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THE ROLE OF DIFFUSION IN THE  
HIGH TEMPERATURE DECOMPOSITION  
OF HYDROGEN PEROXIDE

by

Ralph L. Wentworth

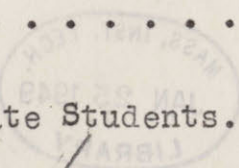
S.B., Harvard University (1944)

SUBMITTED IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE  
DEGREE OF MASTER OF SCIENCE  
AT THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 10, 1948

**Signature redacted**

Signature of Author . . . . .  
Thesis Supervisor . . . . .  
Chairman, Department  
Committee on Graduate Students. . . . .



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..... Chairman, Department  
Committee on Graduate Studies .....



Cambridge, Massachusetts  
September 10, 1948

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

Dear Sir:

I take pleasure in submitting to you this thesis entitled "The Role of Diffusion in the High Temperature Decomposition of Hydrogen Peroxide," in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Very truly yours,

*Ralph L. Wentworth*  
Ralph L. Wentworth

RLW/pr

ACKNOWLEDGEMENT

This research was carried out as part of the Office of Naval Research Contract No. N5ORI-78, Task Order XIX. The author is indebted to Professors C. N. Satterfield and D. B. Broughton for their advice and supervision and to Miss D. B. Thompson, Mr. C. F. Richey, and Mr. E. A. Ploen for their assistance in carrying out the experimental program.

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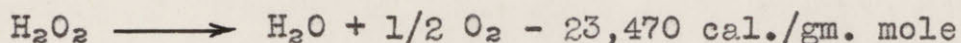
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## I. SUMMARY

The catalytic decomposition of hydrogen peroxide according to the equation,



is a convenient method for producing hot gases for use in certain specialized high power output motors. Considerable study has been made of the catalytic decomposition mechanisms, but the correlation of the data obtained is largely on an empirical basis.

Because of the form of the equations found by Isbin (4) to correlate empirically a large amount of experimental data, it is believed that, at high temperatures, the rate of vapor phase decomposition of hydrogen peroxide on a catalyst surface is limited by the rate of diffusion of hydrogen peroxide vapor to the catalyst surface. This hypothesis could not be substantiated by comparison with calculated diffusion rates predicted by theory because of the irregular shape of Isbin's catalyst bed and the marked temperature and hydrogen peroxide concentration variations in the bed.

The purpose of this investigation was to study vapor phase hydrogen peroxide decomposition on the wall of a tube, a simpler system more amenable to comparison with theory.



A comparison was to be made of the performances of a stainless steel tube and a silver catalyst tube with the performance predicted for such a tube by assuming the decomposition to be limited by diffusion rate.

Direct vaporization of hydrogen peroxide by boiling did not appear to be a safe, dependable way of producing vapor for introduction into the catalyst tube. However, by partially decomposing a stream of hydrogen peroxide in a catalyst bed the stream may be raised to the vapor state. This system was used to produce hot hydrogen peroxide vapor at reasonable concentrations as feed for a catalyst tube directly below the catalyst bed.

Comparison of the per cent decomposition as determined by withdrawing a sample from the tube with the per cent decomposition determined by condensing the entire stream indicated that the stream was not in thermal equilibrium and liquid droplets existed in the stream at points where the bulk temperature was far above the boiling point. It was possible to estimate the overall decomposition occurring in the tube even though the sampling technique was rendered unreliable by the presence of the liquid droplets. The estimate was obtained by measurement of the degree of decomposition attained in the exit stream from the catalyst tube and calculation of the degree of decomposition existing at the end of the catalyst bed by the catalyst

chamber design data of Isbin (4). The actual amount of decomposition determined experimentally by the above calculations was greater than that predicted on the assumption that the rate controlling step was diffusion of hydrogen peroxide vapor from the bulk of the stream to the tube wall. The discrepancy is well within the accuracy with which the diffusion rate can be calculated. It is concluded that diffusion is the controlling feature of hydrogen peroxide decomposition at high temperature in a tube.

## II. INTRODUCTION

Interest in Hydrogen Peroxide The decomposition of a concentrated hydrogen peroxide solution in a suitable apparatus provides gas at high temperature and pressure for use in a power plant. The decomposition is exothermic, and equilibrium for the decomposition is highly favorable. The commercially available solutions are not sensitive to shock and are quite stable in storage. The material is non-toxic and presently available at reasonable cost in large quantity as a water solution in concentrations up to 90 weight per cent. Hydrogen peroxide is not suitable at its present cost for commercial power plants but has application for power units where cost is secondary and high power performance per unit weight or volume is important.

