

EFFECT OF CATALYST GROOVE WIDTH ON DECOMPOSITION RATE  
OF HYDROGEN PEROXIDE

by

ARTHUR F. DERSHOWITZ

Submitted in Partial Fulfillment of  
The Requirements for the Degree of

BACHELOR OF SCIENCE

from the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

1947

Signature of Author, \_\_\_\_\_

Department of Chemical Engineering, January, 1947

Signature of Professor  
In Charge of Thesis \_\_\_\_\_

Signature of Chairman of Department  
Committee on Undergraduate Students \_\_\_\_\_

M.I.T. Dormitories  
Cambridge 39, Mass.  
January 15, 1947

Professor Joseph S. Newell  
Secretary of the Faculty  
Massachusetts Institute of Technology  
Cambridge, Massachusetts

Dear Sir:

In accordance with the regulations of the Faculty, I take pleasure in submitting to you this thesis entitled "Effect of Catalyst Groove Width on Decomposition Rate of Hydrogen Peroxide", in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering from the Massachusetts Institute of Technology.

Very truly yours,

Arthur F. Dershowitz

## ACKNOWLEDGMENT

The author wishes to thank Professor D. B. Broughton and Mr. Herbert Isbin of the Chemical Engineering Department and Mr. Harry Archibald of the Chemical Engineering Machine Shop for their encouragement and many stimulating suggestions.

## CONTENTS

Nr.	Designation	Page
I	Summary	1
II	Introduction	3
III	Procedure	5
IV	Results	13
V	Discussion of Results	24
VI	Conclusions	34
VII	Recommendations	35
VIII	Appendix	37
	A. Historical Survey	37
	B. The Work of Isbin and Associates	49
	C. Summary of Data and Results	53
	D. Sample Calculation	64
	E. Literature Citations	66

## TABLES

Nr.	Designation	Page
I	Comparison of Runs at Same Flow Rate .....	17
II	Average Percent Undecomposed at Various Conditions.....	17
III	Effect of Packing and Waiting On One Catalyst Set.....	18
IV	Low pH Runs.....	19
V	Standard Grooving of Catalyst Plates	19
VI	Batch Test Summary.....	22-23
VII	Possible Causes of Lack of Correlation (Flow Tests).....	32-33
VIII	Appendix C as listed in Contents...	53

## PLOTS AND DIAGRAMS

Fig. Nr.	Designation	Following Page
I	Flow Test Apparatus.....	9
II	Reaction Tube Assembly.....	9
III	Effect of Increased Area .....	16
IV	Effect of Repacking and Waiting....	17
V	Low pH Runs.....	18
VI	Effect of Groove Size on Activity (Batch Tests).....	20
VII	Flow Correlations with Different Pore Sizes.....	52
VIII	Flow Activities for Different Carriers.....	52
IX	Effect of Mesh Size (Flow Test)....	52
X	Effect of Mesh Size (Beaker Tests).	52
XI	Effect of Pore and Mesh Size.....	54
XII	Zeldowitsch's Postulate of log k (activity) vs reciprocal absolute temperature.	44

## SUMMARY

Previous work by Isbin and his associates has shown that changes in the pore width of a catalyst used in the decomposition of hydrogen peroxide had no effect on the activity of the catalyst, although the total area obtained with varying mesh size was in direct proportion to the activity. The analogous case of the effect of groove width has been investigated here.

Lead plates of consistent dimensions were prepared from lead sheet and grooves of widths ranging from 0.005" to 0.125" were cut in the plates. While a consistent groove depth of 1/16" was attempted, this can only be regarded as a good average value, with extreme deviations as great as 0.02" existing.

Flow tests on ungrooved catalyst plates failed to give results that correlated. Some investigation was made into this lack of correlation without positive result.

A single flow test on a grooved catalyst set gave visual evidence that the grooves were not penetrated by the peroxide. Numerical results of this test were within the range of error of the tests on ungrooved plates.

A single flow test on 2 ungrooved catalyst sets, while showing some increased activity, did not show sufficient correlation with area to allow use of the flow system to determine effect of groove size.

Batch tests on ungrooved and grooved catalyst plates were carried out with peroxide acidified with acetic acid. The acetic acid acted to remove colloidal lead from the system,

allowing the lead plate to remain the sole catalyst. Some solution of the catalyst occurred.

Under batch conditions, activity was shown to be linear in total area, i.e. the surface added by grooving the lead was effective. This relation held within reasonable error in spite of a 5°C temperature range and slight variations in the pH of the peroxide used, except for the highest area specimens tested for which results were erratic.

## INTRODUCTION

While the subject of two phase heterogeneous catalysis has been studied both quantitatively and qualitatively for a considerable time,<sup>#</sup> data on three phase heterogeneous catalyses, where one phase reacts on the surface of a second to produce a third, are almost entirely lacking.

Similarly, although some work has been done on the effect of pore size in a catalysis, the effect of linear interstices, i.e. grooves, has not been studied.

Work by Isbin and his associates (See Appendix B) indicates that the pore size of a catalyst has no effect on the steady-state decomposition rate of hydrogen peroxide. This is somewhat confirmed by the statement of Dr. Demant<sup>1</sup> relative to a somewhat analagous situation in the use of catalyst stones. It was also found by Isbin that the mesh size of his catalyst had a definite effect on the rate of decomposition of the peroxide, such that small grains gave faster decomposition per unit weight of catalyst.

These results with varying mesh are in accord with the thesis that decomposition rate is a function of the catalyst area, catalyst activity increasing with increasing mesh (i.e. decreasing grain size). The results with various porosities, on the other hand, do not agree with this thesis as the in-

---

<sup>#</sup> A more detailed review of the relevant work is included in Appendix A.



creased area due to smaller pore size seems to have no effect.

Two questions are raised by Isbin's work. First, to how large a pore size can his results be applied? Second, will grooves of varying width give results similar to pores of the same width or would the addition of a long side to the interstice allow its full area to be attacked? This thesis concerns itself with the second of these questions, using the decomposition of hydrogen peroxide on a lead catalyst as the system.

## PROCEDURE

### 1. Forming of lead plates.

Lead used was American Smelting and Refining Co. sheet lead, 3/16" thick, 99% pure (minimum) lead. Sheet was cut to approximate size on a wood saw and placed in a previously milled steel die. The lead was then pressed into the die by means of an arbor press. Forces as high as 400# were used. After the lead had flowed into the edges of the die sufficiently, the die was removed from the press and excess lead removed with a wood chisel. Some slight surface scratching did occur with use of the chisel but area added by these scratches was negligible. Two die sizes were used, resulting in two plate sizes;  $.140 \pm .002$ " x  $.500 \pm .005$ " x  $.975 \pm .01$ "; and  $.140 \pm .002$ " x  $.825 \pm .005$ " x  $1.000 \pm .01$ ". (These plates will be referred to below as "1/2 inch plates" and ".825 inch plates" respectively). For flow tests, the width of the ".825" plate was filed down to  $.812 \pm .005$ " width.

### 2. Grooving of plates

Three ".825" and six 1/2" plates were held in a specially milled flat steel holder. A ridge 1/16" high ran along the edge of the holder and kept the plates in place. The area in which the plates rested was 5.48" x .980" and the plates were laid side to side along the flat. In general, the plates were filed to  $.975 \pm .005$ " length by  $.815 \pm .005$ " or  $.500 \pm .005$ " width before being fitted into the holder. Fit was tight without buckling.

Grooves of .012", .032", .062", and .125" were cut with a "cutting off" milling cutter. Plates were held down by weights during grooving. Surface burrs were filed down after each groove was cut. In general, four passes were made with the cutter, no burr filing being necessary on the last pass. Where excess metal was left in the groove, it was cleaned out with a .007" spring steel blade. Some scratching of the groove sidewall surface occurred during this cleaning but the added area is small. Some expansion during grooving occurred with the .012" and .033" grooved pieces. In spite of the originally tight fit and weighting of the plates, considerable buckling and movement apparently was present as variation in depth in the extreme case (one of the .062" grooved specimens) was as much as .02". Some of this variation was taken into account in estimating areas of specimens, however.

.005" grooves were cut with a .005" spring steel blade held in a specially turned steel holder. The holder fitted into the spindle of a vertical milling machine, which was tightly clamped after the blade had been aligned with the lead plates. The lead plates, in their holder, were fed manually past the steel blade. A slight surface rise and some expansion of the plates occurred during grooving.

### 3. Flow test procedures

The flow test procedure was designed initially to approximate that of Isbin, Farrell, Thompson and Meadows as described in their Progress Report No. 5. Their procedure, however, involved flowing peroxide past catalyst impregnated granules

whereas the study of grooved plates requires a fairly massive catalyst to support the grooves. Two 1/2" plates and one .812" plate were therefore placed in the reaction tube and separated with glass beads as shown in Figure II. The beads and catalyst plates were then supported with a stainless steel wire support. The whole flow assembly is shown in Fig. I.

Steps in each run were as follows:

- a. Lead plates were washed. (6N NaOH used in first four runs, soap and water or nothing used in remainder)
- b. Glass beads and stainless steel support were washed in 48% H<sub>2</sub>O<sub>2</sub> to which a few drops of nitric acid had been added.
- c. Reaction tube was washed in soap and water followed with nitric acid.
- d. Reaction tube was packed. Beads were in contact and separating lead plates at all points.
- e. Catch flask below reaction tube was filled to 1/4 depth with approximately 5% phosphoric acid.
- f. Burette was filled with peroxide.
- g. Rubber cover on joint above reaction tube was wired down.
- h. 10 psig oxygen pressure was kept above peroxide.
- i. Peroxide was allowed to flow (at about 7ml/min) till activation occurred (as evidenced by fogging below reaction tube).

j. Reaction tube was angled so that flow was as even as possible from all sides of tube.

k. Readings of burette and wet test meter were taken at alternate 30 second intervals (i.e. burette readings were taken each minute).

l. Wet test meter temperature and barometric pressure were taken at the end of each run.

Flow rate was controlled either by stopcock or by micrometer adjustment on rubber tube between burette and reaction tube. Neither adjustment was very satisfactory. Although the micrometer gave satisfactory adjustment on tests made with water running through the burette, flow rate during a peroxide run did not respond rapidly enough to micrometer to be readily controlled. Conditions therefore were only approximately steady-state for each flow rate.

Five types of peroxide were used in flow tests.

These were:

A. Undistilled peroxide; - diluted from Becco 85-93% commercial peroxide to s.g. 1.190. (Used in runs 1-6)

B. Distilled peroxide, - diluted from peroxide distilled at M.I.T. to s.g. 1.190. (Used in runs 6-13, A-E,

G-1, and S-1)

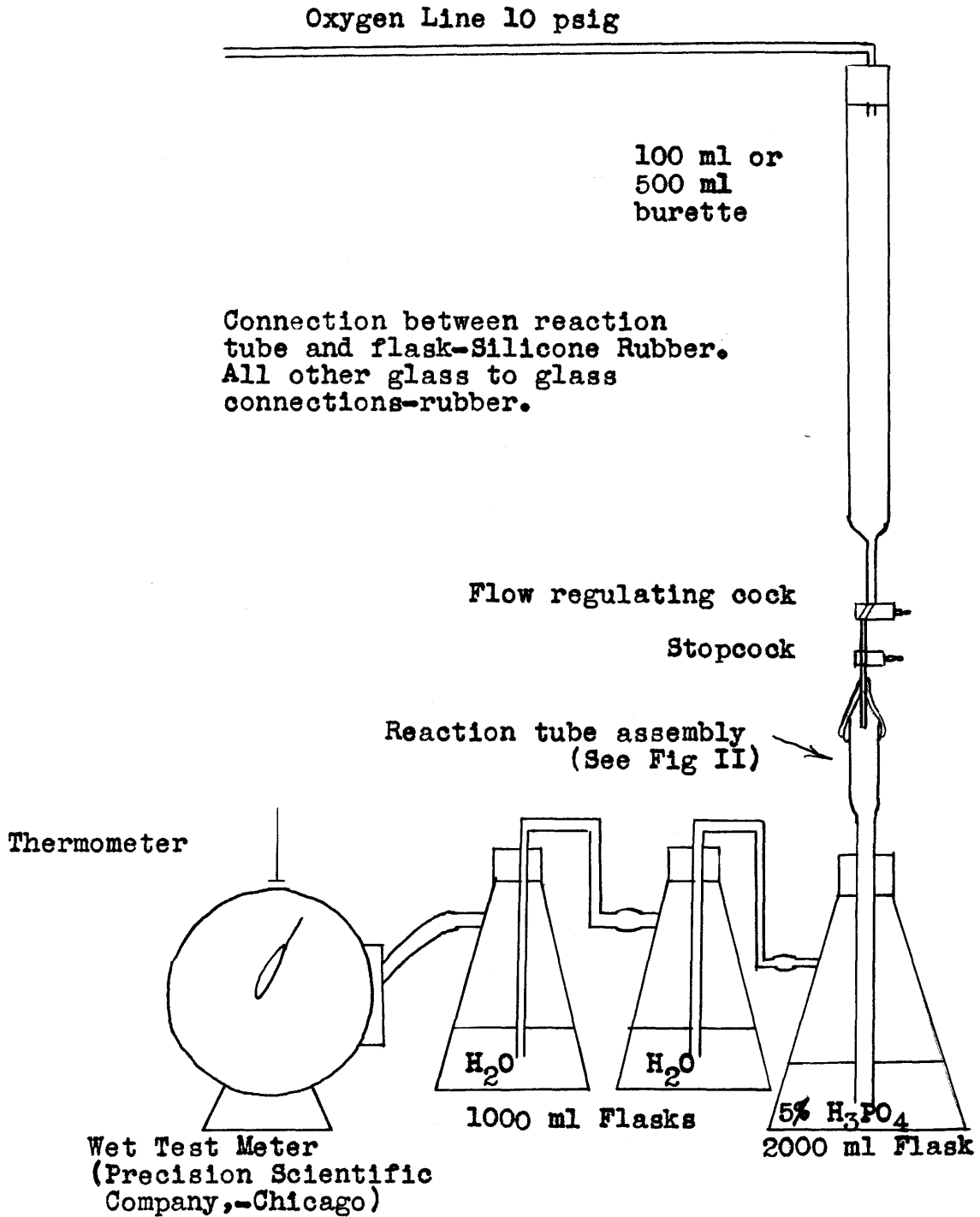
C. Alkaline undistilled peroxide, - Becco 85-93% commercial peroxide diluted to s.g. 1.208 with added NaOH solution sufficient to give .06N Na<sup>+</sup>, and approximately 48% hydrogen peroxide. pH on tenfold dilution 9.0.

