where, a , is the initial concentration of the aniline sulfate; x , is the amount decomposed at time, t ; $(a-x)$ is the amount left at time, t .

The values obtained for the constants by each equation are more nearly constant for K' , although the values obtained for K'' are almost as constant. A plot of the data using $\log(\text{concentration of aniline sulfate})$ against time gave more nearly a straight line than the corresponding graph of $1/(\text{concentration of aniline sulfate})$ against time. This fact, and the fact that the volume of gas is proportional to the concentration of aniline sulfate is additional evidence that the reaction comes nearer to obeying the mono-molecular law

rather than the di-molecular law. The values for K' are given for each experiment in the tables below. A few typical values for K' are also recorded. Both constants are calculated in moles per liter and the time is expressed in minutes.

Since the logarithm expression in the equation for K' is a ratio, it can be evaluated quickly by using the volumes corresponding to the concentrations. Hence, $a = 156.3$ cc., and $x =$ the volume of gas measured at time, t . The purity of the aniline sulfate as determined by analysis was taken into account in calculating the value of "a".

An important part of the study of this research was to determine the promoter effect in the mixtures of salts used as catalysts. To evaluate the promoter effect, the "promotion factor", B , was calculated using the relation: $B = \frac{V_f}{V_o}$; V_f is the volume of gas at time, t , when a mixture is used as catalyst, and V_o is the volume calculated by adding the volumes obtained when the amount of each metal in the mixture is used alone as a catalyst.

The "promotion factor" calculated from the values of K' is called, B' in the tables below. $B' = \frac{K'_f}{K'_{Cu \text{ alone}} + K'_{Hg \text{ alone}}}$

Although the data gives reaction constants which correspond more nearly to the mono-molecular constant, the values of K' are not sufficiently constant to compare the

reaction rate between experiments without taking some arbitrary mean. This has been done, using the values at 45, 60, and 90 minutes, and the average of these values of K' gives the "average" value recorded in the tables. This allows the results of all the experiments to be compared at comparable times.

The unit weight of catalysts were the molar equivalent quantities: 0.0305 grams of mercuric oxide, and 0.0351 grams of copper sulfate pentahydrate. Multiples of these unit weights were used in the experiments, and are shown after the weight of catalyst in each table. These values are important in studying the relationship between the promoter effect measured by the promotion factor and the composition of the mixed catalyst since they give immediately the mol ratio of copper to mercury in the mixture.

The data calculated as described for each experiment is given in the following tables:

Volume of sulfuric acid50 cc.
Temperature275
Weight of catalyst indicated with each Table.
Volumes in cc. at time, t , in minutes, corrected to
0.0500 grams aniline sulfate and to standard conditions.

TABLE 1
 0.0000 Grams HgO (0)
 0.0000 Grams CuSO₄·5H₂O (0)

t	#270	#271	#272	K x 10 ⁶	K ¹
45	(.4)	-	-	-	-
60	(.8)	-	-	-	-
80	(.8)	-	-	-	-
120	(1.0)	-	1.1	.321	.000556
150	(1.3)	-	1.4	.386	.000583
180	(1.6)	1.6	1.5	.344	.000627
240	2.1	2.1	2.0	.345	.000697
300	2.6	2.6	2.6	.361	.000618
360	3.1	3.3	3.1	.359	.000668

AV. *000556

TABLE 2
 0.0305 G. HgO (1)

t	#40	#41	#42	#44	AV. Corrected	K x 10 ⁶	K ¹
5	2.6	3.5	1.0	1.4	2.1	0.5	-
10	2.9	3.9	1.3	1.6	2.4	1.0	.000846
15	3.6	4.8	1.7	2.2	3.1	1.5	.000614
25	4.8	5.7	2.5	3.1	4.0	2.4	.000598
45	6.9	7.7	4.4	5.3	6.1	4.5	.000665
60	8.4	9.3	6.1	7.1	7.7	6.1	.000660
80	11.8	12.8	8.6	11.0	11.3	8.4	.000682
120	15.0	16.1	13.0	14.8	14.7	13.1	.000729
180	21.0	22.4	20.3	22.9	21.7	20.6	.000797

From curve

AV. *000672

TABLE 3
 .0810 E. H₂O (2)

t	#48	#48	Average	Corrected from curve	K ₁
5	1.8	1.8	1.7	0.8	.00680
10	1.8	2.3	2.1	1.1	.00690
15	3.4	2.8	3.1	1.8	.00768
25	-	4.1	4.1	3.1	.00811
45	6.6	7.4	7.0	6.2	.00885
60	9.2	10.5	9.8	8.8	.00968
90	15.2	16.7	15.5	14.5	.0109
120	20.8	21.1	21.0	20.2	.0119
150	27.6	26.2	26.9	25.9	.0121
180	32.9	31.4	32.1	31.6	.0125

TABLE 4

.1220 E. H₂O (4)

t	#49	50	51	Average	Corrected from curve	K ₁ x 10 ⁶
5	1.8	1.6	1.4	1.6	0.9	.00927
10	2.3	2.3	2.1	2.3	1.8	.0115
15	3.2	3.0	3.0	3.0	2.8	.0123
25	5.4	5.6	5.0	5.3	4.8	.0124
45	8.9	9.8	9.7	9.4	9.2	.0135
60	13.4	13.9	13.6	13.6	12.8	.0143
90	23.2	22.2	21.4	22.3	21.8	.0167
120	31.3	29.6	28.9	29.9	29.5	.0174
150	38.6	36.1	35.3	35.1	36.1	.0175
180	44.3	42.8	41.0	41.9	42.3	.0175

AV.

*009769
 '00155

TABLE 5
 .2440 g. HgO (8)

t	#56	#58	#60	#62	#66	#72	Av.	Corr. from curve	K ¹
5	1.5	-	2.0	1.2	1.4	1.2	1.6	0.8	.001060
10	2.5	2.8	3.1	1.9	2.5	2.3	2.5	1.7	.001038
15	3.5	3.1	4.7	2.5	3.6	3.5	3.5	2.7	.001151
25	6.8	6.1	8.3	4.9	6.7	6.5	6.5	5.7	.001475
45	14.5	12.8	15.9	10.9	14.3	13.7	13.7	12.9	.001920
60	20.7	18.1	22.2	15.9	21.0	19.9	19.6	18.8	.002135
90	32.0	28.1	33.3	23.0	33.3	30.5	30.0	29.2	.002308
120	39.3	38.8	42.6	37.0	44.0	39.8	40.3	39.5	.002430
150	50.3	46.4	50.7	45.5	52.0	47.3	48.7	47.9	.002448
								Av.	.00212

TABLE 6
 .0351 g. CuSO₄.5H₂O (1)

t	#57	#59	#61	#65	Average	Corrected from curve	K ¹	
5	-	1.4	1.0	.70	1.0	0.2	.000230	
10	-	1.9	1.6	1.0	1.5	0.6	.000392	
15	-	2.4	2.0	1.4	1.9	1.0	.000492	
25	-	3.5	3.3	2.3	3.0	2.0	.000543	
45	4.9	6.0	5.9	4.7	5.4	4.7	.000676	
60	7.0	8.3	9.0	6.7	7.8	7.1	.000775	
90	11.8	12.7	12.3	11.4	12.0	11.5	.000855	
120	-	17.8	16.7	15.7	16.8	15.9	.000897	
150	21.2	21.9	21.0	20.1	21.0	20.1	.000919	
180	25.4	26.0	24.5	23.9	24.9	23.9	.000924	
							Av.	.000769

TABLE 7
 .0702 S. CUSO₄·5H₂O (2)

z	#90	#100	#101	Average	Corrected From curve	K x 10 ⁶	K ¹
8	-	1.0	0.6	0.8	0.6	-	.000641
10	-	1.7	1.4	1.5	1.2	-	.000784
15	-	2.2	2.1	2.1	1.8	-	.000768
25	-	3.8	3.6	2.7	3.4	5.67	.000675
45	7.3	7.6	8.0	7.8	7.2	6.80	.001074
60	9.9	10.9	10.8	10.8	10.5	7.70	.001154
90	15.6	16.8	17.7	17.2	16.9	8.60	.001333
120	21.1	22.6	22.4	22.4	22.7	8.34	.001313
150	-	28.0	28.4	28.0	27.7	9.18	.001300
180	31.1	32.1	32.8	32.0	31.7	9.03	.001266

AV. #00118

TABLE 8

.1404 S. CUSO₄·5H₂O (4)

z	#67	#69	#95	Average	Corrected From curve	K ¹
8	1.7	1.6	1.6	1.6	0.7	.000816
10	2.6	2.1	2.2	2.3	1.4	.000812
15	3.5	2.8	3.0	3.1	2.5	.001075
25	5.3	4.7	4.7	4.9	4.2	.001088
45	9.9	8.8	9.2	9.3	8.5	.001255
60	13.3	12.5	12.8	12.8	12.3	.001375
90	20.7	20.8	20.8	20.6	19.7	.001498
120	27.0	27.3	27.6	27.3	26.4	.001540
150	32.0	33.8	33.8	33.8	32.7	.001565
180	37.2	39.6	-	38.4	38.5	.001875