Practical exploitation of the use of hydrogen peroxide in high power propulsive units was first realized by the Germans in the late war. Hydrogen peroxide power systems were applied to turbine-driven pumps for propellant fluids in the V-2 rocket, rocket launching units, rocket powered interceptor aircraft, and submarine power plants. The decomposition of the hydrogen peroxide in these units was accomplished in several ways. A stream

of calcium permanganate solution was used as catalyst in the V-2 pump unit. Later, solid catalysts impregnated with manganese, chromium, or lead salts were developed for use in the submarine propulsion unit. In the rocket aircraft, a fuel igniting spontaneously with hydrogen peroxide was used.

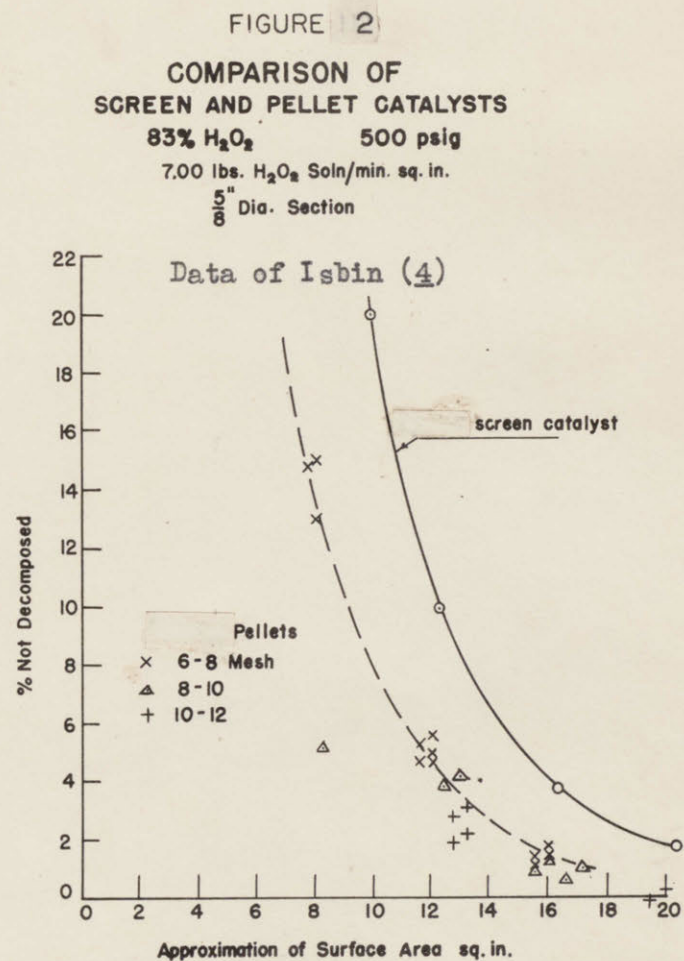
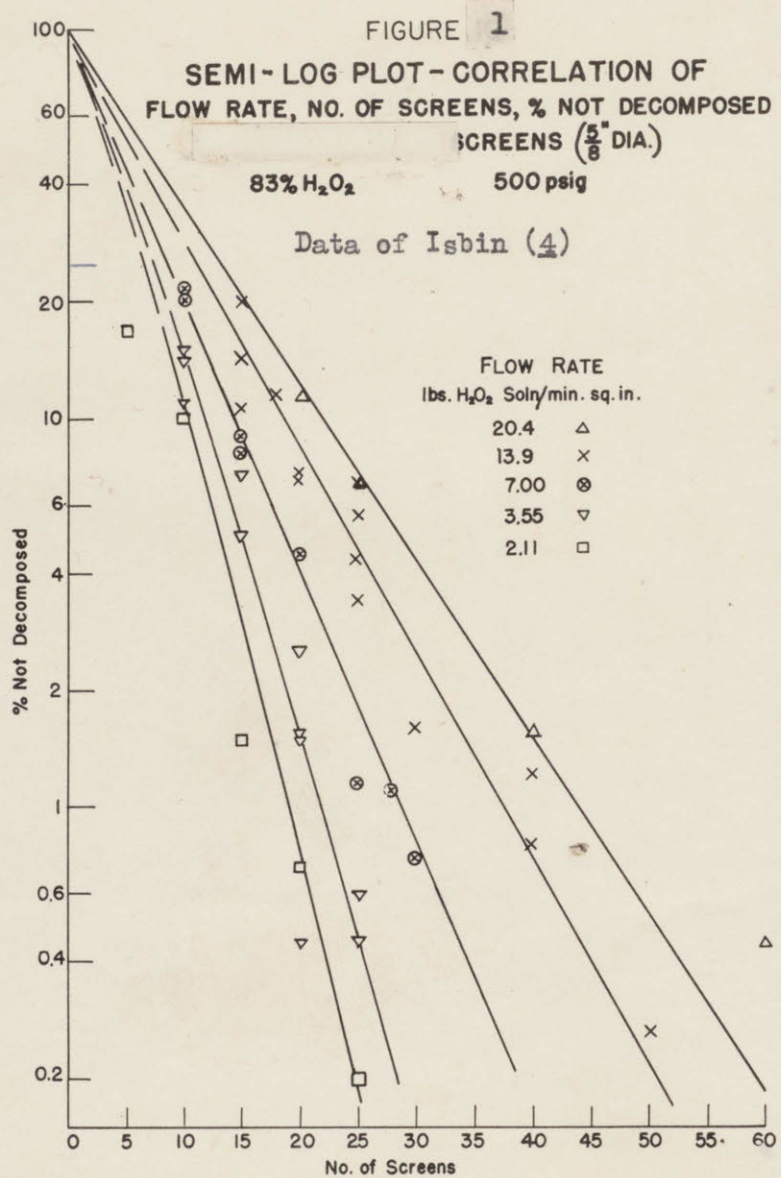
These developments have been the basis for continued research in this country on the improvement of power plants using hydrogen peroxide. This research program, of which this investigation is a part, has been concerned with the subjects of catalytic decomposition mechanism, of hydrogen peroxide stability on storage, investigations of basic physical properties, thermal decomposition of hydrogen peroxide, and catalyst development. The work carried out at M.I.T. has been aimed at the study of basic properties and reactions rather than at the development of power units.