D. Alkaline undistilled peroxide, -Becco 85-93% commercial peroxide diluted to s.g. 1.208 with added NaOH solution sufficient to give .006N Na<sup>+</sup>, and approximately 48% hydrogen peroxide. pH on tenfold dilution 7.5-8.

E. Acid undistilled peroxide, -Becco 85-93% commercial peroxide diluted to s.g. 1.208 with added HNO<sub>3</sub> solution sufficient to give .0015N NO<sub>3</sub><sup>-</sup>, and approximately 48% hydrogen peroxide. pH on tenfold dilution 3.85-4.9. (Used in tests P-3, 14, and 15).

Each run used a different catalyst set with the exception of runs A-E and P-1 to P-3 which all used the same catalyst set. Runs A, B, D, E, and P-1 represent repackings of the same catalyst set. Run C used the set and packing of B after a 2 day wait. Runs P-2 and P-3 used the same set and packing as P-1 but the packed sets were washed between runs and different peroxides

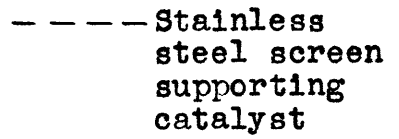
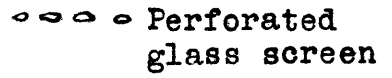
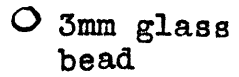
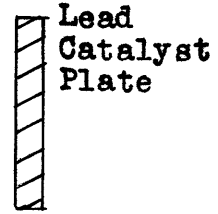
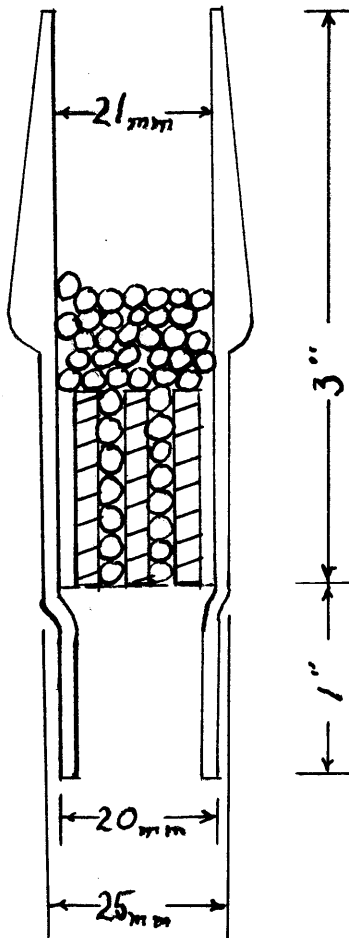
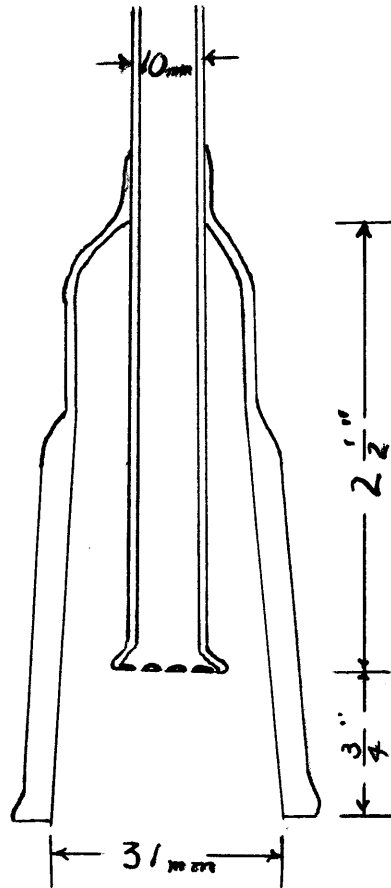
FIG I  
FLOW TEST APPARATUS



CFD  
1/16/1947

FIG II

ZOONCHACH  
 YFWSUSAFWC



Basic Unit is 25 mm  
 Pyrex Glass Joint

Inch (") Dimensions  
 are lengths

Millimeter (mm)  
 Dimensions are  
 diameters

1" 1"

1mm 1mm

WFD  
 1/16/1947



were used on each.

#### 4. Batch test procedures

The main obstacle to a successful batch procedure to test activity of a lead catalyst is the formation of colloidal lead oxides and hydroxides (which are quite active catalysts) throughout the peroxide solution. This would result in a total obscuring of the effect of the lead catalyst and a substitution of the effect of the far higher area colloidal lead particles. To avoid this, batch tests were run in a slightly buffered acetic acid solution as the formation of stable lead acetate molecules in solution would tend to prevent precipitation of colloidal lead. Two adverse effects result from this acid solution, however, - the slowing down of the rate of reaction on the lead and possible introduction of side reactions, -either solution of the lead in acetic acid giving off hydrogen or reduction of the acetic acid by peroxide giving hydrogen and oxygen. The latter reaction is unlikely, and certainly does not occur in the absence of a catalyst. The former reaction occurs only slowly, even at boiling temperature. Therefore, if it occurs in our system, it occurs as a result of three phase heterogeneous catalysis, which is being studied in any case.

Becco 85-93% undistilled peroxide was therefore diluted to s.g. 1.190 and 50 ml glacial acetic acid/liter 48% H<sub>2</sub>O<sub>2</sub> and 40 ml 0.6N NaOH/liter 48% peroxide added. This solution gave pH 3.3 -3.5 upon tenfold dilution.

Lead plates were measured with a micrometer and areas calculated on the basis of perfect rectangular prisms with perfectly rectangular grooves of constant average depth. These calculations can conceivably be in as much as 10% error due to burring, scratching and buckling errors, although average error should be much smaller than this maximum. It should be noted that ungrooved plates were of far more perfect shape than grooved pieces.

Reaction vessel was 500 ml graduate cut down to a height of 300 ml. 25 ml of acidified peroxide solution was used in each test.

Catalyst plate was thoroughly washed with soap and water and dried with a clean towel. Initial temperature of the peroxide solution was taken. The catalyst, held in stainless steel tongs, forceps, or wire, was then lowered into the peroxide. The time for violent bubbling to start and the time for bubbling to end (as estimated by eye) was determined with a stopwatch. Maximum error on this eye measurement is probably  $\pm$  0.1 min, average error considerably less.

Final temperatures of the peroxides were found to be insignificant and were only taken in a few runs. Some variation existed in the height that catalysts were held off bottom of reaction vessel which may or may not be significant. A test with catalyst laying on bottom of vessel resulted in a partially unattacked catalyst and was discarded. Some unattacked area also was present with the higher-area ungrooved tests which necessitated use of several plates (to equal total area secured by grooving plates.)

Stainless steel holders were washed with 48% peroxide with a few drops of nitric acid added. Reaction vessel was washed with concentrated alkali, followed by rinse, then soap and water.

## RESULTS

### 1. Flow Tests

#### A. Organization

Flow test results are shown in this section as percent peroxide undecomposed vs  $100/\text{flow-rate-in-ml/min.}$  For a constant volume system, this would give a result comparable to organization as concentration of reactant vs time. Thus, a semilog plot of some of Isbin's results shown in Appendix B, gives a straight line for a first order reaction. Results by run in the original rate form are listed in Appendix C.

#### B. Percent Deviation

Tables in Appendix C include average percent deviation, calculated from original data found in the Thesis Notebooks, copies of which are in the possession of Prof. D. B. Broughton. Results in which the average percent deviation is greater than 15% are, with a few exceptions not included here but are listed there. Values are not of equal weight as number of readings for a particular flow rate varied for each run and some judgment was used in estimating "steady state". Flow rate varied during run (generally dropping several percent) and the use of averages reflects approximate steady state. It should be especially noted that percentages deviation

merely give range of values of data for the run concerned, and do not include possible errors in method, observation, etc. which are possibly much larger.

### C. Numbering and history of runs.

Runs one through six were made with undistilled peroxide. Run one was made with only one plate which had been preactivated in 48% peroxide. All other runs were made without activation as appearance of catalyst from run two after end of run was the same as that of one. In general, no data were taken until 20 ml after fog of peroxide first passed through bottom of tube indicating that lead was active. Runs one through six showed evidence of decrease of activity as the run went on. For this reason distilled peroxide was used in later runs.

Runs six through thirteen were made with distilled peroxide. Correlation between these runs was not particularly good, differences as great as 39% undecomposed existing between runs at approximately the same flow rate, (cf. Table I).

Considerable difficulty was found in obtaining consistent data within each run. The tabulated data, while reflecting what appeared to be the most consistent part of any run, reflect errors as great as 15%. Examination of Appendix C will show deviations as great as 60% in

some runs at some flow rates.

Runs A, B, C, D, and E used the same lead catalyst, Run C was made after the catalyst from B had been standing in the reaction tube for 2 days. A considerable increase of activity was present (as may be seen from Table II or Fig. IV). For this reason, runs 6E, 8E, and 12E which were similar cases of wait between runs on the same catalyst, are not included in the tabulation of this section, although listed in Appendix C.

Runs P-1 and P-2 were at high pH. Both resulted in visible leaching of lead oxide on to the catalyst tube and glass beads. Inasmuch as lead oxide itself is an active catalyst, these runs were discarded without record of data. A consistent oxide coating was formed on the catalyst plates as well.

Run G-1, made with a 1/16" width grooved catalyst apparently offered no entry of peroxide into the extra catalyst area. Light was visible through the grooves of the catalyst at flow rates up to 10 ml/min.

Run P-3 using low pH peroxide gave good consistency of gas evolution at each flow rate. For this reason, runs 14 and 15 were tried with acid peroxide. Within-run consistency of these runs was only slightly better

than with non-acidified peroxide.

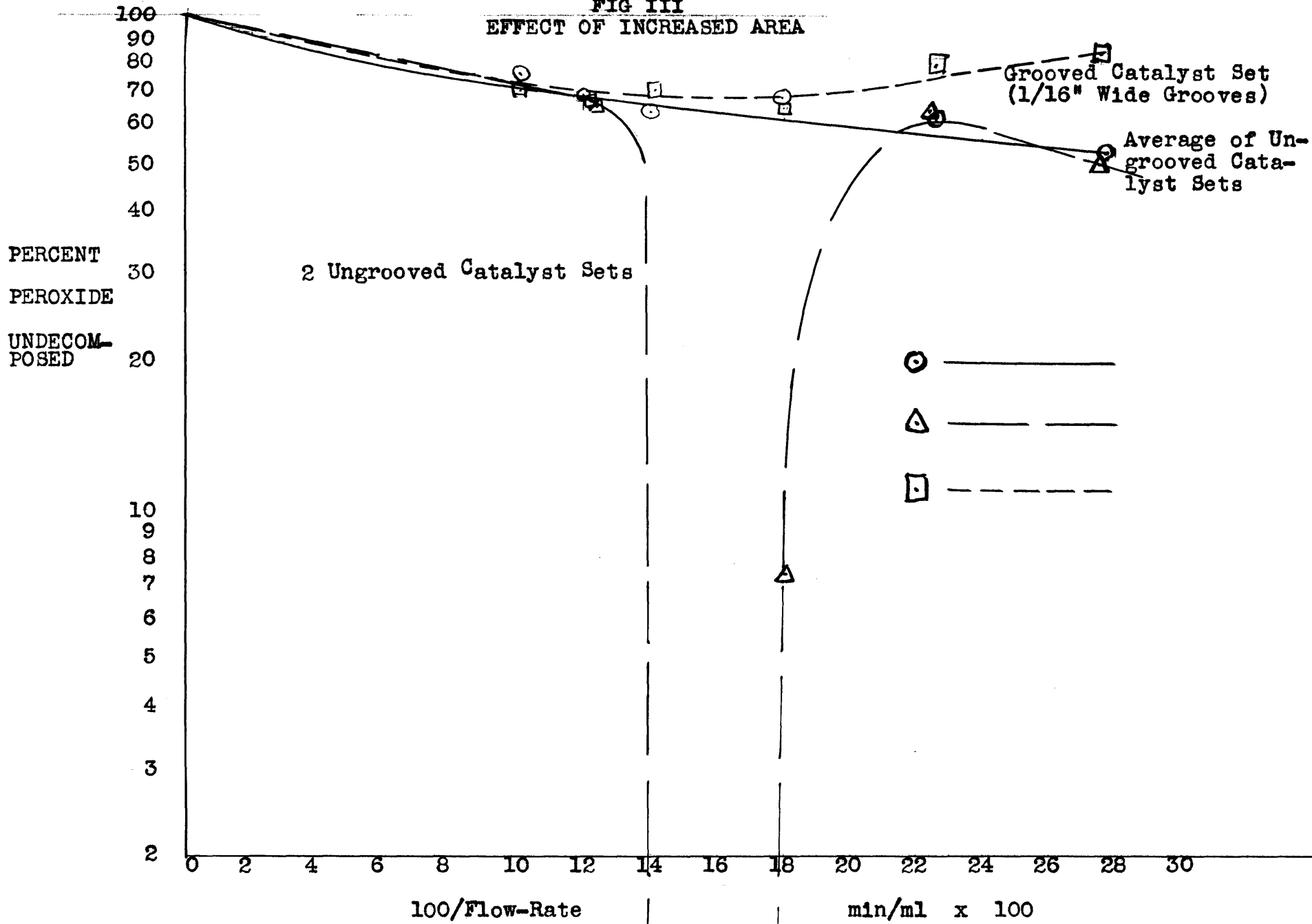
#### D. Appearance of catalyst after runs

With the exception of runs P-1 and P-2, catalyst appearance after each run was approximately the same, consisting of blotches of oxide on the bottom and edges of each catalyst plate which lightened to mere circles at the top of the plate. The pattern of bead packing was visible from the rings of oxide. While the appearance of these catalysts was approximately the same, the blotches, of course, were placed somewhat differently on each catalyst and covered a somewhat different area.