AV. #00137

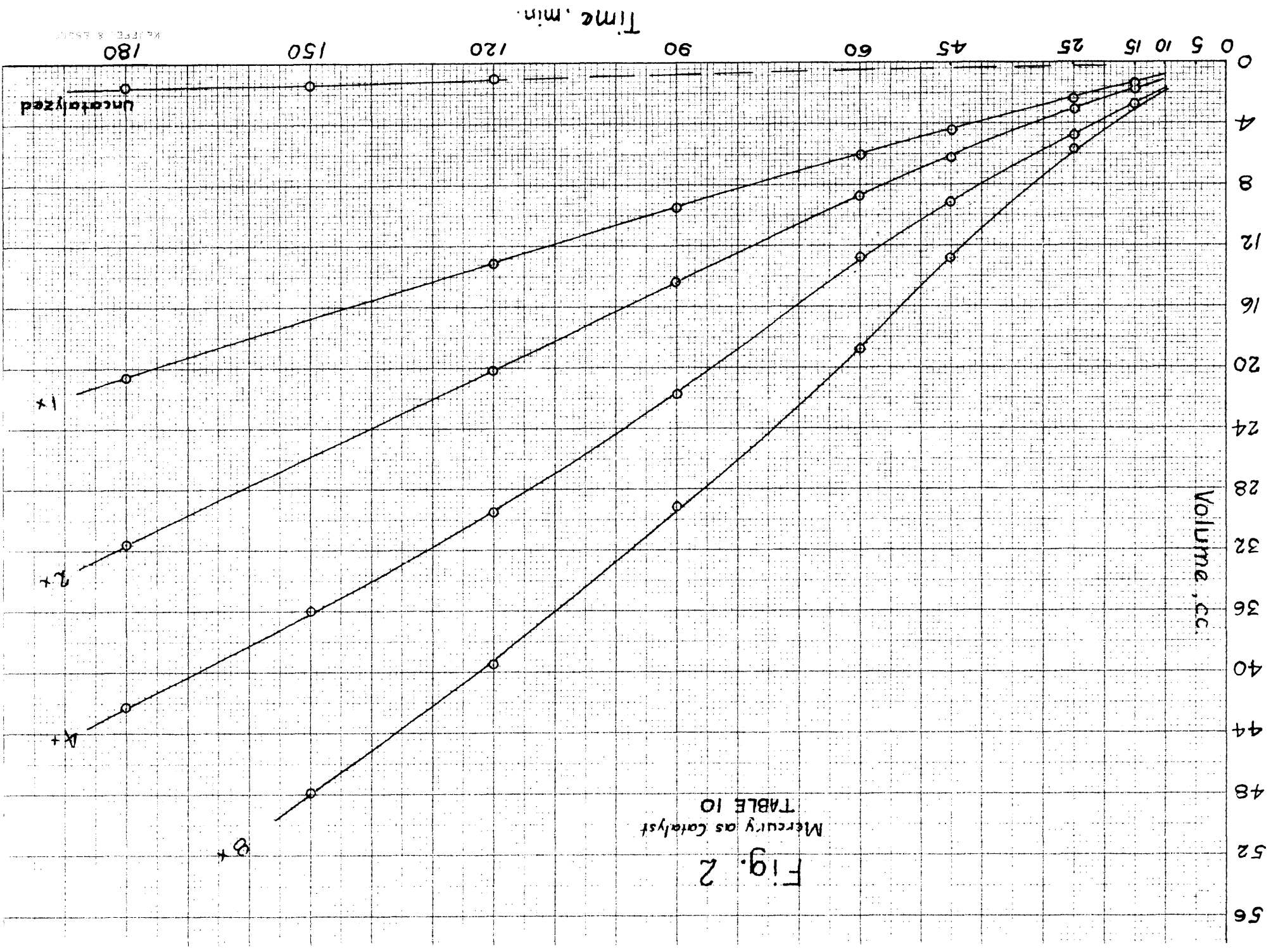


Fig. 2
Mercury as Catalyst
TABLE 10

KAUFER & BROWN

Fig. 3

Copper as Catalyst
TABLE 10

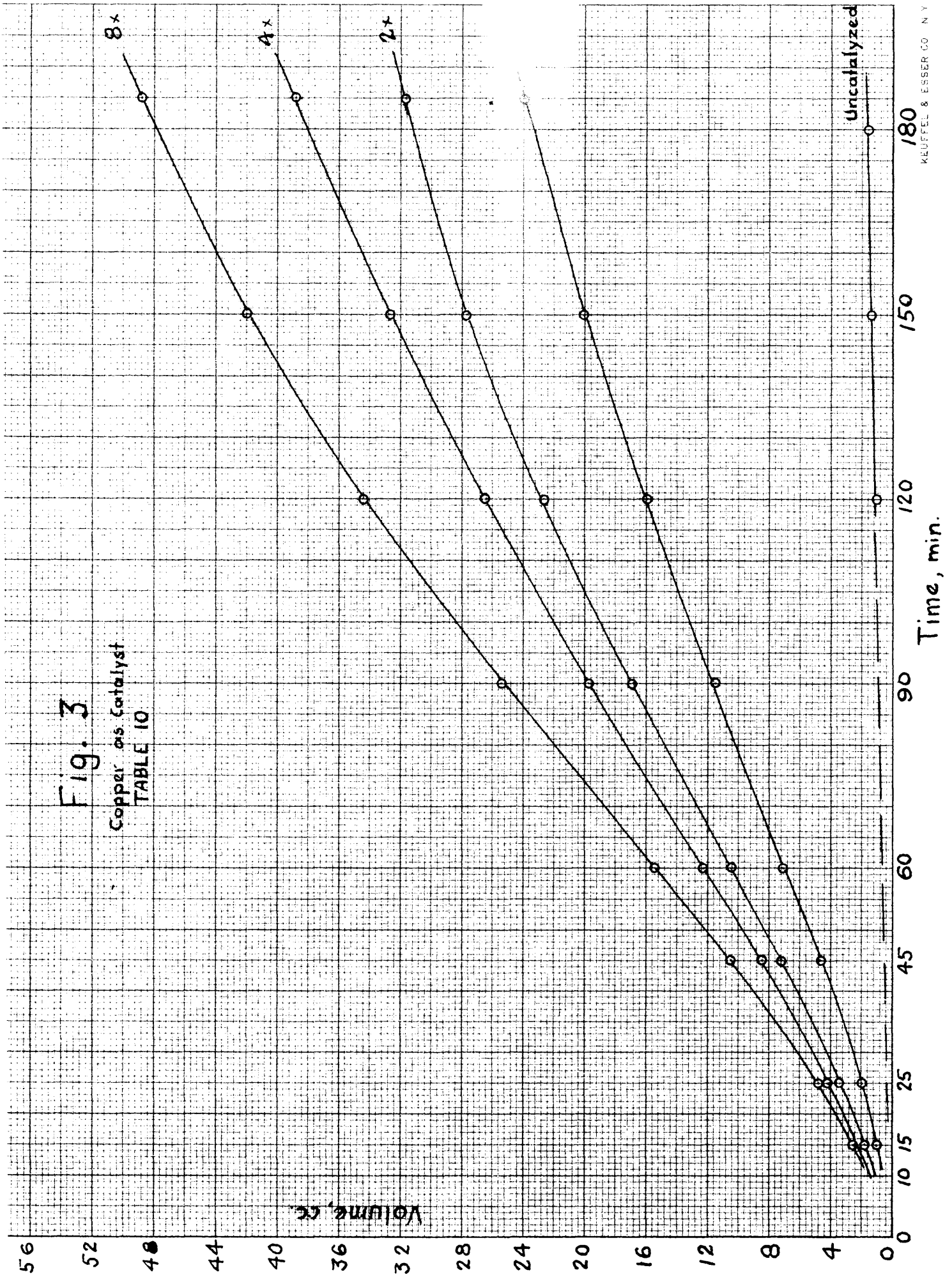


Fig. 4

Mercury as catalyst
TABLE 10