Previous Work on Catalytic Decomposition The subject of this thesis forms a part of the studies on catalytic decomposition mechanisms and proceeds from the work of Isbin (4). Isbin studied the catalytic decomposition of 83% hydrogen peroxide using catalyst coated screens or an impregnated pellet-type catalyst of his own development. His method was to measure the overall decomposition of a

stream of hydrogen peroxide in an adiabatic catalyst chamber at 500 psig with the aim of developing design data for such decomposition chambers. Fig. 1 presents his results obtained with the screen catalyst at various flow rates. Fig. 2 gives a comparison of the screen and pellet catalysts. Isbin has summarized his results in an equation which may be used for the prediction of the length of catalyst bed necessary to attain a given degree of decomposition at a given flow rate.

These results make possible the enlightened design of catalyst chambers using these catalysts. The design parameters of such chambers cannot be predicted closely by theoretical considerations. Part of this difficulty lies in the fact that the results obtained were for overall operation of the catalyst chamber. It can be appreciated that the decomposition is a complex process when it is considered that the peroxide starts as a liquid solution at room temperature and emerges, decomposed, at several hundred degrees Centigrade as a gas or gas-liquid stream. The following characteristics of hydrogen peroxide catalyst beds are pertinent to the discussion and indicate that diffusion of hydrogen peroxide vapor to the catalyst surface is a controlling factor.

1. The temperature of the different portions of the bed is fixed by the degree of decomposition



attained up to that point, the rate of heat loss from the catalyst chamber, and the importance of heat exchange by radiation from different parts of the bed. Heat loss from the catalyst bed relative to the amount of heat developed in the bed is small, so that the system may be considered adiabatic. The temperature level and temperature differences within the bed are not so large as to make radiation of great importance. Therefore, the temperature at any point in the catalyst bed is fixed largely by the degree of decomposition at that point if thermal equilibrium of the stream is maintained. Thermal equilibrium may not be maintained if the flow characteristics of the bed are such as to produce a stream, a portion of which has decomposed and vaporized while the rest of the stream passes along as liquid droplets with little or no decomposition.

2. Isbin's work showed little difference (Fig. 2) at high temperature and pressure between catalysts which show considerable differences in activity at lower temperatures.

3. Even supposedly catalytically inert substances become active at high temperature. For example, it has been found that a thermocouple shielded with stainless steel, to which hydrogen peroxide is substantially inert at low temperatures, often reads the temperature corresponding to 100% adiabatic decomposition when exposed to a stream of hydrogen peroxide vapor at high temperature, indicating that all the hydrogen peroxide reaching the surface is decomposed.
4. Certain runs made by Isbin with hydrogen peroxide containing stabilizers or contaminants demonstrated a constant catalyst activity for the initial portion of the run followed by a constantly decreasing activity for the remainder of the run. This can be explained on the assumption that the reaction rate on the catalyst surface initially was higher than diffusion rate but that diffusion rate was maintained until poisoning eventually reduced the effective catalyst area or the reaction rate to a level such that it became the controlling factor rather than the diffusion rate.
5. The increase in the rate of diffusion with an increase in temperature is generally less rapid than



the increase in reaction rate. The experimentally measured increase in rate of decomposition in a catalyst chamber between room temperature and catalyst chamber temperature is not nearly as high as would be predicted from the usual temperature coefficient for reaction rate.