The catalysts from runs P-1 and P-2 were covered with a fairly even coat of orange-brown lead oxide, broken only at regular points on the faces where the glass bead packing touched.

It may be noted that preactivation tests gave an uneven oxide coating with 48% peroxide, and a fairly even coating with a 10 second dip in 85% peroxide. The latter procedure is dangerous as violent reaction may occur within the ten second period and violent spattering will occur in any case when the catalyst is removed from the solution.

FIG III  
EFFECT OF INCREASED AREA



0% Undecomposed

AFD  
1/16/1947



Table I

COMPARISON OF RUNS AT SAME FLOW RATE

100/F from 11.5 to 13.5

% Undecomposed	100/Flow Rate	Run Nr.	Comment
68.4	13.5	10	One cat. set.
64.3	11.5	11	"
34.1	12.6	12M	"
72.0	12.0	A,B,D,E avg.	"
68.9	12.0	G-1	One grooved set
68.6	11.8	S-1	Two cat. sets
66.8	12.8	S-1	"
0	13.3	S-1	"

Table II

% UNDECOMPOSED AT VARIOUS FLOW RATES FOR

VARIOUS CONDITIONS (Averages)

100/F Range	1 Set, Undist. H <sub>2</sub> O <sub>2</sub>	1 Set, Dist. H <sub>2</sub> O <sub>2</sub>	Grooved Set	Two Sets	Low pH
2.6					83%
5-7					75.8%
7-9					0-75.1%
9-11		75%	71%		0-87.8%
11-13.5		68.2%	68.9%	67.7	5.2-88.1%
13-15	74.9%	64.5%	#70.1%	0	
17-19		68.1%	64.8%	7.4%	0-80%
20-25	86.4%	62.1%	79.7%	#64.1%	3.7%
25-30		52 %	84.1%	51.4%	

---

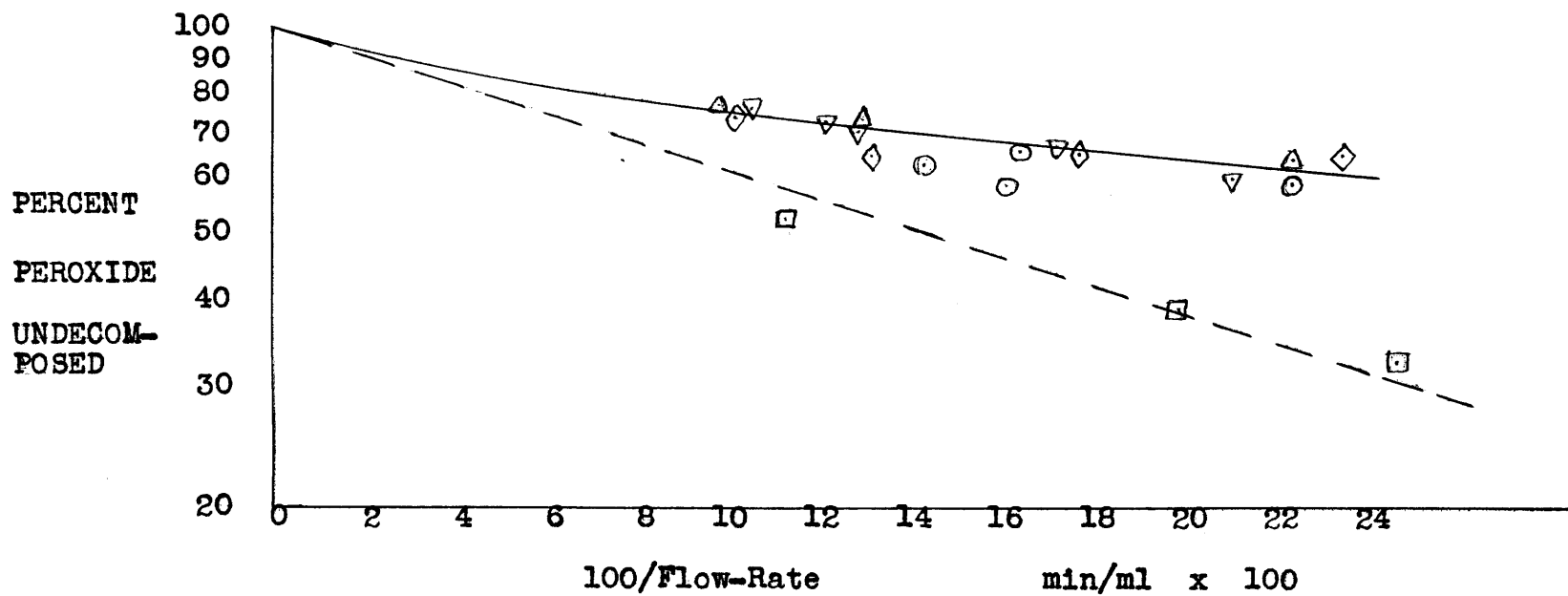
#Error Exceeds 15%

FIG IV

EFFECT OF REPACKING AND WAITING

- Run A
- △ Run B Repacking of A
- Run C B after 2 days
- ◇ Run D Repacking of C
- ▽ Run E Repacking of D

Distilled 48% peroxide  
Ungrooved Catalyst Set



*WFO*  
1/16/1947

Table III

EFFECT OF PACKING AND WAITING ON ONE CATALYST SET

Flow Rate ML/MIN	100/F MIN/ML	%Undecomposed	Run Nr.	Comment
4.5	22.2	59	A	
9.4	16.2	66.8	A	
7.1	14.1	62.8	A	<u>single point</u>
6.3	15.9	59.7	A	" "
4.5	22.2	60.4	B	Repacked cat. A
7.8	12.8	73.0	B	" " "
10.3	9.7	77	B	" " "
4.1	24.4	32.5	C	B after wait
5.1	19.6	38.8	C	" " "
9.0	11.1	52.5	C	" " "
4.3	23.2	65.0	D	Repacked cat. A
5.7	17.5	65.5	D	" " "
7.7	13.0	65.6	D	" " "
10.0	10	74.1	D	" " "
4.8	20.8	#60	E	Repacked cat. D
5.9	17.0	67.0	E	" " "
7.9	12.7	70.8	E	" " "
8.3	12.0	72.4	E	" " "
9.6	10.4	76.2	E	" " "

---

#Error Exceeds 15%



Table IV

Low pH Runs

<u>% Undecomposed</u>	<u>100/F</u>	<u>Run Nr</u>	<u>pH upon dilution</u>	<u>Comment</u>
0.0	23.2	P-3	3.8-4.6	
4.7	21.8	"	"	
12.5	16.1	"	"	
0.0	14.9	"	"	
7.0	12.2	"	"	
5.2	11.3	"	"	
3	10.1	"	"	
15.6	31.2	14	4.1	
6.7	23.8	"	"	
3.5	20.8	"	"	
0.0	19.2	"	"	
0.0	10.7	"	"	
0.	9.6	"	"	
0.0	8.7	"	"	
74.5	4	"	"	Single point
84	2.6	"	"	
80	17.3	15	4.0-4.9	
88.1	12.6	"	"	
87.8	11.0	"	"	
79.1	9.1	"	"	
75.1	8.0	"	"	
80.8	6.5	"	"	
79.8	6.2	"	"	Single point
84.8	5.7	"	"	
62.9	5.5	"	"	
82	2.6	"	"	
84.3	2.3	"	"	Single point

Table V

Standard Grooving of Catalyst Plates

Goove Width (in)	.125	.063	.032	.012	.005
Grooves per Inch	4	7	15	10	10

## 2. Batch Tests

Activity of catalyst in the batch tests is measured as the reciprocal of the time necessary for the decomposition of 25 ml of peroxide solution. Fig. VI is a plot of this activity vs the total area of catalyst in the test. The straight line used was the best line through the points determined for ungrooved catalyst areas. Points for grooved catalysts were then placed on this plot. Points in blue are plotted against surface area of catalyst (i.e. disregarding all area added or inside grooves).

Some spattering occurred during the runs, but its effect is probably negligible. Worst spattering occurred with ungrooved pieces. Liquid remaining in reaction tube was quite viscous and had an odor of vinegar. If the catalyst remained in the solution, further reaction could be obtained by adding hydrogen peroxide solution but not by adding acetic acid. Surface of the catalyst was black and somewhat gummy. The black coating washed off with soap and water and rubbing. Some of the runs on ungrooved catalysts represent plates that were re-used after washing. Results using these plates are not distinguishable from those using fresh plates.

Loss of lead in each run was considerable, amounting

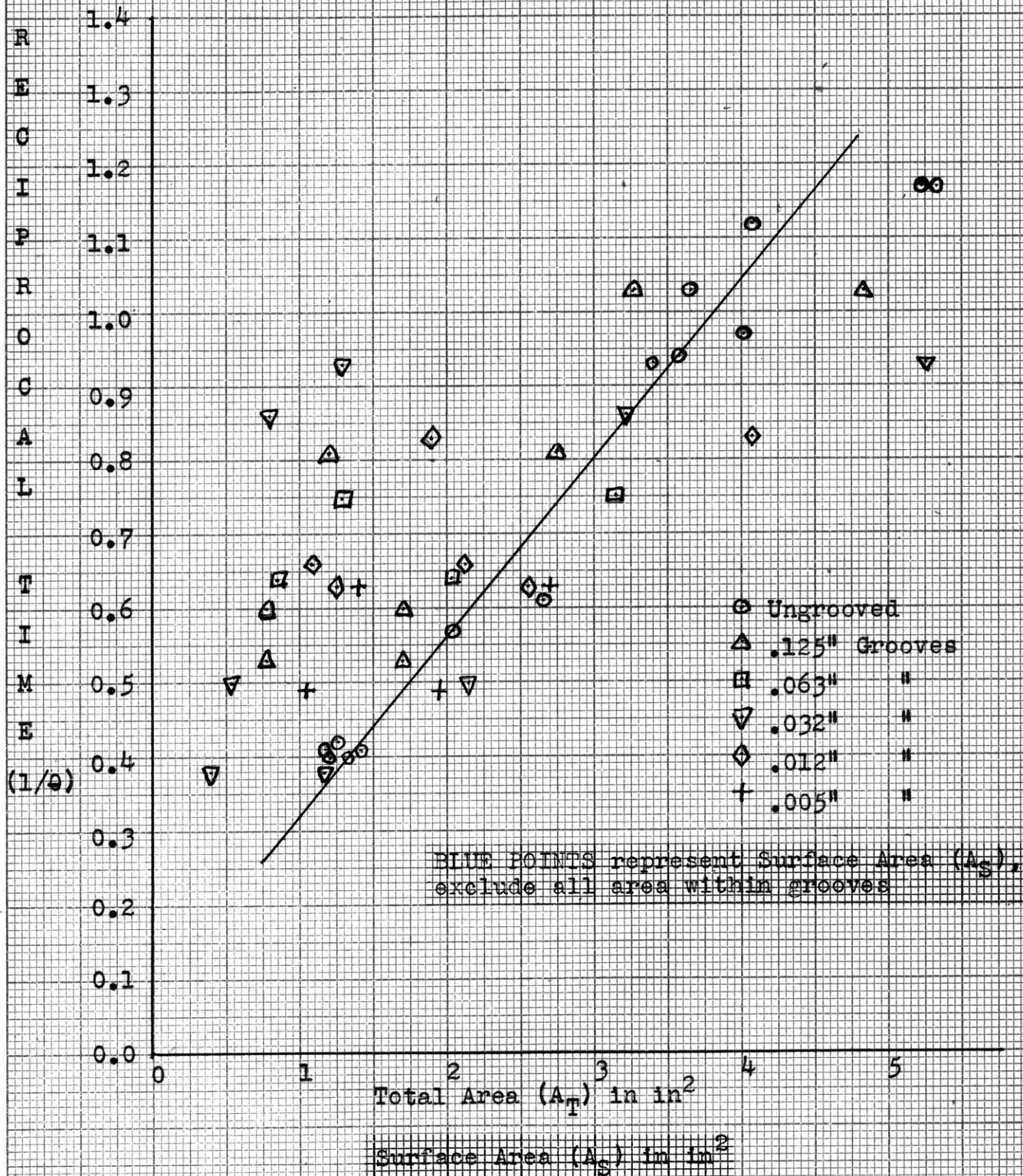
to .002" to .005" from each dimension of the plate. The change in surface area from this effect was neglected.

Observation with a shop microscope of used catalysts showed an average increase in groove width of about .003". Area added by this increase was not significantly large.

High area ungrooved catalysts consisted of several plates resulting in some blocking of peroxide from the plates. Effect of this blocking is not evident in the plot.