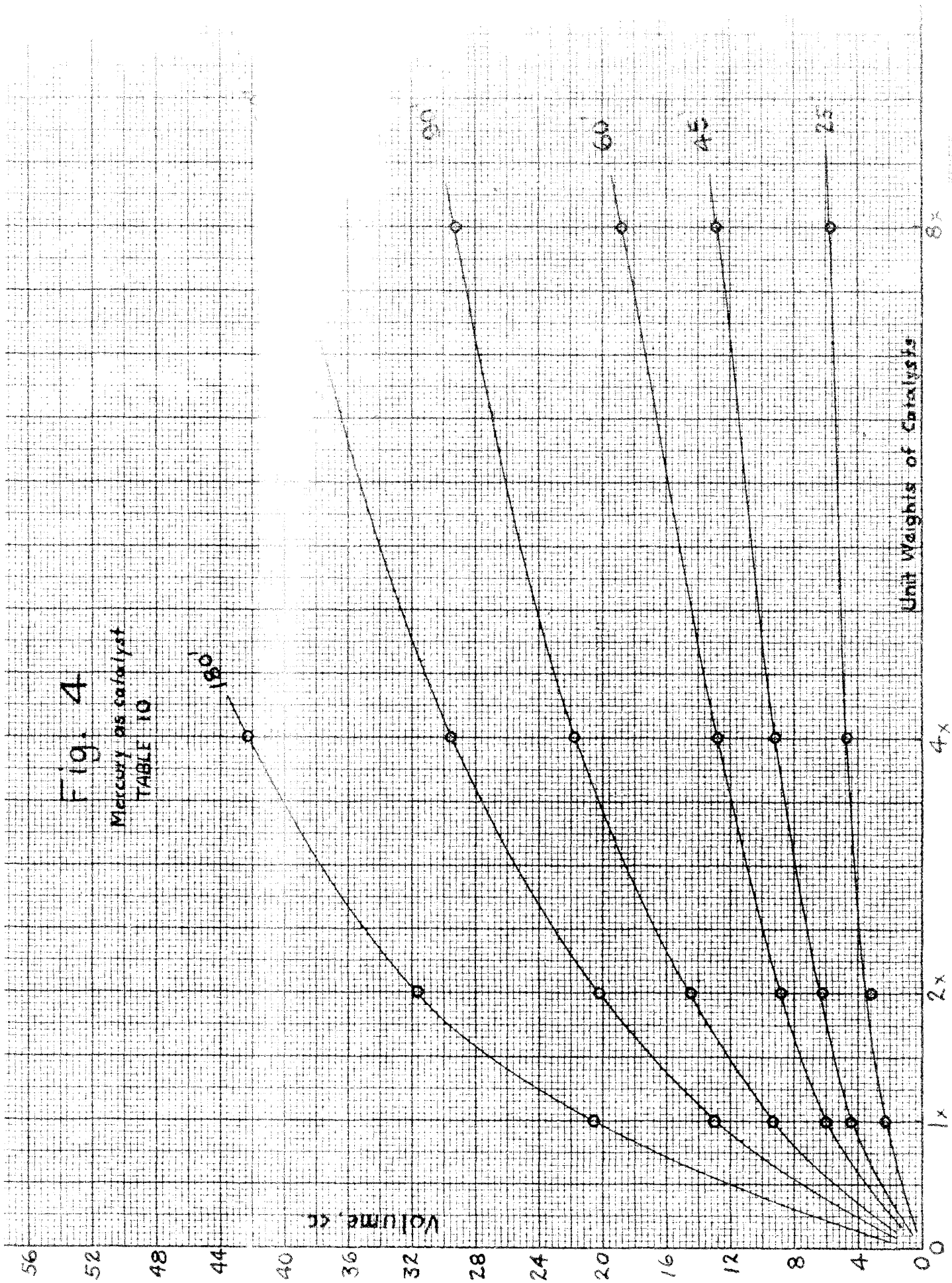


Fig. 5

Copper as Catalyst
TABLE 10

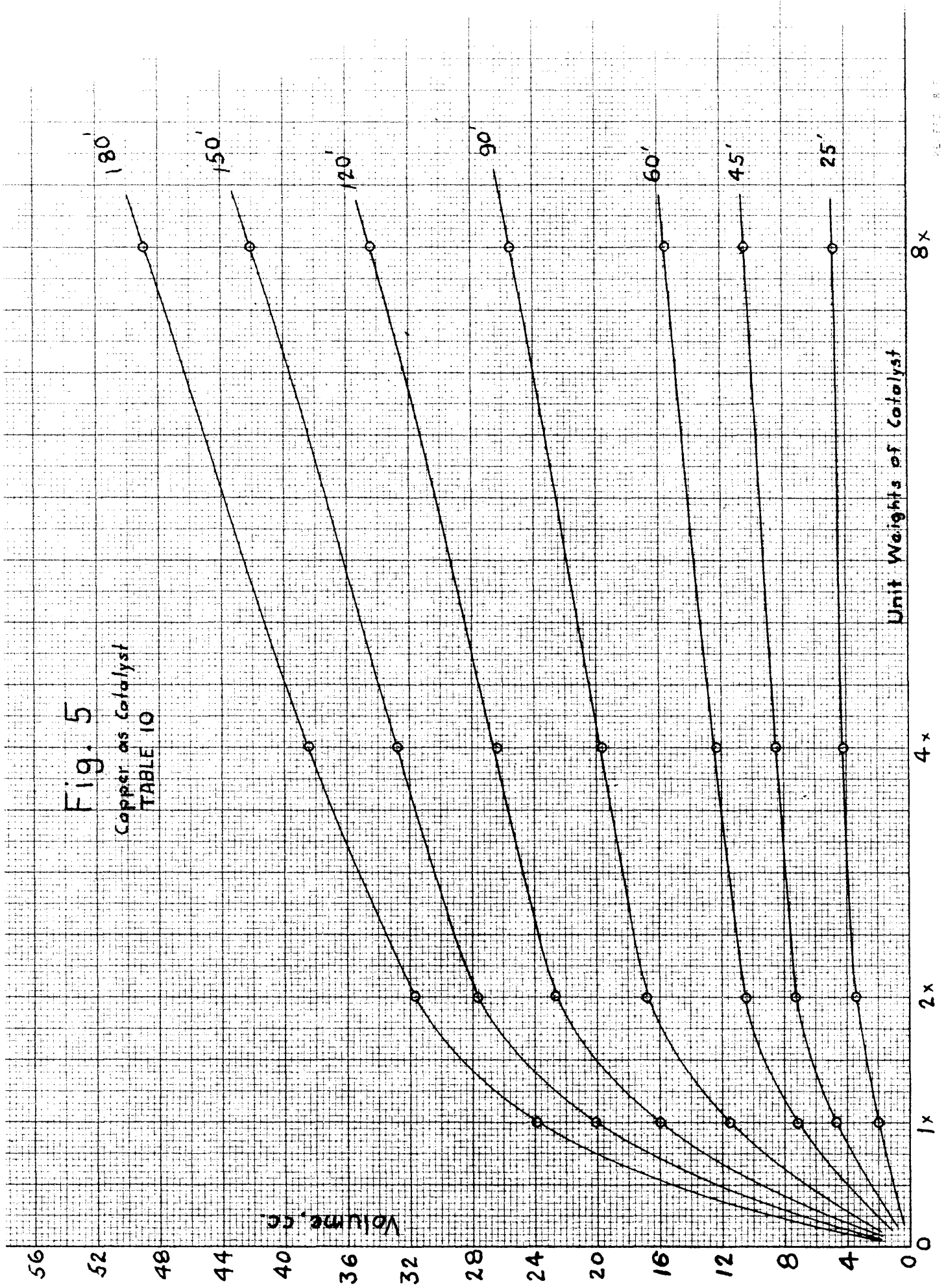


Fig. 6

Variation of K' With
Increase of Catalyst
TABLE 10

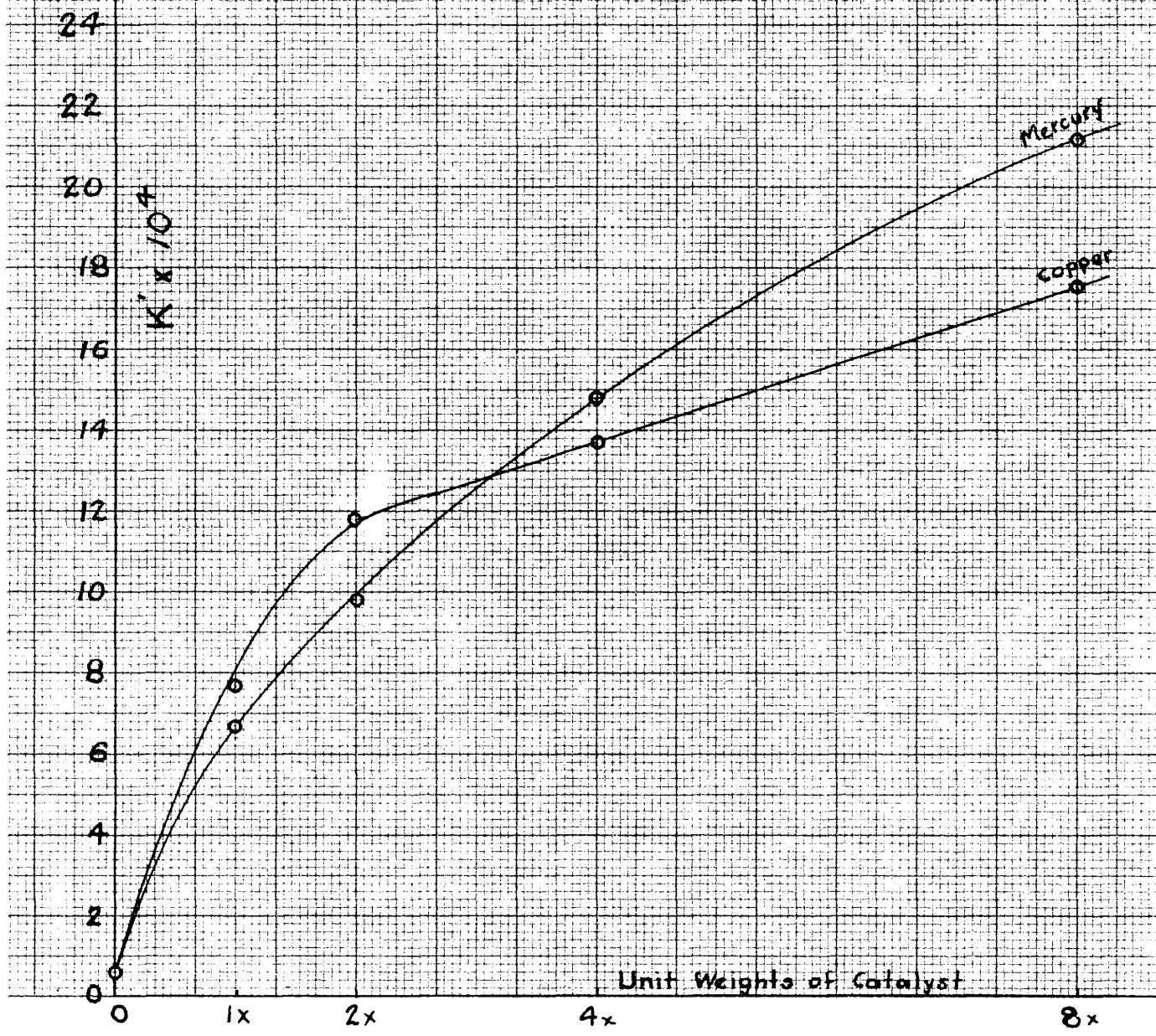


TABLE 11

.0305 g. HgO (1)