6. The most successful attempt made by Isbin to predict his experimental results from theoretical considerations was based on the assumption that decomposition rate was limited by the rate of diffusion of vapor phase hydrogen peroxide to the catalyst surface. It can be appreciated that this is reasonable by reference to Fig. 1. The decomposition of 83% hydrogen peroxide yields sufficient heat to vaporize completely the remaining hydrogen peroxide, the water of solution, and products of decomposition when the decomposition has proceeded to 76.5% of completion. As can be seen from Fig. 1, a large portion of the catalyst bed is required to decompose the small amount of peroxide remaining after this level of decomposition has been reached. Since the bulk of the catalyst bed is supporting a vapor phase

reaction at a high temperature, it is not surprising that the description of the overall action of the catalyst is best approximated by the assumption that decomposition is limited in rate by the rate of diffusion of hydrogen peroxide vapor to the catalyst surface.

Object of the Investigation The facts outlined above provide a reasonable basis for assuming that vapor diffusion is the controlling feature of high temperature hydrogen peroxide decomposition, but the presence of the initial, liquid phase reaction and the complex nature of flow in a screen bed makes theoretical analysis of the operation difficult. The object of this thesis then became to measure the decomposition occurring in a tube through which hydrogen peroxide vapor was flowing. Analysis of the data obtained under these conditions can be made on a more direct and firmer theoretical basis than data which might be obtained by measurement of the performance of a portion of a catalyst bed composed of screens or pellets such as Isbin used.

This problem was attacked by modifying the apparatus used by Isbin, in order to allow a longer catalyst chamber and provision for sampling the stream. It was then intended to compare the performance of tubes both catalytically active and inert with the calculated rates of diffusion for the same system.

### III. EXPERIMENTAL PROCEDURE

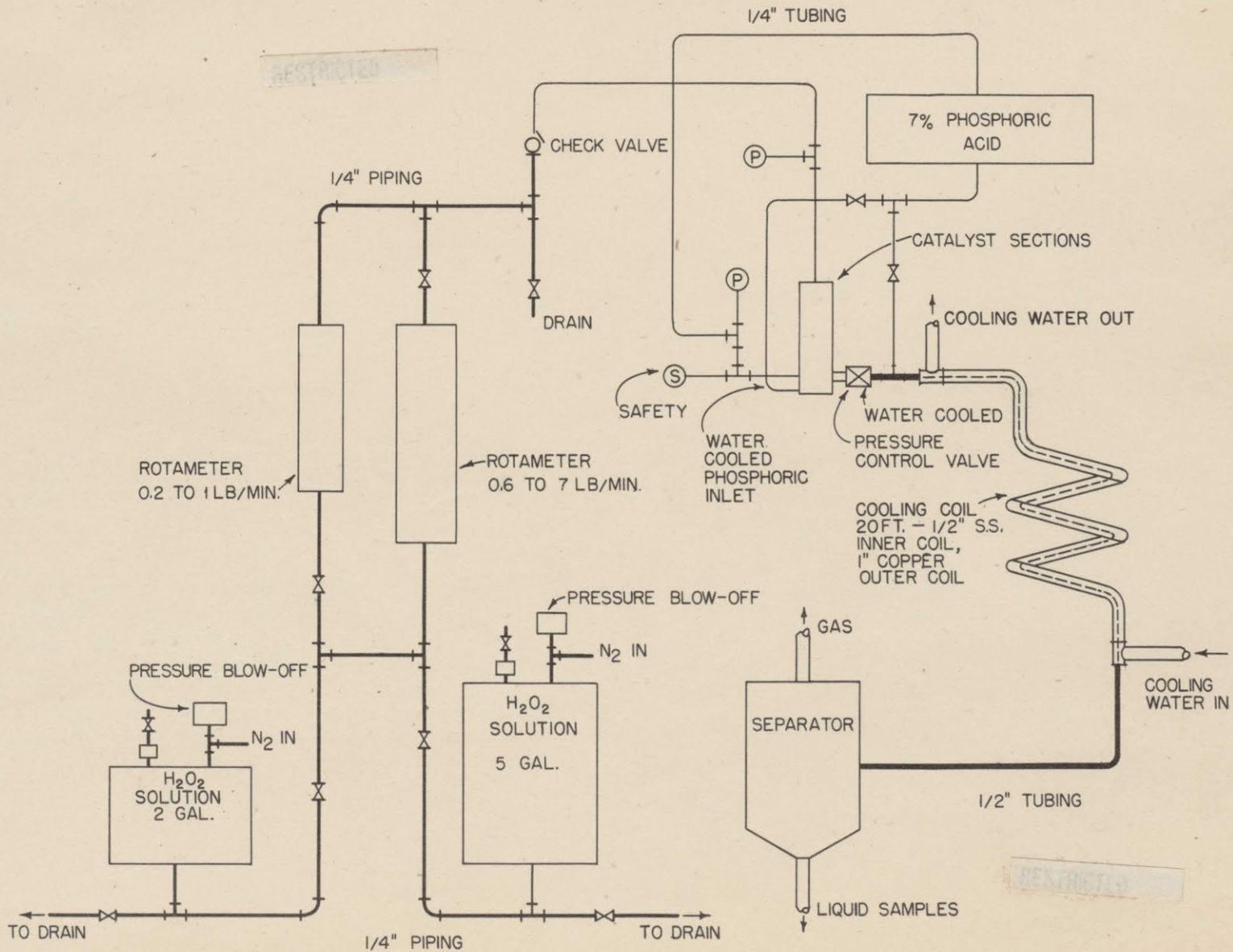
Apparatus The apparatus used in this investigation is that used by Isbin in his work, with certain modifications and additions to the catalyst chamber. Figure 3 is a flow sheet of the apparatus. Figure 4 illustrates the catalyst chamber and auxiliary equipment used in this work.