FIG VI

EFFECT OF GROOVE SIZE ON ACTIVITY  
-Batch Tests-



WFO  
1/16/1947



Table VI

Batch Test Summary

$A_T$ in <sup>2</sup>	$A_S$ in <sup>2</sup>	$\theta_T$ min	$\theta_V$ min	$1/\theta_T$ min <sup>-1</sup>	$1/\theta_V$ min <sup>-1</sup>	$t_o$ °C	G.S. in	pH on dil	Comment
1.42	1.42	2.44	1.14	.41	.88	24	none	3.3.-3.43	avg. of 12 tests; used as standard
3.58	3.58	1.06	.54	.94	1.85	25	none	3.35	single test
2.05	2.05	1.77	1.07	.57	.93	24.5	"	3.35	" "
1.33	1.33	2.53	1.13	.40	.89	22	"	3.43	" "
2.66	2.66	1.65	1.13	.61	.89	24	"	3.31	" "
3.40	3.40	1.08	.83	.93	1.21	24	"	3.31	" "
3.64	3.64	.97	.77	1.03	1.30	24.5	"	3.31	" "
1.19	1.19	2.50	.99	.40	1.01	24	"	3.31	" "
1.26	1.26	2.38	1.12	.42	.89	24.5	"	3.31	" "
4.07	4.07	.89	.57	1.12	1.75	25	"	3.31	" "
4.37	4.37	.96	.66	1.04	1.52	24	"	3.31	" "
1.18	1.18	2.45	1.22	.41	.82	25	"	3.31	" "
4.01	4.01	1.02	.52	.98	1.92	23	"	3.31	" "
5.32	5.32	.85	.65	1.17	1.54	23	"	3.31	" "
5.22	5.22	.85	.61	1.17	1.64	22.5	"	3.31	" "
1.72	.78	1.67	1.47	.60	.68	23.8	.125	3.35	avg. of 2 tests
1.72	.78	1.90	1.68	.53	.59	23.4	.125	3.37	" " " "
2.74	1.19	1.23	1.10	.81	.91	23.5	.125	3.43	" " " "
4.84	3.29	.97	.87	1.03	1.15	25	.125	3.31	single test

Table VI (Continued)

$A_T$ in <sup>2</sup>	$A_g$ in <sup>2</sup>	$\Theta_T$ min	$\Theta_V$ min	$1/\Theta_T$ min <sup>-1</sup>	$1/\Theta_V$ min <sup>-1</sup>	$t_o$ °C	G.S. in	pH on dil	Comment
2.03	.85	1.56	1.30	.64	.77	24	.063	3.38	avg of 3 tests
3.13	1.29	1.33	1.11	.75	.90	24	.063	3.43	" " 2 "
2.15	.54	1.98	1.86	.50	.54	23	.032	3.31	single test
3.22	.80	1.16	1.09	.86	.92	25	.032	3.38	avg of 3 tests
5.26	1.27	1.08	.93	.93	1.08	23.5	.032	3.43	" " 2 tests
1.18	.38	2.64	2.52	.38	.40	24	.032	3.43	single test
2.55	1.23	1.58	1.36	.63	.74	24.2	.012	3.38	avg of 3 tests
2.11	1.08	1.51	1.41	.66	.71	23.8	.012	3.35	single test
4.07	1.90	1.21	1.03	.83	.97	23.5	.012	3.43	avg of 2 tests
2.71	1.39	1.59	1.36	.63	.74	24	.005	3.31	avg of 3 tests
1.95	1.03	2.03	1.73	.49	.58	26	.005	3.31	single test

$A_T$  : Total area of grooved plus ungrooved surface.

$A_g$  : Surface area disregarding all area within grooves.

$\Theta_T$  : Time for decomposition of 25 ml of batch peroxide mix.

$\Theta_V$  : Time from start of violent bubbling in peroxide to decomposition of 25 ml of batch peroxide mix.

$t_o$  : Initial temperature of peroxide before addition of catalyst.

G.S. : Catalyst groove size.

avg. : Average

## DISCUSSION OF RESULTS

### 1. Batch tests

Within the range of error possible in estimating areas of grooved plates and the error inherent in an eye estimation of the "end" of gas evolution, it can be seen from Fig VI that, in general, the total area produced by grooving is as effective catalytically as the area of ungrooved pieces.

With the exception of the .005" groove width, points for each groove width lie on both sides of the "average line". This is particularly significant because the "average line" was drawn on the basis of ungrooved points alone and therefore represents the normal activity-area relationship for the system.

Above 4 sq. in. area, there is evidently some departure from the straight line, both for grooved and ungrooved catalysts, although the effect is apparently the greater for grooved catalysts. Several explanations may be hazarded for this falling off, none of which are completely satisfactory.

At high activities, the effect of error in estimating end of decomposition is multiplied. For example, a 20 second error at a decomposition time of 2 minutes will appear as 0.1 min<sup>-1</sup> error in

activity. For a decomposition time of 1 minute, the 20 seconds will appear as  $0.5 \text{ min}^{-1}$  error in activity. The actual error in estimating end of decomposition, of course, is not nearly this large, but any other errors of a constant time interval effect will be magnified similarly.

If the values are not in error, (and all of these points are the average of two approximately equal values), the explanation may be the necessity for intermittent action at high areas. The volume of oxygen formed at the surface during a small time interval may be so great that no peroxide can enter until the oxygen is dissipated. This action would tend to be worse with decreasing groove width as stability of a hypothetical oxygen film in the grooves is probably greater than at the surface. The objection to this argument is that the oxygen produced per unit area for the large catalyst should be not greater than for the small catalyst, and interference, therefore, should be no greater.

A somewhat more tenable version of the intermittent action idea would be the intermittent production of sufficient oxygen to blow the solution away from the catalyst completely. This would set an upper limit to oxygen production rate, any greater speed resulting in blowing

the solution from the catalyst and a slower net rate. The objection to this proposal is that it does not adequately explain the difference in this effect for various groove sizes at the same area. Moreover, such an effect was not visible during the runs, although it may have been hidden by foaming.

Another explanation might be based on the effect of the edges of the catalyst on its activity. This breaks down on the fact that the groove edges provide so many more edges than the plate itself does that change in the ratio of plate edges to surface should be inconsequential.

Another possibility is the effect of groove length. All the high-area-underactive grooved specimens had a groove length of about "0.825", while most of the pieces following the straight line had a groove length of about 0.500". Objections to this reasoning are that two ungrooved pieces also showed low activity at high area (although not as low activity as the grooved pieces), and that two pieces of the same long groove length and lower area followed the normal "average line" and did not show low activity. This is particularly notable in that the 1/8" groove width, a long groove

length piece of lower area followed the normal line and one of higher area showed the low activity effect.

It is also difficult to ascribe the drop in activity to geometrical effects as, of the four points showing high area-low activity, three represented different shapes.

Of the above explanations for the deviations at high area, a combination of intermittent action and magnification of errors would seem to be the most tenable explanation, although any and all of the others may enter. No one explanation is completely satisfactory.

It may be seen from the blue points of Fig. VI that activity is not a function of surface area. This is more apparent if we consider all ungrooved points as part of the attempted surface area correlation.

An attempt (not shown) to correlate surface area excluding grooves with time of violent reaction ( $\theta_v$ ) was without success. This indicates that even during the violent reaction period, total surface rather than surface excluding grooves is effective.

It should be noted that, although values of .005" width grooves are all within the range of error of the "average line" of Fig IV, they <sup>are</sup> unique in that both points taken are underactive. Correlation of total surface with

the "average line" is, however, considerably better than that of surface excluding grooves. Proof that .005" grooves are completely effective, therefore, may not be considered conclusive.

The reasons for using a straight line which does not pass through the origin to express the data of Fig IV, rather than assuming proportionality as Isbin did in treatment of similar data (see Appendix B) are first, that while zero area exhibits negligible activity (i.e. rate of uncatalyzed decomposition of peroxide is slow), the action of very small areas cannot be assumed without test as the rate of solution of the lead, while negligible at the areas used, is relevant at small areas. The activity at any small area, therefore, must include solution effects unless rate of solution is also directly proportional to area (for which there is no evidence in this test). The more cogent argument, of course, is that a straight line not passing through the origin fits the data better than an assumption of proportionality does. It may also be noted that parabolas or hyperbolas could be constructed to fit the data as well as the straight line used.

## 2. Flow tests

The attempt to use a flow system to measure the effect

of groove width on the activity of the catalyst was unsuccessful.

A. Runs on ungrooved catalyst sets did not correlate particularly well. The best average of the best of these runs gave points which did not fit into a smooth curve but which diverged more or less from a straight line on a semilogarithmic plot (Fig III). Technically sound results, therefore, could only be attained by a very large number of runs (e.g. 50-100) and comparison of good statistical averages. Even if this were done, results would not be good for predicting the action of any single future run.

B. Doubling the amount of catalyst present in one run gave results which did not follow any regular pattern. At the majority of flow rates, activity of the catalyst of double area was not distinguishable from activity of the normal ungrooved catalyst within the limits of error. At some rates there was a greatly increased activity but this increase in activity showed no apparent relation to the amount of area increase. (cf. Fig III). Thus available area is apparently not a factor of unique importance in this system. It is not possible, therefore, to study the effect of grooved specimens on the basis of area increase



to the system.

C. Observation of a single run on a grooved specimen showed that liquid flowed past the grooves without entering, indicating that at the flow rates studied, the mechanical opposition offered by a ridge to flow was sufficient to annul the effect of any area added by grooving. While the data on this run, indicating, in general, a lower activity, agreed with this observation, they are, of course, insufficient to show the actual performance of grooved catalysts in the system. The visual observation of flow pattern interference, however, should be sufficient evidence of the unsuitability of the system.

D. Attempts to improve correlation by changing pH (in the hope of promoting stability and uniformity of the active surface), as can be seen from Fig V were a failure. While evolution of oxygen within any low pH run was very slightly smoother, runs correlated even more poorly than normal pH runs. Theory would indicate that acid peroxide dissolves the catalytically active lead oxides, resulting in a somewhat less active catalyst. This is borne out by one run which was less active and refuted by two runs in which the catalyst was considerably more active than with normal peroxide.

High pH apparently encouraged the formation of active

lead oxides. Lead oxides leached out, however, and precipitated on the reaction tube and glass bead packing. While this offers potentialities as a method of preparing a catalyst to decompose peroxide, it obviously interferes with any attempt to estimate the effect of grooving of the lead.

E. Fig IV shows the effect of repacking on the flow system. For any one catalyst, the effect of repacking is not very great and the four repacked runs correlated considerably better than normal runs with different catalyst sets. Apparently, the packing technique used was consistent and not the cause of the lack of correlation. Moreover, repacking does not seem to effect the portion of lead catalyst activated or its degree of activity.

The effect of time in the reaction tube was shown by one run made after allowing the catalyst to remain in the reaction tube for 2 days. Activity increased considerably, probably due to leaching of oxide on to the glass beads and reaction tube walls by peroxide solution remaining in the reaction tube. Another possible cause of the increased activity is attack of the lead surface by peroxide vapor and air present in the reaction tube, - presumably to form a finer and more adherent catalytic oxide coating.

Table VII

POSSIBLE CAUSES OF LACK OF CORRELATION

Confirmatory Facts

Discrepant Facts

A. Variation in flow pattern with packing

- |  |   |
|--|---|
| 1. Each catalyst was browned over a different amount and in different spots, indicating flow reached different places.           | . 1. Repacking of one catalyst set resulted in fair agreement of data with original packing data. |
| 2. Small differences in thickness and width of catalyst exist and might cause appreciable difference in flow with tight packing. | .   |
| 3. Point of drip from reaction tube varied visibly from run to run.  | .   |

B. Alternate and variable deposition and solution of active surface.

- |   |  |
|---|--|
| 1. Results vary during run with one catalyst set. | . 1. In acid solution, where this effect is slight, results correlated even more poorly. |
|   | .  |

C. Variation in Composition and Mechanical History of Lead

- . 1. Batch tests gave reproducible results.

D. Variation in activation of Lead

- |  |   |
|--|---|
| 1. Amount of lead surface browned during run varied from piece to piece. | . 1. Color of lead similar in several non-correlating cases (e.g. acid runs). |
|  | .   |
|  | . 2. If flow pattern varies, activation variation irrelevant.                 |

Confirmatory Facts (cont)

Discrepant Facts

E. Orientation of Catalyst Tube

- . 1. Repacked catalyst set
- . gave results that correlated.
- .

F. Time of wait during run

- |   |  |
|---|--|
| 1. Repacked catalyst set showed definite increase in activity on waiting. | . 1. Almost all runs were carried out immediately after packing, total time after packing not being greater than two hours |
|---|--|

G. Variation in peroxide and effect of stabilizers

- |  |  |
|--|--|
| 1. Some undistilled peroxide runs showed drop in activity during run, - in general were less active than undistilled peroxide. | . 1. Use of distilled peroxide did not result in correlatable results. |
|--|--|

H. Inconsistent laboratory technique

- . 1. Results that correlated
- . far more consistently were
- . achieved on repacking single
- . catalyst set.

## CONCLUSIONS

1. In acetic low pH solutions, 1/16" deep grooves, 0.005" wide and wider are effective in increasing catalyst activity under batch conditions. For grooves 0.012" wide and wider, the increase in activity is equivalent to the total area increase caused by grooving. This is at least nearly true for 0.005" grooves as well.

2. Under the batch conditions studied, the relation of activity to total area was linear, except for high areas, at which results were erratic.

3. No tenable reason can be cited for this erratic behavior.

4. The flow system studied is unsuitable for determining the effect of groove size on activity because conditions other than area are the controlling variables of the system.

5. Activation of lead catalysts by peroxide alone is not recommended because of uneven surface produced at low percentages of peroxide and excessive spattering (and hence fire hazard) at higher percentages of peroxide. Alkaline solutions of peroxide offer greater promise although they were not specifically tested in this work.

## RECOMMENDATIONS

1. Batch tests at higher surface areas, with various reaction tube diameters, and various initial volumes of peroxide should be made to thoroughly develop the conclusions of this thesis.

2. Lead catalysts probably cannot be grooved satisfactorily with grooves smaller than .001". Thinner grooves should be investigated using manganese catalyst which should hold shape satisfactorily with very minute clearances.

3. The effect of large pore sizes should be investigated for comparison with Isbin's work. Experience with grooving tests on lead would suggest the following approach:

- a. Casting or extrusion of thin walled lead tubes of the proper varying inner diameters;
- b. Slicing of the lead tubes while cold (using ice water or dry ice if necessary) into short lengths with a high speed saw.
- c. Use of these short lengths as a loose packing.
- d. Use of high flow rates or semiflow methods of testing so that temperature is kept down (lead loses shape readily with increased temperature) or/and
- e. Use of batch tests with peroxide and acetic acid on somewhat longer lengths of tubing.

4. As 0.005" wide grooves are effective in increasing activity, the surface of nonporous catalysts may be lacerated to increase activity, provided that the catalyst is completely covered with peroxide during flow.

## APPENDIX A

### HISTORICAL SURVEY

The problem of the decomposition of concentrated hydrogen peroxide by a catalyst on a porous medium touches on several complicated fields, none of which have been explored sufficiently to give either a quantitative or solid theoretical qualitative basis to the study.

In general, the phenomenon of catalysis implies the speeding up of the rate of a chemical reaction by a noncomponent or catalyst suffering no (or little) net chemical change. The mechanism of catalysis may be of several types<sup>2</sup>, - the provision by the catalyst of a substance to engage in intermediate reaction, - the provision by the catalyst of activation energy for the reaction, - the provision by the catalyst of an intermediate energy carrier to sustain the reaction or combinations of these in an ability of the catalyst to cause temporary stresses in the molecules of the reactants (which is a concept included in the first three as well).