.2808 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (8)

t	200	238	240	242	249	250	Av.	Corr. from curve	K^1
5	1.2	2.3	2.5	2.0	1.6	1.7	1.9	1.9	.00240
10	3.7	5.1	5.3	4.7	3.5	4.0	4.4	4.4	.00288
15	7.4	7.6	8.0	7.5	5.9	6.5	7.2	7.2	.00315
25	13.5	14.9	15.3	12.9	10.8	12.9	13.1	13.1	.00348
45	29.2	30.5	31.2	25.6	24.4	25.2	27.6	27.6	.004318
60	41.0	40.5	40.5	35.2	35.5	34.2	37.8	37.8	.004630
90	55.3	55.3	54.4	51.3	52.5	55.5	54.3	54.3	.004755

Av. .00456

TABLE 12

.2440 g. HgO (8)

.0351 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1)

t	201	203	205	207	Average	Corrected from curve	K^1
5	2.7	2.0	3.7	2.7	2.8	2.8	.00368
10	7.3	5.8	8.1	6.1	6.8	6.8	.00449
15	12.9	11.1	13.6	10.7	12.1	12.1	.00538
25	25.1	23.6	26.5	27.8	25.8	25.8	.00723
45	49.2	43.4	43.7	43.8	43.8	43.8	.00732
60	60.6	54.6	55.6	54.0	54.6	54.6	.00716
90	68.7	-	70.2	70.5	70.3	70.3	.00675

Av. .00708

TABLE 13

.0305 g. HgO (1)

.0351 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1)

t	213	216	218	Average	Corrected from curve	$K'' \times 10^6$	K^1
5	2.1	1.0	1.1	1.1	1.1	9.0	.001337
10	2.9	2.1	-	2.5	2.5	10.4	.001614
15	4.0	3.5	3.6	3.7	3.7	10.3	.001614
25	7.0	6.2	6.6	6.8	6.8	10.6	.001796
45	13.9	12.3	13.8	13.8	13.8	13.1	.00206
60	19.3	16.9	19.2	19.2	19.2	14.9	.00218
90	29.8	26.3	29.1	29.4	29.4	16.5	.002325
						AV.	.00218

TABLE 14

.2440 g. HgO (8)

.2808 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (8)

t	225	237	274	Average	Corrected from curve	K^1	
5	2.7	3.7	-	3.2	3.2	.00414	
10	7.8	8.9	-	8.3	8.3	.00849	
15	14.1	15.4	13.3	14.6	14.6	.00653	
25	31.8	29.9	28.0	29.9	29.9	.00849	
45	57.7	51.6	53.0	54.1	53.6	.00933	
60	68.7	62.9	65.7	65.8	65.8	.01108	
90	75.7	77.7	81.0	78.1	82.0	.00841	
						AV.	.00956

TABLE 18

•0915 G. H₂O (3)

•1053 G. CUSO₄·5H₂O (3)

z	239	240	246	Average	Corrected	K ⁿ x 10 ⁶	K ₁
5	1.7	2.5	1.6	1.7	1.7	-	•00184
10	4.8	5.3	5.2	4.7	4.7	-	•00304
15	7.0	8.0	8.0	7.0	7.0	-	•00314
25	13.5	13.3	14.5	13.8	13.8	24.8	•00371
45	26.8	26.8	27.9	27.2	27.2	30.0	•00426
60	36.0	36.2	36.5	36.2	36.2	32.2	•00439
80	50.3	50.0	49.3	49.9	52.2	35.6	•00482

AV. •00439

TABLE 19

•1525 G. H₂O (5)

•0351 G. CUSO₄·5H₂O (1)

z	245	247	Average	Corrected	K ⁿ x 10 ⁶	K ₁
5	2.8	2.4	2.6	2.6	-	•00336
10	5.4	4.8	5.1	5.1	-	•00330
15	8.5	7.4	7.9	7.9	22.6	•00345
25	14.2	13.9	14.1	14.1	25.2	•00378
45	27.3	25.9	26.6	26.6	29.2	•00415
60	36.2	35.6	35.9	35.9	31.7	•00437
80	52.8	50.7	51.8	51.8	35.3	•00486

AV. •00436

TABLE 17

.0610 g. HgO (2)

.1404 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (4)

t	203	210	212	219	224	228	230	234	236	Av.	Corp. from curve	K^1
5	-	-	1.7	1.7	1.9	2.1	2.4	2.2	1.9	2.0	2.0	.00263
10	5.4	-	3.6	4.3	4.6	5.0	5.1	4.3	4.3	4.6	4.6	.00295
15	8.1	7.3	6.7	6.5	7.5	7.3	7.3	7.3	6.2	7.2	7.2	.00318
25	10.1	12.4	11.1	11.2	12.7	13.2	13.6	13.5	11.5	12.4	12.4	.00330
45	28.8	25.6	23.0	22.1	24.7	26.5	24.7	27.6	23.4	24.8	24.8	.00385
60	39.0	34.7	28.4	28.3	32.9	36.1	32.9	36.2	32.6	33.4	33.4	.00403
90	48.1	49.7	43.7	43.5	43.4	51.5	43.6	52.4	47.7	49.5	49.5	.00424

Av. .00403

TABLE 18

.1220 g. HgO (4)

.0702 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (2)

t	226	232	235	Average	Corrected from curve	K^1
5	2.5	2.3	2.5	2.5	2.5	.00322
10	4.8	5.0	5.3	5.0	5.0	.00330
15	8.3	8.4	8.3	8.3	8.3	.00367
25	15.4	14.8	14.8	15.0	15.0	.00405
45	30.2	29.4	28.6	29.4	29.4	.00465
60	40.0	39.8	37.6	39.8	39.8	.004915
90	55.7	55.0	53.5	55.0	55.0	.00480

Av. .00480

TABLE 19

.1372 g. HgO (4.5)

.1579 g. CuSO₄.5H₂O (4.5)

t	255	257	265	Average	Corrected from curve	K"x10 ⁶	K ¹
5	7.0	-	3.1	3.1	3.1	-	.00400
10	7.0	7.3	6.2	6.8	6.8	-	.00443
15	11.4	12.4	9.7	11.2	11.2	32.9	.00495
25	22.8	23.6	19.5	21.9	21.9	41.6	.00606
45	39.2	40.4	38.4	39.3	39.3	47.7	.00644
60	50.4	53.8	49.0	51.1	51.1	51.8	.00661
90	-	73.4	66.0	69.7	67.2	53.7	.00612
						Av.	.00639

TABLE 20

.1220 g. HgO (4)

.0351 g. CuSO₄.5H₂O (1)

t	262	263	Average	Corrected from curve	K ¹	
5	2.2	2.2	2.2	2.2	.00285	
10	4.6	3.5	4.0	4.0	.00265	
15	6.9	5.3	6.1	6.1	.00266	
25	12.4	9.4	10.9	10.9	.00281	
45	24.1	20.9	22.5	22.5	.00346	
60	32.3	28.1	30.2	30.2	.00357	
90	46.8	42.4	44.6	44.6	.00374	
					Av.	.00357

TABLE 21

0308 S. H₂O (1)

1404 S. C₂H₅O₂·H₂O (4)

5	10	15	25	45	60	80
1.8	3.1	4.7	8.3	17.4	25.3	-
1.6	2.5	4.2	8.8	17.8	24.6	39.8
1.5	2.9	4.7	8.8	17.8	25.0	38.9
1.5	2.7	4.5	8.6	17.6	25.0	37.9
1.5	3.0	4.8	8.8	17.6	25.0	38.8
00198	00196	008078	00223	00266	00290	00328