Flow of hydrogen peroxide to the catalyst chamber is caused by pressurizing the supply tank with nitrogen at about 650 psig. The flow is controlled by a needle valve placed immediately before a rotameter for measurement of the flow rate. After reaching the catalyst bed through which the stream flows vertically downward, and decomposing, the stream is joined at the end of the catalyst chamber by a stream of fluid containing an agent which inhibits decomposition. The quenched stream then passes through a valve which controls the pressure level in the catalyst chamber. The valve is followed by a water cooled coil in which vapor is condensed. A gas-liquid separator then passes the liquid to a sampling station.

The catalyst chamber consists of sections of 1-1/4

FIGURE 3

PRESSURE FLOW APPARATUS



Nitrogen Pressure

Quench Fluid Tank

Quench Fluid Line

Water Jacket

Gas-Liquid Separator

Wet Test Meter

Catalyst Screens

Baffle

Catalyst Chamber

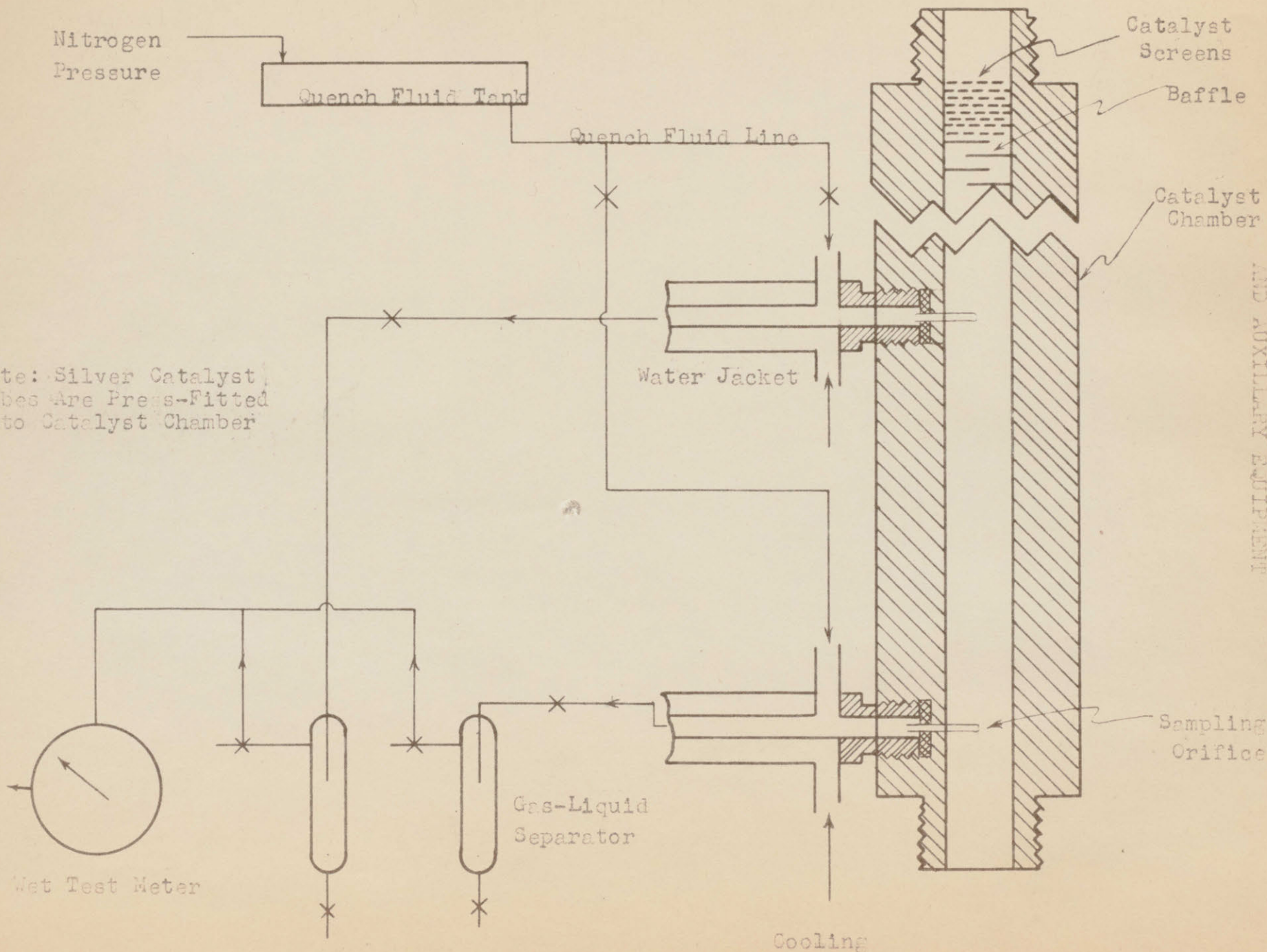
Sampling Orifice

Cooling

Note: Silver Catalyst Tubes Are Press-Fitted Into Catalyst Chamber

DIAGRAM OF CATALYST CHAMBER AND AUXILIARY EQUIPMENT

FIGURE 4



inch stainless steel hex stock through which a 5/8 inch diameter hole is longitudinally bored. Three sections of tube make possible a total length of 26 inches of catalyst chamber. At various points along the side of the catalyst chamber holes have been provided for the insertion of a sampling tube. These sampling tubes are made of 1/8 inch stainless steel tubing with an appropriate sized orifice hole drilled in the peaned-over end. The orifice in the sampling tube withdraws, even at the lowest flow rate used, less than 5% of the stream passing through the catalyst chamber. The sample withdrawn passes immediately into a water jacketed tube and is mingled with a stream of quenching fluid amounting in volume to several times the condensed volume of the sample. The gas and liquid in the sample are then separated, the liquid being collected, and the gas passed through a wet test meter. This condensing and sampling equipment is duplicated for each sampling tube inserted in the catalyst chamber during a particular run.

A record of the pressure and temperature in the catalyst chamber is kept by means of recording instruments. Further details of the apparatus will be found in the Appendix.

Operation of Apparatus The sequence of operations in making a run was the same in all cases. 83% peroxide was

used at a pressure of 500 psig throughout the work in order that a comparison might be made with the work of Isbin. In each run a sufficient number of catalyst screens was used to give at least 76.5% decomposition of the stream before passing to the sampling points. At the flow rates used in this work the stack of 20 mesh catalyst-coated screens is about one inch in length. Mass flow rates of hydrogen peroxide solution used ranged from 3 to 13 lb./min./sq. in.