By means of radioactive tracers, Broughton and his associates<sup>3</sup> determined the decomposition of hydrogen



peroxide by colloidal manganese dioxide to be of the intermediate reaction type, with manganous hydroxide as the main intermediate. There is also evidence that the decomposition of peroxides by silver is of the same type.<sup>4</sup> The mechanism of decomposition with lead has also been studied<sup>5</sup> and although radioactive tracers were ineffective, "the phenomena observed are all consistent with the hypothesis that catalysis of hydrogen peroxide decomposition by lead and its compounds is the result of a cyclic oxidation and reduction of lead."

Catalysis by intermediate reaction may be of a "trace catalysis" type, in which the catalyst supplies a necessary component for intermediate reaction although the reaction velocity constants are such that further addition of a catalyst does not speed the reaction. In this case, reaction rate would be independent of catalyst surface and volume.

Alternatively, as is more common, the reaction rate is a function of the amount of catalyst available for reaction. In the case of solid catalysts, this implies the amount of surface available for reaction.

Work by Isbin and his associates (see Appendix A) definitely shows that the decomposition of 48% peroxide

by manganese dioxide is a function of the amount of catalyst present. Similarly, the work of Hoffman and Satterfield<sup>6</sup> with anodized lead screens shows that for any flow rate, through such screens, there is a definite minimum number of screens for complete decomposition of the peroxide to occur. This indicates the positive effect of catalyst area.

The work of Isbin further indicates that for the same weight of catalyst, decomposition increases with decreasing particle size, but there is no change in decomposition rate at constant mesh size with varying pore sizes. (See Appendix B). It therefore follows that for the pore and grain sizes he studied, the catalyst external surface was the only "surface available for reaction."

The treatment of catalytic reaction in the pores of materials of various grain and pore sizes has received some study in the literature. In general, the work has been done on two phase systems, using a solid catalyst and gas phase reaction components. A considerable number of experimental cases have been found where the grain size had no effect on the rate of reaction, at least in some size ranges.<sup>7,8,9A,10</sup> The

postulated explanation of this experimental phenomenon has in general been the existence of extremely small pores which provided a reaction surface so large that changes in the external surface of the grains by subdivision had no effect.<sup>7</sup>

Of somewhat greater interest are the theoretical treatments of pore-diffusion catalysis. The more mathematical treatments, because of their limiting assumptions, cannot be applied. All, for example, make the assumption of a single phase of reaction components active on the surface of a second phase catalyst. Inasmuch as the decomposition of peroxide liberates oxygen, these derivations all fail. Moreover, as neither the mechanism of removal of gas from the surface of a catalyst nor the diffusibility of gas through a liquid medium in capillaries has been studied, it is difficult to postulate even semi-quantitatively what is occurring. (It may be mentioned that the mechanism of gas removal from the catalyst surface is being studied at this time. It will probably be wise to re-examine this thesis in the light of the results of that work.) It is possible, however, to hazard some qualitative guesses.

Inasmuch as, in the technique used, (see Procedure Section), an atmosphere of oxygen has been maintained above the peroxide, there should be enough oxygen in solution to make the normally negligible solubility of oxygen in water infinitesimal. We are thus concerned with the problem of transfer of an insoluble gas through a liquid medium in pores of very small width. When this transport is slow, the film thickness of oxygen about the pore surface must perforce increase, sealing off the pore surface from further reaction. The transport may be by bubbles of various sizes, diffusion (??), or combinations of and additions to the above. In any case, it is probable that the gas is transported more slowly, if at all, in a small pore than in large pores. Temperature decrease may decrease turbulent bubble eruption, but will also decrease gas volume/mole and chemical reaction rate<sup>#</sup>.

Taylor in the "Twelfth Catalysis Report" <sup>11</sup> cites the five steps in the progress of a heterogeneous catalytic reaction as (1) the diffusion of the reactants to the catalyst (2) formation of the adsorption complex-catalyst surface (3) the chemical change at the surface (4) the

---

<sup>#</sup>And liquid diffusion rate, - see below

decomposition of the adsorption complex-product surface; and (5) the diffusion of the reactants from the surface. The theoretical work of Zeldowitsch<sup>12</sup> implies and the work of Milleville<sup>13</sup> agrees that a more usable hypothesis in the case of porous materials would be:

(1)<sub>0</sub> Diffusion of the reactants to the external surface of the catalyst.

(2)<sub>0</sub> Reaction at the external surface, possibly simultaneous with

(3)<sub>1</sub> Diffusion into the inner surfaces of the catalyst,

(4)<sub>1</sub> Reaction at the inner surfaces of the catalyst, and

(5)<sub>1</sub> Expulsion of the products from the inner surfaces by diffusion, turbulent expansion, or other mechanism.

(6)<sub>0</sub> Return of the products of the reaction to the main stream by diffusion or other mechanism.

The theoretical derivations of Thiele,<sup>14</sup> Damkohler,<sup>15</sup> Zeldowitsch,<sup>12</sup> and Milleville,<sup>13</sup> (which as mentioned above are limited to 2-phase heterogeneous catalysis) all derive a region of reaction rate equivalent to full

pore utilization, tapering off into partial pore utilization as the relative depth to width of the pore increases. (The Thiele curve of relative activity is drawn against the parameter  $x_s \sqrt{\frac{c}{kr}}$  where  $x_s$  is a depth measure and  $r$  is a width measure. The Zeldowitsch and Milleville derivations involve  $x \sqrt{\frac{ks}{D}}$  where  $x$  is a depth measure and  $S$  and internal surface area per unit internal volume, i.e. a reciprocal width. For a full discussion of these interesting derivations see Zimens<sup>16</sup> and Milleville<sup>13</sup>).

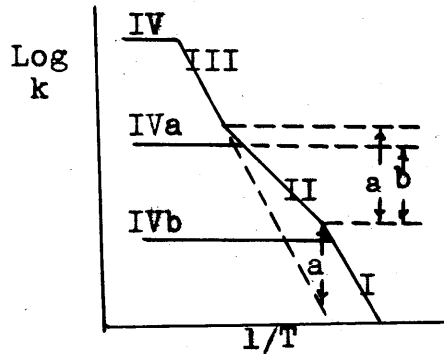
Zeldowitsch, however, has also postulated a curve for the most general case of a gas phase reaction on a porous solid catalyst<sup>#</sup> being limited in turn by (1) rate of chemical reaction on total surface (2) diffusion or other transfer rate into and out of pores (equivalent to chemical reaction at only part of the full pore depth) (3) chemical reaction rate at external surface (diffusion rate to external surface from main stream very fast; (4) diffusion rate to catalyst external surface. Zeldowitsch postulated curves for a system of constant grain and pore size and varying reaction temperature (see curves

---

<sup>#</sup> This limitation to gas phase was not stated by Zeldowitsch but is implied by his use of a constant diffusion rate line at varying temperature. See some of the discussion of diffusion below.

below:

FIG XII



Postulate of log k (activity) vs reciprocal of absolute temperature (Zeldowitsch)<sup>12</sup>

Diffusion was assumed to remain almost constant with temperature (note this as point of limitation of argument to gas phase. The remainder of Zeldowitsch's argument seems equally applicable to liquid and three phase heterogeneous reactions), while chemical reaction rate was exponential in temperature, ( $K \sim e^{-\frac{A}{Rt}}$ ). He also pointed out that either step (2) or (3) may not and step (3) most often will not be apparent unless proper relative rates of reaction and diffusion exist. For example, with very wide pores, diffusion into the pores is practically instantaneous with diffusion to the external surface and neither (2) nor (3) will appear. The

plot will thus appear like IVb above, - limiting effect being either diffusion to the surface of chemical reaction. Case (3) (III) appears only if diffusion to external surface is almost instantaneous, surface chemical reaction very rapid, and pore diffusion very slow. The reaction will thus proceed exactly as if the grains were impermeable. Experimental examples of curve sections I, II, and IV (cases 1, 2, and 4) are quoted by Milleville from Chufarov, Tatievskoya, and Kul'pina, Chang; and Uchida and Nakajima but Milleville found no experimental evidence that Zone III exists.

If, however, we make an assumption that gas travel through liquid in a pore is necessarily much slower than gas evolution from a particle surface in a stream, (which seems eminently reasonable) or that gas covers the pore surfaces as a vapor sheath preventing reaction, the characteristics of Zeldowitsch's Zone III may be seen to fit the characteristics of decomposition of peroxide on a porous catalyst (subject of course to the effect of temperature on liquid diffusion as discussed below.) However, before jumping into a theory, it may also be noted that with as rapid a reaction as peroxide exhibits, it may well be diffusion to the external particle surface



(Zeldowitsch's Zone IV) that limits the reaction. Increasing area by the means Isbin used, - decreasing particle size, - would also increase the reaction rate by speeding diffusion#. (The channels being smaller, at any mass flow rate the velocity is greater, decreasing the film to be diffused through. The increased area, moreover, acts as a "resistance in parallel", providing more area to be diffused to.)<sup>17</sup>

Since the viscosity of liquids varies far more with temperature than that of gases, the diffusivity is much more sensitive to temperature.<sup>17</sup> Thus the diffusivity of a liquid is likely to rise sharply with temperature. (Correlation for as polar a liquid as hydrogen peroxide is likely to be abominable). Thus, the diffusion rate-reaction rate relationship, although it may be of types analogous to curves I, II, III, and IV of Zeldowitsch (i.e. the controlling factor for any reaction-grain-pore system will still fall into one of the above categories) will be confined to one type over a far greater temperature range. (This implies that the diffusivity is also an inverse exponential to a power

---

#However, plots of log undecomposed peroxide vs reciprocal flow rate (see Appendix B for example) are linear. If diffusion was limiting, there should be curvature at high flow rates.

proportional to the reciprocal of absolute temperature which can be assumed to be true approximately (for curve fitting purposes) over any small temperature range).

For our gas product-liquid reactant system, the temperature effect depends on the mechanism of gas flow through liquid and the net effective diffusion-temperature relationship resulting.

For the pores, on the other hand, there is really no evidence to show that gas, once in a pore, will have any tendency to leave at an appreciable rate. The very small highly capillary pores of a sponge, for example, will retain air almost indefinitely under water if no compressive pressure is exerted. The standard procedure of Isbin and associates<sup>18</sup> in placing porous carbon rods in permanganate solution in order to prepare a catalyst, was to place the rods under a vacuum because gas would tend to remain in the pores and the rods would not sink into the solution. There is certainly a limit to this phenomenon, however, for if you drop a clean porcelain filter plate into a pail of water, to take an extreme case, the air will certainly leave the filter holes, - although the presence of air in the micropores of the filter is debatable.

Another factor to consider in a gas-liquid-solid catalyst system is surface tension. Evacuated small pores, by surface tension, will resist entrance of liquids unless pressure is applied.<sup>19, 20</sup> Thus for pores of 43,00  $\text{\AA}$  and mercury, it takes a pressure of 25 psia to force entrance.<sup>19</sup> The size and shape of gas bubbles also depends on surface tension.<sup>21</sup> Thus while the term "diffusion" has been rather loosely used in discussing possible reaction in the pores, the limiting parameter for transfer may well be surface tension or some function of it, pore size, and various contact angles. It may also be noted that adherence of bubbles, is affected by vibration as well as surface structure. In the absence of work on the mechanism of gas transfer from the catalyst surface (both internal and external) to the main stream, these consideration must be dealt with lightly.

It would seem from all the above, that some further data on the effect of pore size (and interstice or groove size as well) are necessary before we can analyze the peroxide catalysis liquid-gas-solid catalyst system.

## APPENDIX B

### Work of Isbin on Mesh and Porosity

#### Summary

In the course of a general research on hydrogen peroxide, Isbin and his associates have made flow and beaker tests of the rate of decomposition of hydrogen peroxide on the surface of various catalysts. Among these tests were included the effect of varying mesh and pore sizes on the activity. For the ranges of pore and mesh sizes studied; varying mesh size showed an increase in activity proportional to the reciprocal of grain diameter.

#### Discussion of Curves

##### I. Flow Correlation With Different Pore Sizes (Fig VII)

Other experiments with colloidal manganese hydroxide have shown the order of reaction of the decomposition of hydrogen peroxide to be approximately first.<sup>25</sup> The plot of log concentration vs t for peroxide on a material of constant surface activity would therefore be straight<sup>#</sup>. If, however, the area of a catalyst affected the rate of

---

<sup>#</sup>  $-dA/dt=kA; -\int_{A_0}^A dA/A = \int_0^t k dt; \ln A/A_0 = -k(t-t_0)$  which, if plotted as log A vs t gives a straight line. ("A" is concentration of substance decomposing)

reaction, while the plot for any one surface is a straight line, each surface of different area gives a different straight line. For a flow system, a plot of log percent reactant undecomposed vs the reciprocal of flow rate for a constant length of catalyst tube is equivalent to a plot of log concentration vs time (the volume of liquid being approximately constant).\*

Inasmuch as points for the same mesh size and varying pore sizes fall on the same straight line in this type of plot, the pore size cannot have any effect on the activity of the catalyst.

## II Flow Activity for Different Carriers (Fig VIII)

As hinted above, the slope of the line of the log percent undecomposed-reciprocal flow rate curve may be taken as a measure of activity, i.e. a very active catalyst bed will decompose a particular percentage of peroxide in a shorter time which is equivalent to a higher flow rate. The slope of the curve will thus be steeper for more active carriers and less steep for less active carriers.

Curve VIII plots the relative slopes found in a series of flow tests on each of several different carriers. In

---

\* Liquid volume varies as the amount of vaporization of the liquid. As 50.0wt% peroxide distills 5.2 wt % peroxide vapor, this assumption is false at higher temperatures.

spite of the varying pore sizes, it would found that for the same mesh size, activity was proportional to the number of pellets used. Again it can be seen that the varying pore diameters had no effect on activity.