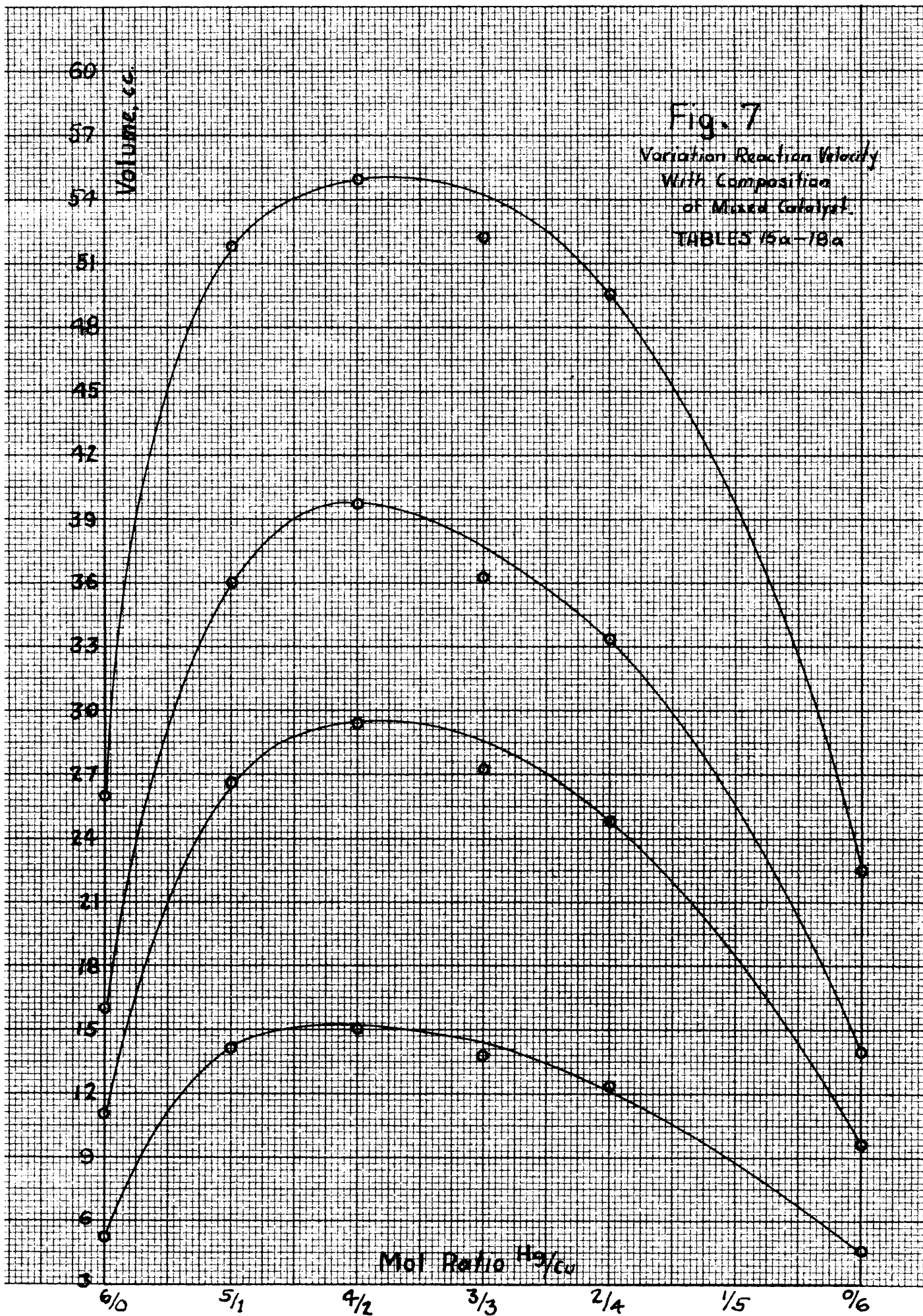
Corrected
from curve

X
1

AV.
00294

Fig. 7

Variation Reaction Velocity
With Composition
of Mixed Catalyst
TABLES 15a-18a



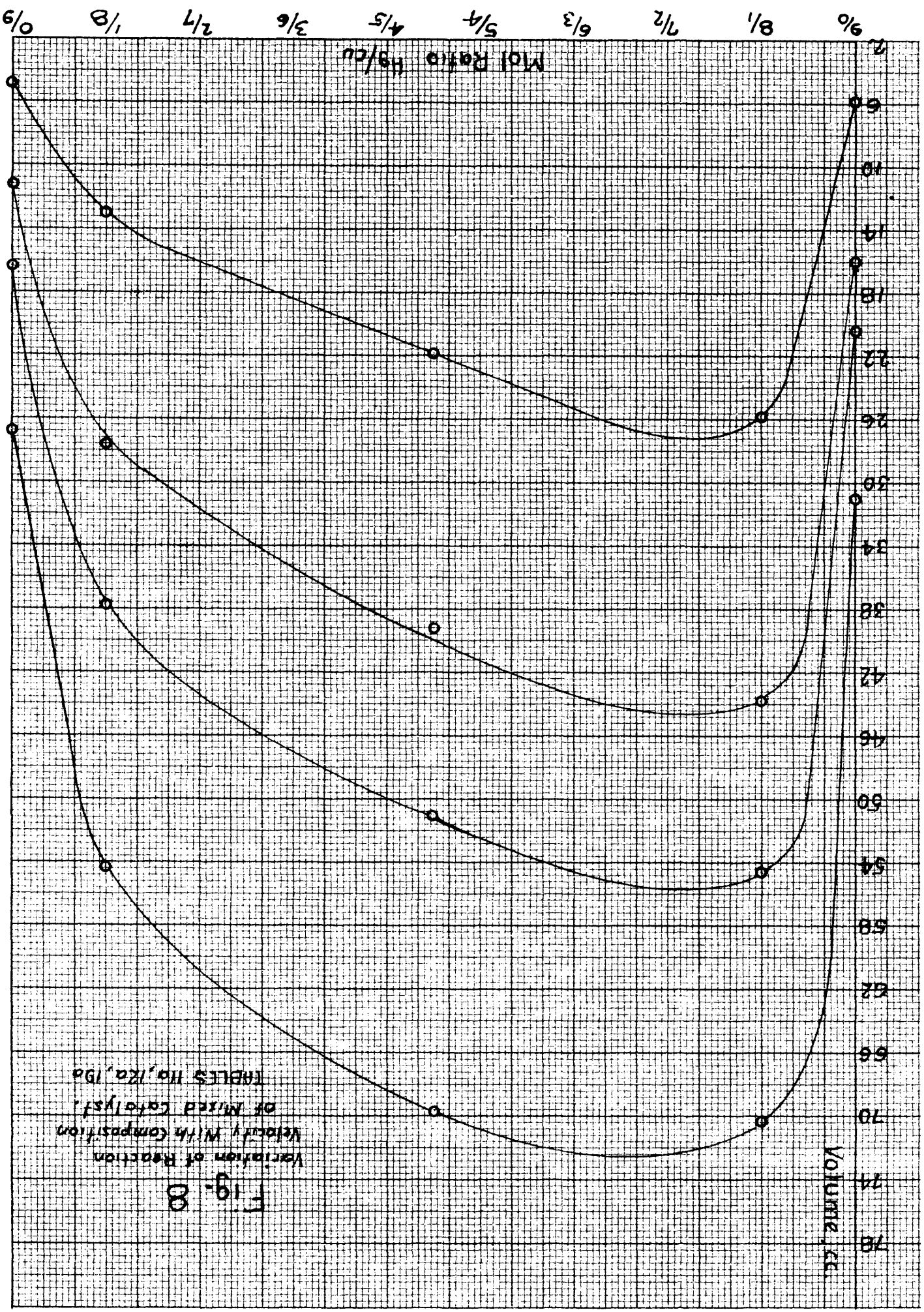


Fig. 8
 Variation of Reaction
 Velocity With Composition
 of Mixed Catalysts
 TABLES No. 12a, 12b

	Kx10 ⁴		
	21.8	14.4	1.82
8	1.1	0.7	1.97
10	2.5	1.6	1.66
15	3.7	2.5	1.48
25	6.8	4.4	1.65
45	13.8	9.2	1.65
60	19.2	13.2	1.48
90	29.4	20.9	1.41

15a
1 HR - 1 CU
14a
8 HR - 8 CU

	Kx10 ⁴		
	45.6	24.2	1.88
8	1.9	1.6	1.19
10	4.4	2.8	1.67
15	7.2	4.1	1.75
25	13.1	7.1	1.85
45	27.6	15.0	1.84
60	37.8	21.6	1.75
90	54.3	34.8	1.56

11a
1 HR - 8 CU
12a
8 HR - 1 CU

	Kx10 ⁴		
	38.7	98.6	2.48
8	1.9	3.6	1.89
10	3.5	6.9	1.97
15	5.0	15.0	2.84
25	10.4	29.9	8.87
45	23.4	64.0	2.32
60	34.3	63.9	1.70
90	54.6	76.2	1.39

	Kx10 ⁴		
	28.9	70.8	2.36
8	1.0	2.8	2.80
10	2.3	6.8	2.90
15	3.7	12.1	2.27
25	7.7	25.8	3.35
45	17.6	43.8	2.50
60	25.9	54.6	2.11
90	40.7	70.3	1.72

15a

3 Hg - 3 Cu

t	F	C	B
5	1.7	-	-
10	4.7	-	-
15	7.0	-	-
25	13.8	(8.2)	1.61
45	27.2	(16.9)	1.61
60	36.2	(23.0)	1.57
90	52.2	(37.0)	1.41