After assembling the catalyst chamber into the apparatus, loading the supply tank with sufficient hydrogen peroxide for 10-20 minutes running time, and attending to the instruments, the run was started by opening the valve to the rotameter. Thereafter one operator watched the rotameter continuously, making the necessary adjustments of the control valve to keep the flow rate constant. When pressure in the catalyst chamber reached 500 psig the control valve below the catalyst chamber was opened. The operator in charge of this valve made adjustments during the run to keep the pressure at the 500 psig level. When operating pressure had been reached in the system the valves on the lines from the sampling tubes were opened and sampling begun. As the run progressed the operator of the sampling station allowed the condensed liquid from the sampling tubes to collect over a period of one or two

minutes then withdrew the total sample into a flask. At some time during the collection of each sample a reading of the quantity of oxygen accompanying the liquid was taken from the wet test meter. The reading of the wet test meter was timed with a stop watch.

During the run, another operator measured the rate of collection of the liquid condensed from the exit stream of the catalyst chamber and set aside samples from each minute's collection. The operators of the two sampling stations called out the numbers of the sample flasks, sample volumes, and time for a given gas volume to the operator in charge of the pressure control valve. This information was entered on a form sheet.

After exhausting the hydrogen peroxide supply, the system was depressurized and purged. The liquid samples from the exit stream and the sampling tubes were titrated with permanganate to measure the amount of hydrogen peroxide remaining. Calculation of the degree of decomposition attained at the sampling points and in the exit stream from the data obtained is a straight forward procedure, and is outlined below.

#### Expression of Results

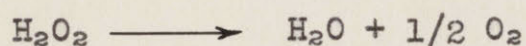
The degree of decomposition has been calculated and recorded in terms of "per cent not decomposed" throughout



this work. This refers to the fraction of the entering peroxide which remains undecomposed at the particular point of measurement.

The total amount and rate of collection of hydrogen peroxide remaining in the exit stream from the catalyst chamber is measured. Knowledge of the flow rate and original hydrogen peroxide concentration then allows direct calculation of the per cent not decomposed in the exit stream.