### III Effect of Mesh Size (Flow Test) (Fig IX)

Relative activities were measured similarly for a single carrier of constant pore size and different mesh sizes. The activity of the catalyst bed was found to be proportional to the mesh.

### IV Effect of Mesh Size (Batch Test) (Fig X)

The time for complete decomposition of a batch of peroxide was measure on catalysts of various mesh size in a beaker. It was found that the time for decomposition was proportional to particle size. In other words, the average decomposition rate was inversely proportional to particle size.

### V Effect of Pore and Mesh Size (Fig XI)

Runs at constant flow rates were taken at three different mesh sizes for varying pore sizes. It seems probable from the results that pore size has no effect, although the points are not sufficiently numerous or

consistent to be a proof in themselves. Mesh size definitely is shown to affect the decomposition rate.

Conclusion:

The rate of decomposition of hydrogen peroxide on a porous manganese oxide impregnated catalyst is proportional to the external surface of the carrier,<sup>#</sup> and independent of the pore size of the carrier within the limits tested. These included a range of meshes of 4 to 10 and of pore sizes of 0.0002" to 0.025".

Note:

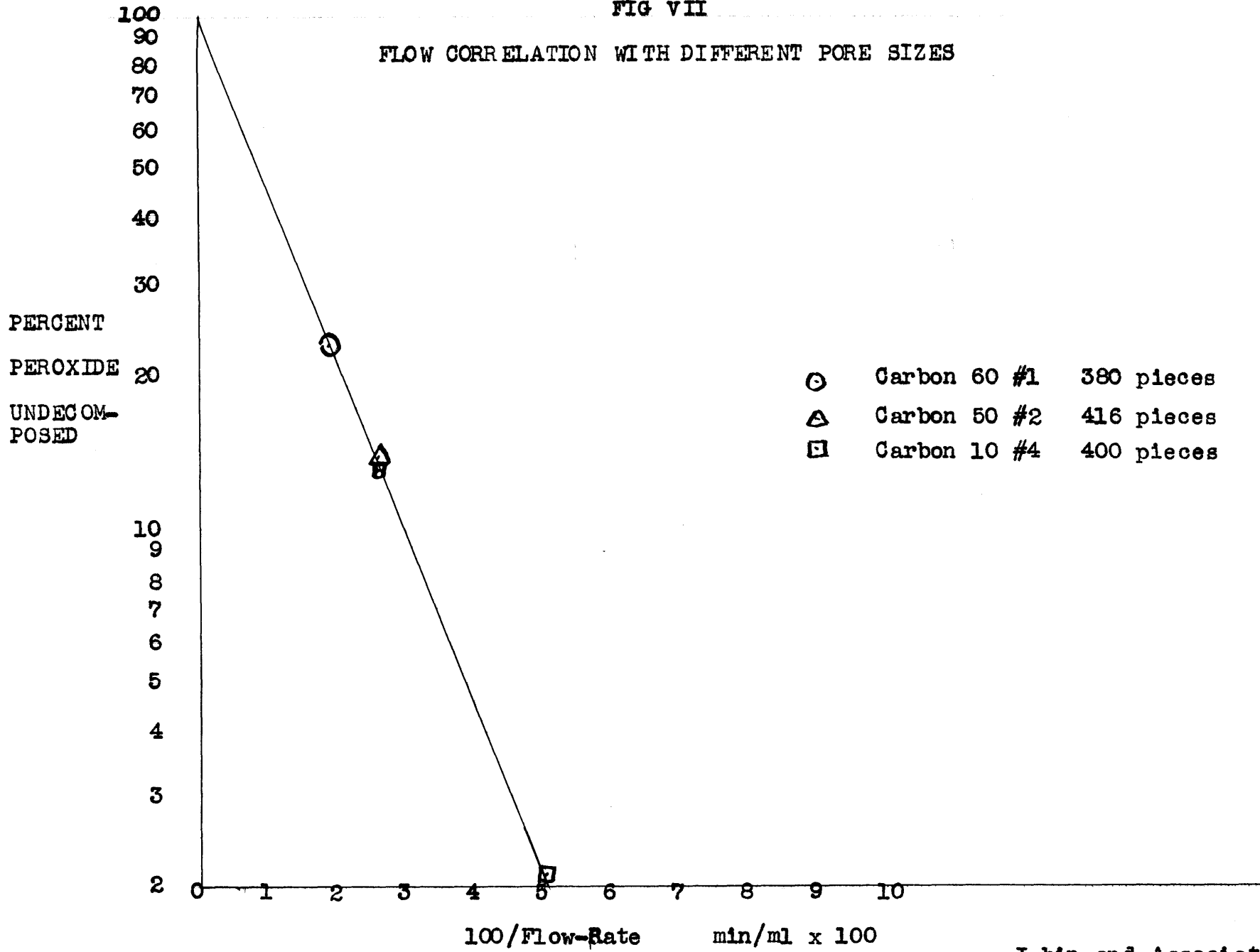
This is a short summary of Isbin's work and conclusions from his collected data and verbal comments. This work will probably be published separately by Isbin in a more collected and precise form.

---

<sup>#</sup>This is obvious particularly from curve VIII. Curves IX and X imply rate is a square root function of surface.

FIG VII

FLOW CORRELATION WITH DIFFERENT PORE SIZES



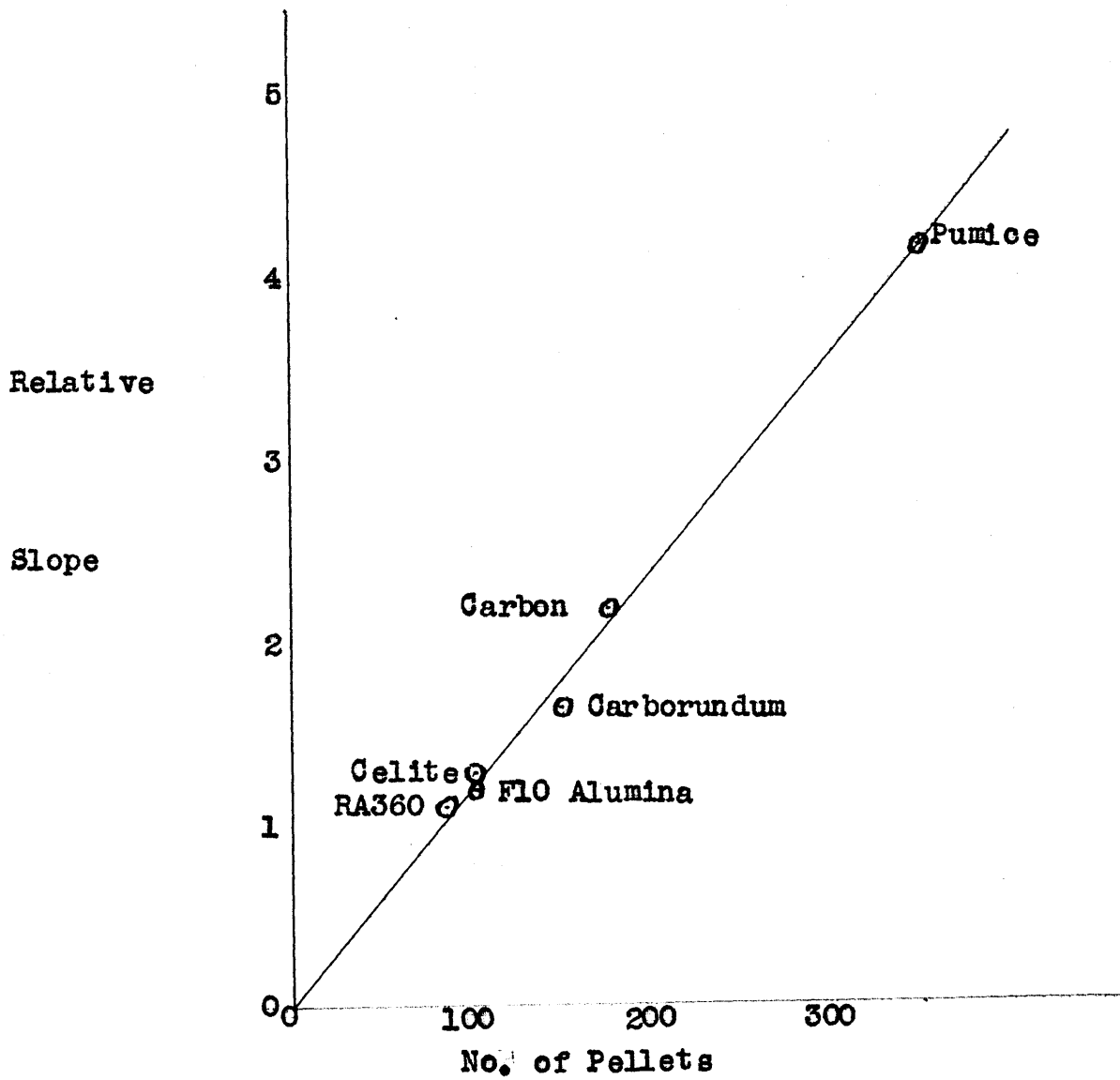
Isbin and Associates  
Summer 1946



FIG VIII

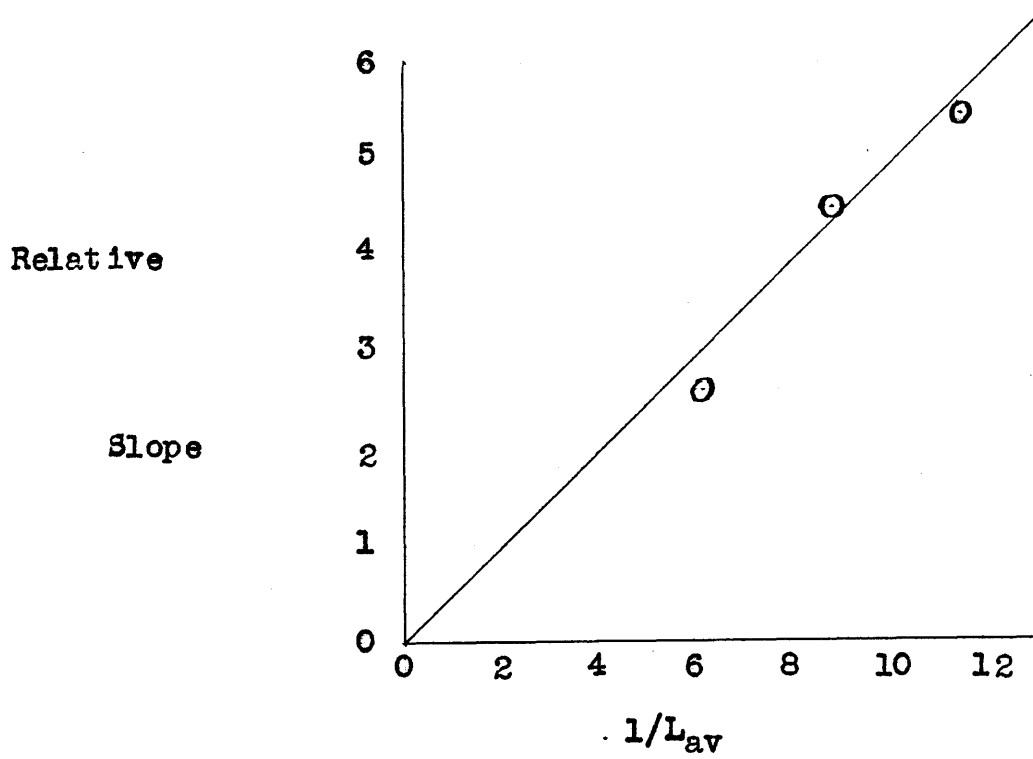
FLOW ACTIVITIES FOR DIFFERENT CARRIERS

6-8 mesh 16mm (id) catalyst tube  
Mn(NO<sub>3</sub>)<sub>2</sub> impregnated, dried at  
175°C. Pore sizes from .0001"  
to .025".



Isbin and Associates  
Summer 1946

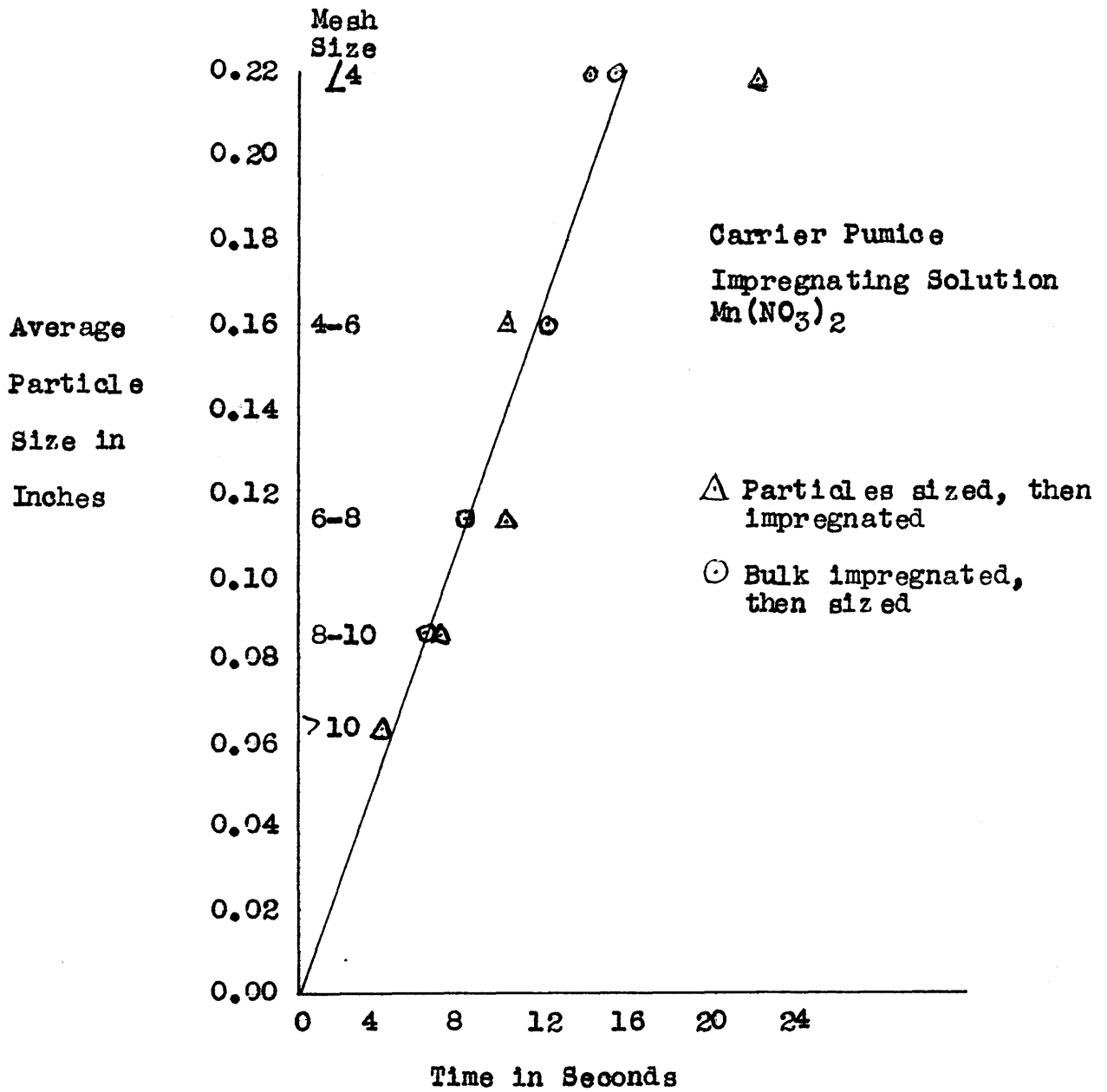
FIG IX  
EFFECT OF MESH SIZE  
(Flow Test)