$K \times 10^4$ 43.9 (26.4) 1.66

16a

5 Hg - 1 Cu

F	C	B
2.6	-	-
6.1	-	-
7.9	-	-
14.1	(7.0)	2.00
26.6	(14.9)	1.78
35.9	(21.7)	1.65
51.8	(35.7)	1.45

43.6 (24.4) 1.78

17a

2 Hg - 4 Cu

t	F	C	B
5	2.0	1.2	1.67
10	4.6	2.5	1.84
15	7.2	4.3	1.72
25	12.4	7.3	1.70
45	24.8	14.7	1.69
60	33.4	21.1	1.58
90	49.5	34.2	1.45

$K \times 10^4$ 40.3 23.5 1.72

18a

4 Hg - 2 Cu

F	C	B
2.5	1.4	1.79
5.0	3.0	1.60
8.3	4.6	1.81
15.0	8.2	1.83
29.4	16.4	1.79
39.8	23.3	1.71
55.0	38.7	1.42

48.0 26.6 1.80

19a

4.5 Hg - 4.5 Cu

t	F	C	B
5	3.1	-	-
10	6.8	-	-
15	11.2	-	-
25	21.9	(9.2)	2.58
45	39.3	(18.5)	2.12
60	51.1	(26.8)	1.91
90	67.2	(43.8)	1.54

20a

4 Hg - 1 Cu

F	C	B
2.2	1.1	2.0
4.0	2.4	1.66
6.1	3.8	1.60
10.9	6.8	1.63
22.5	13.9	1.62
30.2	19.9	1.52
44.6	33.3	1.34

$K \times 10^4$ 63.9 (30.0) 2.13

35.7 22.5 1.59

21a

1 Hg - 4 Cu

t	F	C	B
5	1.5	1.2	1.25
10	3.0	2.4	1.25
15	4.8	2.0	1.20
25	8.6	6.6	1.30
45	17.6	13.0	1.35
60	25.0	18.4	1.36
90	39.8	29.1	1.37

$K \times 10^4$ 29.4 20.4 1.44

5. Discussion of Results

Bredig and Brown^{3,4} determined the rate of oxidation for five concentrations of mercury, for one concentration of copper, and for one mixture of copper and mercury.

The data of this investigation extends the study to: 1) four concentrations of copper; 2) eleven mixtures of copper and mercury; 3) checks the work of the previous investigators for four concentrations of mercury and for the rate without catalysts present.

The data may be compared on the basis of the volume of gas given off at definite time intervals, or, by comparing the values of the reaction constant. The "average" value for K' for this comparison was taken as the average of the values at 45, 60, and 90 minutes as mentioned on page 13.

The summary of the data in Table 10 and in Figs. 2 - 6 shows that copper is a better catalyst than mercury at the lower concentrations but a poorer catalyst at the higher concentrations on a mol for mol comparison. Weight for weight, copper sulfate is a better catalyst for the reaction than mercuric sulfate. The presence of 1.4 millimoles of metal causes the oxidation reaction rate to increase about thirteen fold. (Table 10).

The catalytic effect is proportional to the amount of metal present, but is not directly proportional as Bredig and Brown decided⁷. It is generally true in homogeneous catalysis that the catalytic effect increases proportionately with the increase of catalyst concentration. The optimum amount of catalyst to promote the destructive oxidation of aniline sulfate by sulfuric acid is therefore the maximum amount which will dissolve in the reaction mixture¹⁰.

The data obtained using mixtures of metal salts as catalysts is shown in Tables 11 - 21. As with single catalysts, the catalytic effect is again proportional to the total amount of metal present. The mixtures with a high mercury content are better catalysts than those with a high copper content. This may be expected from the fact that mercury is a better catalyst than copper when used alone at high concentrations. Two experiments are recorded for a series of mixtures in which the total amount of metal is six units, and nine units. The data for these is shown in Figs. 7 and 8, respectively. The data shows that for a given amount of metal catalyst, the optimum composition of the mixed catalyst is approximately one mol of copper to two of mercury.

The values of the promotion factor "B" and "B'" are

given in Tables 11a-21a. An inspection of the values shows the interesting fact that the promoter effect as measured by the promotion factor is practically constant for all the mixtures. The variation from the lowest value of B, (Table 21a) is in most cases about 15-20%, and in the extreme cases (Tables 12a, 14a, 19a) about 65-70%. The relationship between the promotion factor and the composition of the catalyst is an important relationship in classifying promoter action, and is the most important information sought in this research. In many instances the promotion factor varies as much as 300-400% with varying composition of the mixed catalyst.^{28b}

Another interesting fact about the value of "B" is that it decreases steadily with time. This may mean that before the oxidation is complete the value of "B" may become equal to unity; then no promoter action occurs. This indicates, also, that the mixed catalyst is particularly effective during the early stages of the oxidation.

The values of the reaction rate constant, K' , are not all that is desired if one is to assign a definite order to the reaction. The mono-molecular constant is more nearly constant than the corresponding values for K'' or K''' as has been previously stated. The only conclusion that the data permits is that the reaction is "pseudomono-molecular" with respect to aniline sulfate.

The value of K' is not constant, no doubt, because of the number of reactions which occur in the reacting system. Evidence of the existence of concurrent reactions may be obtained by an inspection of the volume-time curves in Figs. 2-3 where it is seen that the curves go through a change in slope at about sixty minutes. The reason for this change, noted also by the previous workers^{3,4}, cannot be explained except on the assumption that there is a change in the velocity of a concurring reaction.

A cursory examination of the data in the preceding tables might lead one to the conclusion that the apparent lack of agreement between the volumes recorded is the result of poor experimental measurements. The purpose of this research was to evaluate the promoter effect and does not require precise measurements. However, in the opinion of the writer the recorded values are the best that the method of study permits.

The error in the weights of the reacting materials, in the pressure, temperature and volume of collected gas were of the usual ^{order} accuracy and were less than 0.10%. The temperature regulation of the thermostat was \pm 0.10 degree and did not introduce an appreciable error in the results.

The values for the volumes recorded in the previous tables show in some cases a deviation of four to five cubic

centimeters. Part of this deviation is due to the entrance of air with the sample of aniline sulfate and was corrected for by the method of correcting the average curve through the origin. An error which cannot be corrected for is that caused by adding the cold solution of salt to the reaction mixture; the initial time for the start of the reaction is in error by about one-quarter to one-half minute.

Another source of error which apparently did not interfere greatly with the determinations recorded in this research is that due to the solubility of sulfur dioxide in rubber. Although that solubility is appreciable, (10a) the rubber was exposed to the gas in many experiments before those recorded, the pressure of the gas was always less than one-half atmosphere, and the time of exposure was not more than 180 minutes. These facts would lead one to expect a small source of error due to the reaction between the gas and the rubber connections. The apparatus could have been constructed entirely from glass but then it would have been too fragile to be serviceable.

The solubility of CO_2 and SO_2 in the reaction mixture is considered negligible at 275 degrees. The previous investigators have shown that the formation of water as the oxidation proceeds does not interfere with the measured rate with the excess of sulfuric acid present.

6. Comparison of Results with those of Bredig and Brown^{3,4}

It was expected at the start of this work that the values obtained by the previous investigators for the reaction rate without catalysts and for four concentrations of mercury as catalyst could be used in this research. However, attempts to check the data as recorded by Bredig and Brown in these cases were not successful.

The catalytic effect due to the presence of mercury is greater than Brown calculated and recorded in his thesis³, Table 52, page 65. His data recalculated, yields values comparable to those recorded in Table 10 for the increased rate in the presence of 1.4 millimoles of mercury.

The promotion factor "B" for the one mixture recorded by Brown in his thesis³, page 76, has the value 1.37 which is in close agreement with the data of this study.

The values which Bredig and Brown obtained for the volumes of gas and for the value of K' at definite time intervals are all uniformly higher than the values obtained in this study, and we agree, therefore, only in the general conclusions. A close inspection of the data leaves only

the possibility that the sulfuric acid used by the previous workers may have contained copper or mercury sulfates as an impurity.

The values for K' obtained in the previous research are somewhat more constant than those obtained for this data. However, Brown applies a correction to his data, as explained on page 39 of his thesis³, the application of which is not made clear. At times the correction is too large to appear reasonable.

7. The Reaction Between Sulfuric Acid and
Aniline Sulfate¹¹

1. In absence of Mercury and Copper.

At 190 degrees aniline sulfate and sulfuric acid give no evidence of reaction. The solution remains clear and no odor of sulfur dioxide is noticeable.¹² A reaction which does occur, however, is the rearrangement of aniline sulfate to sulfanilic acid.

Heated at 275 degrees, a solution of aniline sulfate in sulfuric acid slowly darkens going through a color change to green to black and finally to yellow which color is due to the formation of quinone after long heating. The black color is that due to the formation of aniline blacks. These are quinoid addition products having formulae of the following type:



The aniline blacks are valuable dyes and are usually made by the oxidation of aniline with dichromate or chlorate in the presence of copper as a catalyst.

Un-Catalyzed at 275 degrees, the main reactions in the mixture are the slow oxidation of aniline sulfate to form aniline blacks, or quinone, accompanied by sulfonation of the

benzene ring. The tri-sulfonic acid is very probably formed.