The data obtained from the sampling tube are treated as follows, on the basis of unit time: Entering the catalyst chamber are X mols of hydrogen peroxide and Y mols of water. By stoichiometry from the equation



there will be, at any point in the catalyst chamber, Z mols of oxygen, (X - 2Z) mols of hydrogen peroxide, and (Y + 2Z) mols of water. Let n be the fraction of the main stream withdrawn through a sample tube. Then in the stream withdrawn there will be

nZ mols of oxygen

n(X - 2Z) mols of hydrogen peroxide

n(Y + 2Z) mols of water

If the ratios of the constituents in the sample and the main stream are the same the fraction decomposed, f, is

$$f = \frac{2Z}{X} = \frac{2nZ}{n(X - 2Z) + 2nZ} .$$

The per cent not decomposed is then  $100(1 - f)$ .

#### IV. RESULTS AND DISCUSSION OF RESULTS

Preliminary Work A number of preliminary runs were made in order to develop the technique of using the sampling system. In the previous work done by Isbin, phosphoric acid solution was used as a quenching agent, but this resulted in serious corrosion of the catalyst chamber pressure control valve. A number of other agents were tested in this work as substitutes for phosphoric acid solution. A dilute solution of sodium stannate was found to be equal to phosphoric acid in retarding decomposition of the stream. The addition of a stream of sodium stannate solution to an unquenched stream would decrease the measured degree of decomposition by 2.5 units of per cent not decomposed. Stannate solution was used as the quenching agent in all runs reported below.

Rapid cooling of the sampled stream was also found to be important in keeping decomposition in the sampling tubes to a minimum. The addition of quench solution afforded some cooling action, and the line through which the sample stream flowed was kept cold by tap water flowing through a jacket extending 12 inches from the point of sampling. In order to make the cooling and quenching most effective, the quantity of material sampled was made as

small as possible. In the earlier work a sampling orifice of 0.013 inch diameter was used. Later, this orifice diameter was reduced to 0.008 inch by the use of the smallest available hypodermic tubing. The stream withdrawn by this orifice was cooled to tap water temperature by passage through the jacketed line.

No measure of the absolute efficiency of this cooling and quenching technique is possible, but it is believed that further effort toward improvement would bring little change in results. The Appendix contains a resume' of this preliminary work.

Results of Sampling Procedure The results of the sampling technique can be divided into groups of runs in which the position of the samplers with respect to the catalyst screens differed and in which different conditions for decomposition were imposed on the hydrogen peroxide stream. These experimental conditions will be described and the results then tabulated. A summary of all runs containing more complete details will be found in the Appendix.

Table I contains the results of runs made with an 8 inch catalyst chamber. In these runs the screen bed was supported by the upstream sampling tube, the downstream sampling tube being 6.25 inches below the screen bed. Quenching and cooling of the exit stream from the

catalyst chamber occurred about 1.5 in. below the downstream sampling tube. In all but one of these runs the stream passed through a 5/8" diameter stainless steel tube. In one run a 0.555 in. diameter silver tube formed the passage between samplers.

TABLE I  
DECOMPOSITION IN AN 8 INCH CATALYST  
CHAMBER

Run No.	Mass Flow Rate lb./min./sq.in.	Average % Not Decomposed			Notes
		Upstream Sampler	Downstream Sampler	Exit Stream	
371	3.1	3.0	2.8	4.0	Stainless steel tube
372	"	7.5	6.8	3.4	" " "
373	"	6.3	10.5	7.2	" " "
374	"	10.3	12.0	8.0	" " "
375	"	9.4	11.0	5.5	" " "
376	"	15.1	12.5	5.7	" " "
377	"	12.0	12.5	6.7	" " "
378	"	12.0	8.2	6.0	" " "
379	"	9.0	8.5	4.9	Silver tube

Table II contains the results of runs made with a 26 inch catalyst chamber. The upstream sampling tube was located 18 inches below the screen bed and the downstream sampling tube placed 6.25 inches below the upstream sampling tube. Quenching and cooling of the exit stream from the catalyst chamber occurred about 1.5 inches below the downstream sampling tube. Most of these runs were made with a simple segmental baffle placed in the stream immediately after the screen bed in order to provide better

mixing and evaporation of any liquid droplets issuing from the screen bed. These runs were made with both stainless steel and silver tubes as noted.