Alundum Carrier  
L=Mesh Size in Inches

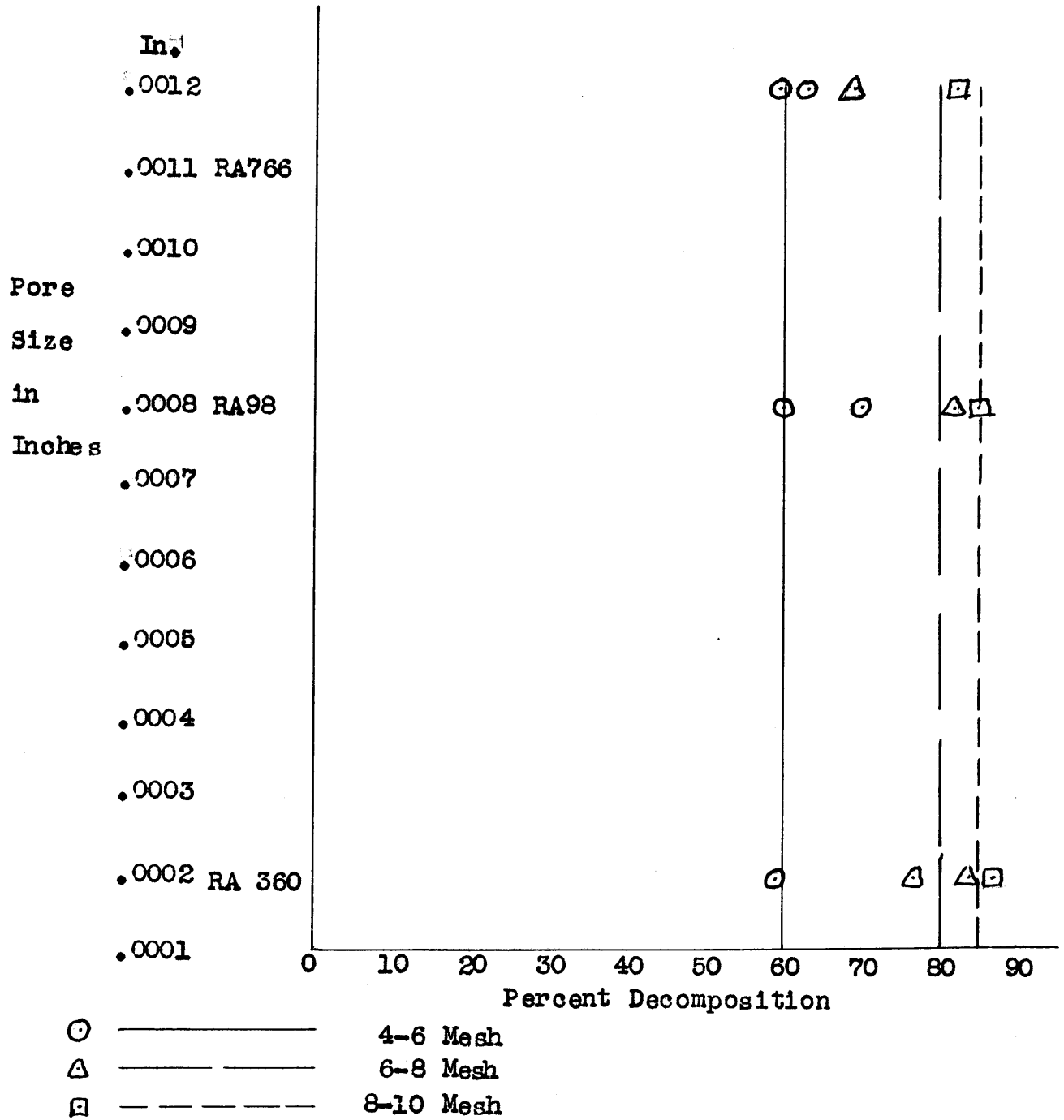
Isbin and Associates  
Summer 1946

FIG X  
 EFFECT OF MESH SIZE  
 (Beaker Tests)



Isbin and Associates  
 Summer 1946

FIG XI  
EFFECT OF PORE AND MESH SIZE



Isbin and Associates  
Summer 1946

Appendix C

TABULATED SUMMARY OF ORIGINAL DATA AND RESULTS BY RUN

1. Flow Tests

Run Nr	Burette Rate - ml H <sub>2</sub> O <sub>2</sub> /min	Wet Test Rate ml wet O <sub>2</sub> /min	P-T corr.	% decom- posed	Comment
2	2.70±25%	227±8.3%	.90	39.2	undist. peroxide
3	2.9 ±19%	254±10.1%	.89	39.6	" "
3	7.1±12%	452±7.5%	.89	29.6	" "
4	1.3±26%	24±36%			" "
5	7.1±9%	306±4%	.90	20	" "
6M	4.6±12%	147±12%	.90	13.6	" "
6E	5.5±6%	412±5%	.88	34.4	distilled "
7	6.8±6%	465±11%	.88	31.6	distilled "
8M	6.7±7%	610±11%	.91	43.5	" "
8E	6.8±5%	793±5%	.90	54.9	" "
9	7.3±1%	530±3%	.89	33.6	" "
10	7.4±1%	503±5%	.89	31.6	" "
11	8.7±2%	686±4%	.88	36.6	" "
12M	7.9±3%	1108±5%	.89	65.9	" "
12E	5.5±4%	1003±6%	.89	83.5%	" "
A.1	4.5±9%	405±11%	.87	41%	" "
2	9.4±3%	683±2%	.87	33.2	" "
3	7.1	580	.87	37.2	" "
4	6.3	550	.87	40.3	" "
B.1	4.5±2%	396±1%	.87	39.6	" "
2	10.3±2%	523±2%	.87	23	" "
3	7.5±1%	443±4%	.87	27	" "
C.1	4.1±4%	593±4%	.89	67.5	" "
2	3.6±4%	538±16%	.89	70.4	" "
3	5.1±5%	663±4%	.89	61.2	" "
4	9.0±4%	950±2%	.89	47.5	" "
D.1	10.±4%	550±1%	.88	25.9	" "
2	7.7±1%	570±1%	.88	34.4	" "
3	5.7±3%	425±15%	.88	34.5	" "
4	4.3±6%	350±4%	.88	38	" "
E.1	3.3±3%	350±18%	.91	51	" "
2	3.9±2%	394±25%	.91	46.3	" "
3	4.8±5%	414±17%	.91	40	" "
4	5.9±4%	413±11%	.91	33	" "
5	7.9±2%	485±6%	.91	29.2	" "
6	8.3±2%	487±3%	.91	27.6	" "
7	9.6±2%	485±7%	.91	23.8	" "

Run Nr	Burette Rate - ml H <sub>2</sub> O <sub>2</sub> /min	Wet Test Rate ml wet O <sub>2</sub> /min	P-T corr.	% decom- posed	Comment	
13:	4.0±6%	322±10.4%	.89	37.8	distilled peroxide	
	5.2±7%	483±15%	.89	43.4	" "	
	5.8±3%	363±7%	.89	28.8	" "	
	6.9±3%	630±17%	.89	42.5	" "	
	9.1±4%	713±4%	.89	36.4	" "	
	9.7±2%	653±9.5%	.89	31.1	" "	
	14:	3.2±9%	600±3%	.87	85.4	dis. perox. pH
4.2±7%		850±6%	.87	93.3	on dilution	
4.8±3%		1005±5%	.87	96.5	4.1	
5.2±2%		1123±5%	.87	100		
9.3±5%		2042±13%	.87	100%		
10.4±3%		2495±1%	.87	110%		
11.6±1%		2530±1%	.87	100		
25		1400	.87	25.5		
37.7±1%		1340±5%	.87	16%		
15:		7.9±3%	210±5%	.87	11.9	dist. perox. pH
	9.1±1%	250	.87	12.2	on dilution	
	11±0%	510±0%	.87	20.9	4.0-4.9	
	16	720	.87	20/2		
	18.3±2%	1490±7%	.87	37.1		
	43	1510	.87	15.7		
	5.8±4%	256±7%	.87	20.0		
	7.1±2%	313±60%	.87	19.9		
	12.5±5%	633±2%	.87	24.9		
	15.5±0%	660±2%	.87	19.2		
	17.5±0%	630±2%	.87	16.2		
	38.5±1%	1540±3%	.87	18%		
	G-1	3.7±4%	140±17%	.89	15.4	dist. peroxide
		4.1±3%	324±61	.89	37.1	grooved catalyst
4.6±4%		200±7%	.89	20.3	set.1/16" wide	
5.6±4%		377±15%	.89	31.6	grooves, 7 grooves	
6.4±2%		396±9.6%	.89	29.2	per inch	
7.4±4%		482±16%	.89	29.9		
8.3±2%		545±1%	.89	31.1		
10.9		680	.89	29		
S-1	3.7±11%	390±6%	.89	48.6	dist. perox.	
	4.5±5%	345±23%	.89	35.9	2 catalyst sets	
	5.3±6%	1042±8%	.89	92.6		
	7.5±1%	1637±3%	.89	102		
	7.8±0%	573±15%	.89	33.2		
	8.5±3%	573±2%	.89	31.9		

Run Nr	Burette Rate - ml H <sub>2</sub> O <sub>2</sub> /min	Wet Test Rate ml wet O <sub>2</sub> /min	P-T corr.	% decom- posed	Comment
P-1					dist. peroxide pH on dilution 9.0
P-2					dist. peroxide pH on dilution 7.8-8.0
P-3	4.3±4%	907±7%	.90	100	dist. peroxide
	4.6±2%	925±3%	.90	95.3	pH on dilution
	6.2±3%	1143±2%	.90	87.5	3.8-4.6
	6.7±1%	1417±3%	.90	100	
	8.2±1%	1605±1%	.90	93	
	8.8±1%	1755±3%	.90	94.8	
	9.9±5%	2005±3%	.90	97	

Notes on Flow Test Summary:

- Two copies of the original data itself are available. The first is in the possession of Prof. D.B. Broughton, M.I.T., Cambridge, Mass. The second is in the possession of the author who may be addressed at 47 Arden Street, New York, 34, New York.
- Flow test peroxide was approximately 48% (by weight) H<sub>2</sub>O<sub>2</sub>. Specific gravity of peroxide unless pH is listed was 1.190. Alkaline and acid peroxides were made up as described in Procedure Section of this report.
- Rates tabulated are average rates of flow. Wet Test Rate refers to the rate of wet gas flow as measured by a

wet test meter at one minute intervals.

4. P-T correction is applied to the difference of the wet test and burette rates. The correction is a multiplying factor as determined from a nomographic chart prepared by Mr. Joseph Boscoff<sup>#</sup> and corrects gas volume to standard temperature, pressure, and zero moisture conditions.

5. % decomposed is percentage of incoming peroxide decomposed at given flow rate. Method of calculation is given in sample calculations. A slight error is present in this calculation for the acid and basic peroxide runs which does not affect the conclusions.

6. "M" and "E" refer respectively to earlier and later runs on the same set up with catalyst remaining in reaction tube. The "E" runs were discarded from the correlations listed in the "Results" section of this report on the basis of the results of run "C" which indicated error in such procedure.

7. Percent deviation listed refers to average percent deviation of the numerical results as taken. It does not include estimated errors of method, etc. In obtaining the averages for this summary, all values of greater than five times average deviation were discarded.

---

<sup>#</sup> Available at Rm 2-034, Chem Eng Dept., M.I.T.



8. Values without percent deviation listed were based on a single point, and should be considered only in the light of their consistency with the other data for the run.

9. pH was determined by diluting a sample to ten times original volume and testing with standard calomel-glass electrode pH meter. Meter was standardized against pH 10 buffer solution for high pH runs and against pH 4.1 buffer solution for low pH runs.