2. In the presence of mercury or copper

That copper and mercury have a profound effect upon the rate of destructive oxidation of aniline is evident from the preceding data. This fact was also noted by Holderman¹², who found that the odor of sulfur dioxide became apparent when even a small amount of mercury was added to a solution of aniline sulfate and sulfuric acid at 190 degrees. Thus while the presence of mercury is desirable in the reaction between sulfuric acid and some compounds, as in the preparation of phthalic acid from naphthalene, and the preparation of the b-sulfonic acid of anthraquinone in place of the a-compound, with aniline sulfate the presence of mercury causes only destructive oxidation.^{12,13}

3. Other possible reactions in the System.

In considering the mechanism of the catalytic effect of the added metals, it will be necessary to consider all the possible reactions in the system. These might be mentioned at this time.

James Kendall and co-workers have shown definitely that in almost every solution, complexes of solute and

solvent are formed. Thus we might expect such complex formation between the sulfuric acid, aniline sulfate and the dissolved metal salts.

That aniline may form such complexes is shown by the following which are recorded in the literature:

$\text{HgBr}_2(\text{An})_2$; $\text{HgBr}(\text{An})$; $\text{Hg}(\text{CN})_2(\text{An})_2$; $\text{Hg}(\text{CN})_2(\text{An})_4$ ¹⁴; and
 $\text{Cu}(\text{NH}_2\text{CH}_2\text{Ph})_3(\text{NH}_4\text{SO}_4)_2$; $\text{NiCl}_2 \cdot \text{HgCl}_2(\text{An})_6 \cdot 2\text{H}_2\text{O}$; $\text{CoCl}_2 \cdot \text{HgCl}_2(\text{An})_4$ ^{15,16}

Another type of reaction which may possibly occur is one in which mercury or copper replaces hydrogen in the benzene nucleus and forms an organometal compound. This reaction is very readily carried out with mercury which has a great affinity for carbon. Such mercuriated aryls are rather stable compounds. Thus, if aniline is added to a solution of mercuric acetate in water solution, p-aminophenylmercuric acetate separates after standing a short time along with some of the o-compound.¹⁷ The copper compounds are less easily prepared and are not as stable.¹⁸

8. Homogeneous Catalysis; Theoretical Discussion¹⁹.

Catalytic effects are classified into two types depending upon the reacting system. Heterogeneous catalysis is concerned with systems containing more than one phase and deals mainly with reactions at solid surfaces. Homogeneous catalysis, on the other hand, is concerned with one phase systems and deals with reactions in the liquid or gaseous state. In this research we are concerned with a case of homogeneous catalysis since the aniline sulfate and the added metal salts were soluble in the sulfuric acid at the temperature and concentrations employed.

In studying catalytic effects we deal with two factors; the first, is the mechanism attending the decomposition of the system; the second, is the mechanism of the catalytic action which hastens this decomposition.

The simplest reacting system theoretically possible is the mono-molecular system in which the reactant is one molecule. But there is little evidence at hand to prove that true mono-molecular reactions occur. The only decomposition which approaches the mono-molecular state is that of nitrogen pentoxide. However, evidence has accumulated to show that the rate of decomposition does not obey the mono-molecular law at all pressures.

On the other hand, bi-molecular reactions are very common and their nature may be definitely established; therefore, many regard the bi-molecular system as the simplest possible. The theoretical treatment of reaction velocity has been based almost entirely on the bi-molecular change.

Before a molecule may decompose, it must collide with another molecule, and must possess a definite amount of energy of decomposition. To account for the source of this energy has been a difficult task, and is a problem which has met but slight experimental proof.

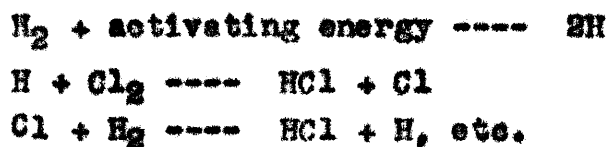
A study of the reaction rates of bi-molecular systems led Arrhenius to two important conclusions. He observed that the number of molecules decomposing represent but a small fraction of the number of collisions actually occurring in the system, and, that the temperature coefficient of reaction velocity is much ^{greater} ~~less~~ than one would expect on the basis of the increased number of collisions due to the temperature rise. On these facts, Arrhenius postulated that there were two types of collision between molecules. An elastic collision, and an inelastic collision. The latter only resulting in the activation of the molecule capable then of decomposition. Thus, he proposed that an equilibrium existed between active and inactive molecules, A A'.

Whatever the source of activating energy, a catalyst apparently operates to increase the number of activated molecules, and increases the reaction velocity by shifting the above equilibrium to the right.

If the mechanism of activation were definitely explained, then the mechanism of catalytic action could perhaps be understood. However, the theories of activation advanced have met but little successful experimental verification.

Studies of the reaction rate in the gaseous state have given rise to the "radiation hypothesis" which suggests that the energy of activation comes from radiant energy existing in or passing through the reacting system. This theory would require the existence of mono-molecular reactions as a sustaining argument and would also require that the activating radiation be defined by the photochemical law, $E = Nh\nu$. In neither respect has it been substantiated. The theory of "activation by collision" is based on the assumption that the kinetic energy resulting from the inelastic collision of reactant molecules appears as quantized energy of activation. In the case of bi-molecular reactions this theory finds sound theoretical explanation since it can be shown that the rate of activation by collision is sufficiently great to account for the required energy of activation. While

the number of proofs is somewhat limited, much experimental evidence is at hand to prove this hypothesis. For that reason it is the most successful hypothesis in explaining the source of activating energy in bi-molecular reactions. In the cases where the photochemical law is not obeyed as required by the radiation theory of activation, some investigators point to the possibility of chain reactions. By this mechanism, only a small amount of radiant energy is required to initiate the decomposition of a few molecules, and then this energy may be handed on from one molecule to another in a series of atom chains. This may be exemplified by the following:



The theories mentioned in accounting for the activation of molecules in the gaseous state should be generally applicable to the liquid state, but this has not met with success. The reason is that the liquid state is much more complex and little understood, and, does not lend itself to precise theoretical treatment. Also, reactions in the liquid state are complicated by the formation of various types of complexes between the reactant, solvent, and catalyst. Theories of activation and catalysis in solution therefore have been based mainly on the idea that reaction proceeds through the formation of an intermediate

complex.

To justify such a theory it must be shown that such complexes can exist, that by their formation the molecules of the reactant may be activated, and that the formation of the complex corresponds to a diminution of the free energy of the system.

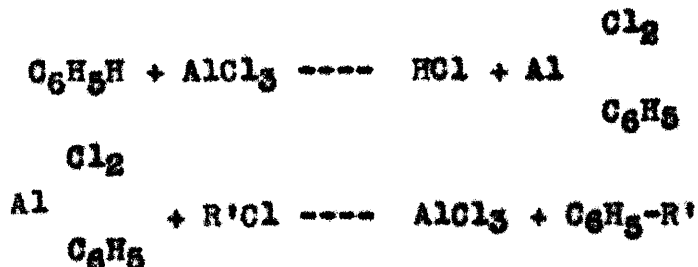
The existence of complex compounds in almost every type of system has been definitely shown by Kendall and co-workers. In many cases these complexes may be isolated from the system. Such evidence has caused the idea of complex formation to be accepted as an adequate explanation of the mechanism of catalytic effect by many workers, more particularly Sabatier²⁰.

Studies of the hydrolysis of esters, the mutarotation of sugars, the decomposition of nitramide, and many reactions which are catalyzed by hydrogen or hydroxyl ion have been best explained by the existence of a ternary complex between reactant, solvent and catalyst²¹.

Reactions like the Friedel-Crafts reaction, the decomposition of diazo-compounds, and others have also been explained by the existence of intermediate complexes²¹.

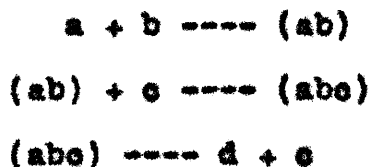
Thus it is postulated that in the hydrolysis of sucrose, catalyzed by H^+ , catalysis results from the formation of the complex: $(\text{sucrose}) \cdot (\text{water})_n \cdot (H^+)_x$. And that the

Friedel-Crafts reaction proceeds through the formation:



Hence, while a system may ordinarily decompose:

$a + b \text{ ---- } (ab) \text{ ---- } d$, the catalyst may hasten the reaction by:



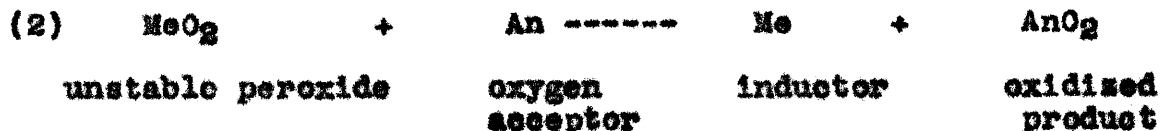
In the case of oxidation catalysis the catalytic effect is supposed to proceed through the formation of a peroxidized intermediate.

We may represent such a state of affairs by the following in which Me represents the active form of the metal ion, O₂ the oxidizing agent, and An, the material to be oxidized. Other than the oxidizing action, the following reaction may take place and produce a catalytic effect:



The peroxide may then spontaneously decompose, or may react

with the oxygen acceptor:



If equation (2) results in only partial reduction of the peroxide to MeO, for example, then the action will not be strictly catalytic according to the definition of catalysis because the inductor will not then be continually regenerated.