## 2. Batch Tests

AT	AS	$\theta_T$	$\theta_A$	$\theta_T - \theta_A$	$t_0$	Code	Groove Width	pH on dilution
1.42	1.42	2.35	1.28	1.07	24	A	none	3.35
1.42	1.42	2.42	1.13	1.13	24	A	none	3.35
3.58	3.58	1.06	0.42	0.54	25	AB	none	3.35
1.72	0.78	1.63	0.15	1.48	25	A	.125	3.35
2.03	0.85	1.68	0.30	1.38	25	A	.063	3.35
2.55	1.23	1.86	0.15	1.71	26.5	A	.012	3.35
1.42	1.42	2.31	1.11	1.20	26	A	none	3.35
3.22	0.80	1.18	0.03	1.15	27	A	.032	3.35
1.72	0.78	1.90	0.15	1.75	25	A	.125	3.35
1.42	1.42	2.43	1.13	1.30	25	A	none	3.35
3.22	0.80	1.16	0.03	1.13	25.5	A	.032	3.35
2.05	2.05	1.77	0.70	1.07	24.5	B	none	3.35
2.55	1.23	1.30	0.30	1.00	24	A	.012	3.35
2.03	0.85	1.40	0.15	1.25	24	A	.063	3.35
2.11	1.08	1.51	0.10	1.41	23.8	A	.012	3.35
1.72	0.78	1.70	0.15	1.45	22.5	A	.125	3.35
1.42	1.42	2.76	1.47	1.29	23	A	none	3.43
3.22	0.80	1.15	0.15	1.00	22.5	A	.032	3.43
2.03	0.85	1.59	0.33	1.26	22	A	.063	3.43
1.42	1.42	2.54	1.50	1.04	22	A	none	3.43
2.55	1.23	1.67	0.25	1.42	22	A	.012	3.43
1.72	0.78	1.90	0.30	1.60	21.8	A	.125	3.43
1.33	1.33	2.53	1.40	1.13	22	A	none	3.43
4.07	1.90	1.18	0.20	0.98	23	B	.012	3.43
2.74	1.19	1.25	0.15	1.10	24	B	.125	3.43
5.26	1.27	1.09	0.15	0.94	24	B	.032	3.43
3.13	1.29	1.35	0.25	1.10	24.5	B	.063	3.43
1.42	1.42	2.20	1.09	1.11	26.5	A	none	3.43
1.18	0.38	2.64	0.12	2.52	24	A	.032	3.43
4.07	1.90	1.23	0.15	1.08	24	B	.012	3.43
2.74	1.19	1.20	0.10	1.10	23	B	.125	3.43
3.13	1.29	1.31	0.20	1.11	23.5	B	.063	3.43
5.26	1.27	1.07	0.15	0.92	23	B	.032	3.43
1.42	1.42	2.35	1.20	1.15	24.5	B	none	3.31
2.66	2.66	1.65	0.52	1.13	24	AA	none	3.31
3.40	3.40	1.08	0.25	0.83	24	AB	none	3.31
4.84	3.29	0.97	0.10	0.87	25	C	.125	3.31
3.64	3.64	0.97	0.20	0.77	25	AAA	none	3.31
1.19	1.19	2.50	1.51	0.99	25	A	none	3.31
1.26	1.26	2.38	1.26	1.12	24.5	A	none	3.31
4.07	4.07	0.89	0.32	0.57	25.5	BB	none	3.31

$A_T$	$A_S$	$\theta_T$	$\theta_A$	$\theta_T - \theta_A$	$t_0$	Code	Groove Width	pH on dilution
4.37	4.37	0.96	0.30	0.66	24	BB	none	3.31
1.18	1.18	2.45	1.22	1.23	25	A	none	3.31
4.01	4.01	1.02	0.50	0.52	23	BB	none	3.31
5.32	5.32	0.85	0.20	0.65	23	ABB	none	3.31
5.22	5.22	2.46	1.42	1.04	23	ABB	none	3.31
2.71	1.39	1.67	0.30	1.37	22	A	.005	3.31
2.71	1.39	1.56	0.24	1.32	25	A	.005	3.31
1.42	1.42	2.21	1.22	0.99	25	A	none	3.31
2.71	1.39	1.54	0.15	1.39	25	A	.005	3.31
1.42	1.42	2.41	1.23	1.18	25	A	none	3.31
2.55	1.23	1.49	0.18	1.31	24.5	A	.012	3.31
1.95	1.03	2.03	0.30	1.73	26	A	.005	3.31
1.42	1.42	2.78	1.60	1.18	22	A	none	3.31
2.15	0.54	1.98	0.12	1.86	23	A	.032	3.31

Notes on Batch Test Summary:

1. Copies of original data are available as cited in "Notes on Flow Test Summary" above.
2. Batch Test peroxide was made up of 50 ml glacial acetic acid/liter 48% peroxide plus 40 ml 0.6N NaOH/liter 48% peroxide. Peroxide strength, therefore, was slightly under 48%.
3.  $A_T$  refers to the total area of lead plate used in the test. For grooved specimens, this includes area of sidewalls and bottom of grooves as well as area of outer surface.
4.  $A_S$  refers to the surface area of lead plate used in the test. Area of the walls and bottom of the grooves are not included in this area.
5. Surface areas were determined from dimensions as measured with a micrometer. Areas within grooves were estimated from

width of cutter used (which checked with the average width observed with a shop microscope) and depth as determined with rule graduated in 1/100 of an inch. Errors in estimation of this depth as well as the area added by burrs and scratches causes some error in this estimation.

6. Areas and groove widths are based on dimensions before testing.

7.  $\theta_T$  refers to time for complete decomposition or "end of bubbling" of the peroxide. Some error in judgement can occur in determining this point.

8.  $\theta_A$  refers to the time required for large bubbles to start emerging from the solution. This is usually accompanied by a large increase in foaming.

9.  $\theta_T - \theta_A$  is the time from the start of violent bubbling to the end of reaction. This is the same as " $\theta_V$ " referred to in Table VI.

10. Areas are measured in square inches; groove width in inches; and time in minutes.

11. Two widths of plate were used, - approximately .50" and .82". From one to three plates were used to make up the areas cited. "A" is used in the code to designate .50" plates. "B" is used to designate .82" plates. One letter is used for each plate used. Thus "AB" means that a .50"

plate plus a .82" plate were used to make up the area. "AAA" means that three .50" plates were used. Plates of short length are not specifically designated as the ratio of grooved to ungrooved length remains constant. Case "C" was a special case in which two .82" plates were used. One was ungrooved. The other was grooved with a .125" grooves.

## Results of Miscellaneous Beaker Tests

### 1. Lead Preactivation Procedures and effect on activity

Activation Procedure	$\theta_T$ (sec)	Observations
1. Lead Plate dipped 10 sec. in 90% H <sub>2</sub> O <sub>2</sub> to give even orange oxide coating	90±10	immediate violent bubbling; some thinning of oxide coat without color change
2. Lead Plate dipped 1 min in 48% H <sub>2</sub> O <sub>2</sub> to give uneven rust-brown oxide coating	90±10	immediate violent bubbling; some thinning of oxide coat. without color change
3. Lead Plate dipped 30 sec. in 30% H <sub>2</sub> O <sub>2</sub> to give slight dulling of lead surface.	90±10	quiet bubbling for 1 min; then violent bubbling for 30 secs. Catalyst color changed to that of 48% preactivated catalyst. Considerable dispersion of lead oxide in solution.

Above tests were made by placing preactivated catalyst in 20 ml of 48% hydrogen peroxide and observing until decomposition of peroxide was complete.

### 2. Beaker reaction tests

- a. 48% peroxide + lead subacetate give violent reaction
- b. 48% peroxide + lead subacetate + acetic acid give no reaction
- c. 48% peroxide + acetic acid + lead plate give fair amount of reaction, increasing in violence as NaOH is added. Some lead dissolves during the reaction
- d. Solution from (c) when separated from lead plate during violent reaction period ceases violent bubbling

immediately, and all bubbling very shortly thereafter.

e. Solution from (d) + NaOH gives a brown precipitate, violent reaction.

f. Procedures (c) or (e) carried out with a very small volume of peroxide causes evaporation and leaching out of lead oxide and hydroxide suspension all through solution.

g. Reaction (c) left by itself will become quiescent, giving lead + a colorless solution non reactive to additional acetic acid but reactive to additional hydrogen peroxide.

h. 48% peroxide + acetic acid gives no reaction (or very mild bubbling)

Appendix D

SAMPLE CALCULATION

BASIS: Flow Run 10, distilled peroxide s.g. 1.90,  
48% H<sub>2</sub>O<sub>2</sub>

BURETTE RATE: 7.4 ml 48% H<sub>2</sub>O<sub>2</sub>

WET TEST RATE: 503 ml wet gas/min

CORRECTION FOR GAS DISPLACED BY INCOMING

PEROXIDE: 7.4 ml/min

WET OXYGEN FLOW RATE: 496 ml/min

P-T CORRECTION: .89 atm. O<sub>2</sub>/atm wet gas at standard  
temperature and pressure.

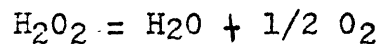
DRY OXYGEN FLOW RATE: .89 x 496 = 436 ml dry O<sub>2</sub>/min  
at 0°C and 1 atmosphere

OXYGEN MOLAR FLOW RATE: 436/22,400 = .0197 mols O<sub>2</sub>/min

LIQUID WEIGHT RATE OF FLOW: 7.4 x 1.190 = 8.81 g/min

H<sub>2</sub>O<sub>2</sub> WEIGHT RATE OF FLOW: .48 x 8.81 = 4.23 g H<sub>2</sub>O<sub>2</sub>/min

H<sub>2</sub>O<sub>2</sub> MOLAR FLOW RATE: 4.23/34 = 0.1242 mols/min





OXYGEN FLOW RATE FOR 100% DECOMPOSITION

OF PEROXIDE:  $.1242/2 = 0.0621$  mols  $O_2$ /min

% DECOMPOSITION:  $100 \times 0.0197/0.0621 = 31.6\%$

## APPENDIX E

### Literature Citations

1. Demant, Dr. Botho; "Interrogation of Dr. Demant at Wimbledon on October 15, 1945"; O.S.R.D. Liason Office Ref No WA 5624 1C; p.3.
2. Schwab, G., Taylor, H.S., and Spence, R.; "Catalysis"; translated from First German Edition; Chaps. III and IV; D.Van Nostrand Co, Inc.; 1937
3. Broughton, D.B., Wentworth, R.L., Laing, M.E., and Mauke, D.M.; "Mechanism of Catalytic Decomposition of H<sub>2</sub>O<sub>2</sub> Solutions with Manganese Dioxide"; Report #1, NavBuOrd Contract NOrd-9107 Task C; M.I.T. DIC 6351; Nov. 1, 1945
4. Schwab, Taylor, and Spence; loc. cit. p. 258
5. Broughton, D.B., Wentworth, R.L., Laing, M.E., and Mauke, D.M.; "Mechanism of the Decomposition of Hydrogen Peroxide by Oxides of Lead"; NavVuOrd Contract NOrd-9107 Task C; M.I.T. DIC 6351; June 1, 1946
6. Satterfield, C.N.; and Hoffman, W.H.; "Decomposition of 50 Weight Per Cent Hydrogen Peroxide Solution Using Anodized Lead Plated Screen"; Progress Report C-2, NavBuOrd Contract 9107 Task A; p. 16; M.I.T. DIC 6249 and 6354; September 15, 1945
7. Julliard; Bulletin de la Societe Chimique de Belgique; 46, 587, (1937)
8. Levi and Haardt; Gizzeta Chimica Italiana; 56, 424, (1926)
9. Emmett, P.H.; "Physical Adsorption in the Study of the Catalyst Surface", which is Chapter V of:  
National Research Council "Twelfth Catalysis Report" John Wiley and Sons (1940), cites to the same effect:
- 9A. Emmett and Brunauer; Trans. Am. Electrochem. Soc.; 71, 383-395; (1937)

10. Cawley and King; Dept. Sci Ind Research (Brit) Fuel Research Tech Paper 45; (1937)
11. Taylor, Hugh S.; "Activated Adsorption", which is Chap III of "Twelfth Catalysis Report" as cited in (9)
12. Zeldowitsch, J.; "On the Theory of Reactions in Powders and Porous Substances"; Acta Physicochimica, U.R.S.S.; 10, No. 4; 583-592; (1937)
13. Milleville, H.P.; "Chemical Engineering Factors in Heterogeneous Catalysis; Fluid Reactants, Solid Catalysts"; Preliminary Report, D. Sc. Thesis, Chem Eng. M.I.T. (1940)
14. Thiele, E.W.; Ind Eng Chem; 31, 916-920; 1939
15. Damkohler, G.; "Der Chemie-Ingenieur"; Book III, Part I, p. 359ff, Berlin (1937 as cited in Milleville, loc. cit. and
16. Zimens, Dr. K.E.; "Porose Stoffe"; Transactions of the Chalmers University of Technology, Gothenburg, Sweden; Nr 40; (1944) p. 140 & ff.
17. Walker, Lewis, McAdams, and Gilliland, "Principles of Chemical Engineering"; Third Edition; Chap XIV, particularly pp 446-449; McGraw-Hill Book Co.; (1937)
18. Isbin, H., Farrell, J., Thompson D., Meadows, A.; "Flow Studies of the Catalytic Decomposition of H<sub>2</sub>O<sub>2</sub> Solutions"; Progress Report #5, NavBuOrd Contract NOrd 9107 Task C; p. 11; M.I.T. DIC 6351; March 1, 1946
19. Ritter, H.R., and Drake, L.C.; Ind Eng Chem Analytical Edition 17, No 12, 782-786, (1945)
20. Washburn, E.W.; Proceedings of the National Academy of Sciences; 7, 115, (1921)
21. Lewis, W.K.; Squires, L., and Broughton, G; "Industrial Chemistry of Colloidal and Amorphous Materials"; p. 40; MacMillan Company, (1943)

22. McAlpine, R.K., and Soule, B.A.; (based on Prescott and Johnson); "Qualitative Chemical Analysis", p. 152, D.Van Nostrand & Co., (1933)

23. Wernlund, C.J.; "Procedures Used in Silver Plating and Activating Wire Screen"; Dupont Progress Report for NavBuOrd; June 28, 1946

24. Broughton, D.B., Mauke, D.M., Laing, M.E., and Wentworth, R.L.; "Activity of Metal Hydroxides as Catalysts for the Decomposition of  $H_2O_2$ "; Progress Report #7, NavBuOrd Contract NOrd-9107 Task C; Fig III; M.I.T. DIC 6351; Feb. 28, 1946

25. Broughton, D.B., Mauke, D.M., Laing, M.E., and Wentworth, R.L.; "Mechanism of Catalytic Decomposition of  $H_2O_2$  Solutions by Manganese Dioxide"; Progress Report #6, NavBuOrd Contract NOrd-9107 Task C; p.1, M.I.T. DIC 6351; Feb. 28, 1946