Many instances of oxidation catalysis have been explained by the mechanism given above.²²

That the mechanism of the catalytic effect produced by metal ions is not a simple oxidation-reduction of the ion ($\text{Me}^{++} \text{ ---- } \text{Me}^{+++}$, for example) can be shown in some cases where thermodynamic data is available. Johnson and Robertson have pointed this out in their study of the ferric salt decomposition of hydrogen peroxide^{28b}. By approximating the ΔF of formation of FeO_4^{\ominus} , they were able to show that the reciprocal oxidation-reduction of $\text{Fe}^{++} \text{ ---- } \text{Fe}^{+++}$ was very improbable.

The presence of the intermediates which a catalyst may form may be proven by isolating such complexes, by spectographic studies, by studying the relation of catalytic effect to the activities of the components of the system, by

ideas based on molecular structure, and by the use of available thermodynamic data.

In postulating the existence of intermediates which exert a catalytic influence, it is important to remember that such an intermediate must be unstable, and that the velocity of the reaction through the postulated path must be more rapid than by the uncatalyzed.

19. The Mechanism of the Catalysis by Mercury and Copper.

That the presence of either copper or mercury sulfates has a profound effect upon the rate of oxidation of aniline sulfate by sulfuric acid is evident from the preceding data.

What we are concerned with here is the behavior of the metal ions acting as inductors of the oxidation reaction. The catalysis may be accomplished through a physical effect in that the added salts may form ternary complexes which are more easily oxidized than aniline sulfate itself; or, the effect may be chemical in that the metal may form a peroxidized complex or react chemically in some other way.

With the data at hand, the problem of assigning a mechanism to the reaction is very difficult. The lack of thermodynamic data and the lack of evidence of any intermediate compound formation makes it necessary to draw only general conclusions. The complexity and number of possible reactions which may occur in the system also increases the difficulty of postulating a mechanism for the catalytic effect.

Dismissing the possible formation of ternary complexes as being untenable and too complicated to explain the catalysis, we may account for the behavior of the added metal salts through two chemical effects.

The first of these is the possible formation of an organometal compound in which the metal present substitutes in place of hydrogen in the phenyl nucleus. Such a compound may then hydrolyze yielding a hydroxy compound which is more easily oxidized than aniline sulfates. We have noted the possibility of the formation of such compounds on page 37 .

That mercury may act in such a way to produce a hydroxyl group in the benzene ring has been shown by Davis, et al²⁵. Benzene and nitric acid in the presence of mercury nitrate give tri-nitro phenol very readily, whereas, in the absence of mercury salts the reaction yields only nitrated benzene. They were unable to account for the formation of the OH group, but were able to show that it was due entirely to

the presence of mercury and was not formed by the oxidizing action of nitric acid. They were able to isolate an intermediate complex from the system whose constitution was not determined; the mercury apparently acts in its catalytic role through the formation of this complex. They also observed that the presence of sulfuric acid in the mixture decreased the yield of picric acid probably through destructive oxidation.

The catalytic decomposition of H_2O_2 has been the subject of a number of investigations²². This system is well suited to a study of the mechanism of homogeneous catalysis because of its simplicity.

The catalytic decomposition of hydrogen peroxide by iron and copper salts has been extensively studied^{28a,b}, and it has been shown that the catalysis proceeds through the formation of ferric and cupric acids. The existence of these compounds has been shown by spectographic measurements on the reaction mixture, and in the case of iron, also by the action of barium ferrate on H_2O_2 . Such a mechanism follows the peroxide theory outlined above and suggests a very probable mechanism for the catalytic effect noted in this investigation.

Both mercury and copper may exist in the form of higher oxides which are rather unstable compounds although readily formed. Copper may form two peroxides: $CuO_2 \cdot H_2O$,

and, Cu_2O_3 ²⁴; mercury, the peroxide, HgO_2 ²⁵. Robertson assigns the formula H_2CuO_3 to the active form of copper in the decomposition of H_2O_2 ²⁶.

This suggests a possible mechanism for the catalytic effect in the aniline sulfate-sulfuric acid system. The copper or mercury sulfates give rise to the peroxidized intermediate represented by the formula, H_2MO_3 . These compounds are readily formed, and are unstable, being readily reduced by the aniline sulfate. Thus the oxidation proceeds more readily by this path and a catalytic effect results.

10. Promoter Action in Homogeneous Catalysis; Theoretical Discussion¹⁹.

An interesting phenomenon in catalytic action is that produced in many instances by a mixture of metal salts acting as a catalyst. Thus, it has been found that in some cases the addition of a relatively inert material may enhance the catalytic activity of a catalyst, or, that a mixture of two catalysts is more active than their single activities would suggest. This enhancement of catalytic activity is known as "promoter action". The term was suggested in patents of the Badische-Anilin und Soda-Fabrik²⁷

which is the first literature use of the term.

Examples of promoter action are more numerous in heterogeneous catalysis than in homogeneous systems. The best known examples in the latter case are the well known neutral salt effect in the hydrolysis of esters, many instances of the action of metal salts in the decomposition of hydrogen peroxide, and the promoter effect of copper salts on the ferric salt catalysis of the reaction between KI and $K_2S_2O_8$, and between H_2O_2 and HI²⁸.

Pease and Taylor²⁹ have collected most of the literature on promoter action up to 1920, and have attempted to set forth a definition of promoter action as: "all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present".

They acknowledge the breadth of this definition, and, in order to define the term further suggest the terms "activation" and "co-activation". The former to refer to the activation of a catalyst by a relatively inert material; the latter to the activation of a catalyst by another catalyst.

Any attempt at defining promoter action, especially in homogeneous systems, is difficult because of the lack of

measurements in a large number of cases. As Robertson has pointed out^{28b}, the term "activation" has no significance after the mechanism of the "promoter effect" is determined. As an aid to study, however, the terms are useful as a means of classifying examples of promoter action.

No general theories have as yet been advanced to account for promoter action in homogeneous catalysis. In a few instances, theories suited to a particular case have been advanced, as for the promoter effect which copper and ferric salts show in the decomposition of hydrogen peroxide. This mechanism will be discussed in the following section.

11. Mechanism of the Promoter Action Between Copper and Mercury.

The extent of promoter action in the mixed catalysts has been evaluated by calculating the promotion factor which is recorded in Tables 11-21a. We have previously noted that the value of the promotion factor does not vary to a marked extent for any mixture of the two catalysts, and that it approaches unity as the oxidation proceeds. The mechanism which produces this result cannot be explained at this time.

Referring to the suggested mechanisms for the catalytic effect produced by the salts acting alone, two

possible mechanisms may be considered.

The first is, that one of the metals may form a complex, either a ternary complex salt or organometal compound, which is readily oxidized by sulfuric in the presence of the other metal. The enhanced oxidation may proceed either by replacement of the combined metal by the uncombined to form a still more easily oxidized complex, or by the formation of a peroxide which reacts with the complex as the metal peroxide was considered to react with aniline sulfate alone.

The second is, a mechanism similar to that which Robertson has shown to exist in the ferric salt decomposition of hydrogen peroxide which is promoted by copper salts^{28b}. This follows from the mechanism suggested for the simple catalysis based on the assumption that peroxides existed in the reaction mixture and produced the catalytic effect.

Robertson has shown for the decomposition of hydrogen peroxide, that: 1) ferric salts are the primary catalysts and act through the formation of H_2FeO_4 ; 2) copper salts are secondary catalysts and act through the formation of cupric acid, H_2CuO_3 ; 3) when present together, H_2FeO_4 is readily formed and oxidizes Cu^{++} readily to H_2CuO_3 which ordinarily is formed slowly; H_2CuO_3 then rapidly auto-oxidizes hydrogen peroxide. The change in path of the reaction thus produces

the promoter action.

Applying this mechanism to the system under study, we have: 1) copper is rapidly oxidized by sulfuric acid to cupric acid which would normally be reduced by the aniline sulfate; 2) cupric acid oxidizes the mercury rapidly to mercuric acid which in turn oxidizes the aniline more rapidly than does cupric acid.

This mechanism postulates a shift in the path of the reaction so that one metal actively oxidizes aniline sulfate through the formation of a peroxide while the other metal continually regenerates it in the peroxide form.

No definite stoichiometric relationship between the metals can be drawn from this data since there is no maximum promoter effect at a definite composition of mixed catalyst. Nor, is there any evidence to indicate the active form of the peroxide or metal ion which operates in the catalysis. Therefore, the mechanism will not be represented by a series of equations.

That copper can exhibit catalytic power in oxidizing mercury ions has been shown by Germuth^{22b}. He has shown that the rate of oxidation of Hg_2^{++} ---- 2Hg^{++} in air, can be appreciably increased by the presence of Cu^{++} .

SUMMARY

The kinetic study of the rate of oxidation of aniline sulfate in the presence of mercury and copper sulfates has been extended to include now, measurements for four concentrations of copper and for eleven mixtures of copper and mercury sulfates acting as catalyst.

Where the work was repeated, the general conclusions of the previous investigators have been confirmed.

The catalytic effect is proportional to the total amount of dissolved metal and for a given number of moles of metal acting as a mixed catalyst, the rate of decomposition is greatest for the mixture whose composition is one mol of copper to two mols of mercury.

The promoter effect as measured by the promotion factor is practically constant for all mixtures of copper and mercury; no definite maximum effect for a particular mixture was found.

Promoter action between copper and mercury may be classified as an example of "co-activation."

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