TABLE II

DECOMPOSITION IN A 26 INCH CATALYST CHAMBER

Run No.	Mass Flow Rate lb./min./sq.in.	Average % Not Decomposed			Notes
		Upstream Sampler	Downstream Sampler	Exit Stream	
380	3.1	55.0	35.0	5.7	Stainless steel tube
381	"	1.8	4.8	8.0	" " "
385	"	- -	2.2	4.7	" baffle used
386	"	2.3	1.7	2.3	" " "
387	"	4.5	2.0	4.1	" " "
388	"	4.5	2.5	5.0	" " "
395	4.2	1.3	0.5	0.7	" " "
390	8.0	7.7	4.5	9.9	" " "
391	"	4.6	1.8	4.9	" " "
393	"	9.5	5.3	9.5	" " "
396	11.8	4.1	2.2	4.5	" " "
397	5.3	0.4	0.3	0.25	Silver tube "
400	5.3	2.5	1.2	2.0	" " "
401	"	0.1	0.01	0.01	" " "
398	10.2	0.6	0.3	10.0	" " "
402	"	7.6	4.7	8.1	" " "
399	12.5	2.1	1.2	2.2	" " "

The values listed under the "Average % Not Decomposed" columns for each position in a given run have been selected from the data collected for each run at such a time during the run when performance was most steady. For example, the values for per cent not decomposed registered by the upstream sampler during run 390 varied from 10.3 to 7.6. The value listed, 7.7, was taken at the eighth minute, and

the values listed for the downstream samples and exit stream are taken at the same time. The level of decomposition in each run is determined by the number of screens used at the flow rate chosen. Thus runs 390, 391, and 393, all made at the same flow rate, differ in level of decomposition since runs 390 and 393 were made with 8 screens and 391 was made using 10 screens. Variations in performance during a run are largely due to changes in the activity of the screen bed. This is particularly noticeable in runs at high flow rates with a small number of screens. In these runs the performance tends to become steadily poorer as the run progresses. However, it is the differences in decomposition between sampling points which is of interest here and, if errors do not enter, the contemporary values listed in the tables provide a measure of the decomposition in the catalyst chamber.

The difference in degree of decomposition between upstream and downstream sampling tubes were to be compared with the differences to be predicted by calculation of the rate of diffusion of hydrogen peroxide to the walls of the catalyst chamber. It is apparent, however, that there is a serious inconsistency in the results. Table I shows there to be a negative difference between the values of per cent not decomposed for the upstream and downstream samples in many cases. In nearly all cases the difference

between the values of per cent not decomposed for the samples and the exit stream is positive. Table II shows the results of runs with the longer catalyst chamber to differ in the opposite way. Thus, all but one of the differences between the values of per cent not decomposed for the upstream and downstream samples are positive, while the differences between the downstream samples and the exit stream are negative in nearly all cases.

The signs of these differences are listed in Table III. In all cases the differences represent the subtraction of the value of the per cent not decomposed at a downstream position from the value for an upstream position.

TABLE III  
ALGEBRAIC SIGNS OF DIFFERENCES OF DECOMPOSITION  
AT SAMPLING POINTS IN CATALYST CHAMBER

	Stainless Steel Catalyst Chamber		
	8 in. <u>without baffle</u>	26 in. <u>without baffle</u>	<u>with baffle</u>
Upstream sampler			
- Exit stream	+6, -2	+1, -1	+2, -6
Upstream sampler			
- Downstream sampler	+4, -4	+1, -1	+8, -0
Downstream sampler			
- Exit stream	+7, -1	+1, -1	+0, -8
	Silver Lined Catalyst Chamber		
	8 in. <u>without baffle</u>	26 in. <u>with baffle</u>	
Upstream sampler	+1, -0	+3, -3	
- Exit stream			
Upstream Sampler	+1, -0	+6, -0	
- Downstream sampler			
Downstream sampler	+1, -0	+1, -5	
- Exit stream			



The explanation of this anomalous behavior apparently lies in the fact that the stream of hydrogen peroxide and products of decomposition leaving the screen bed is not in thermal equilibrium. Although a degree of decomposition sufficiently high to provide heat for complete vaporization may have been attained, channeling in the screen bed allows totally or partially undecomposed hydrogen peroxide in the liquid phase to pass through. This must be accompanied by vapor which is superheated relative to its state in thermal equilibrium.

The degree of decomposition as measured in the exit stream is independent of the state of the stream since all hydrogen peroxide, either as liquid or vapor, is measured. The measurement of the degree of decomposition at the sampling points depends upon obtaining a representative sample of the stream. If droplets of liquid in the stream tend to pass by the sampling orifice by virtue of their greater momentum, the sample withdrawn will be deficient in hydrogen peroxide, resulting in the impression to the observer that decomposition has proceeded further than it has in fact.

In the short catalyst chamber the upstream sampling tube receives a sample from a position directly under the screen bed. Although the sample is relatively deficient in hydrogen peroxide, here the vapor is rich in hydrogen

peroxide and the quantity sampled is sufficient to give a positive difference between the values of per cent not decomposed of the upstream sampler and the exit stream. As the stream of vapor and liquid droplets passes to the downstream sampler, decomposition must occur as well as evaporation of hydrogen peroxide from the liquid into the vapor. In the short catalyst chamber, at this short distance from the screen bed, droplet size is largest, thus giving the most rapid rate of evaporation. If the quantity of hydrogen peroxide as liquid issuing from the screens is large, it is possible that the rate of evaporation might outstrip the rate of decomposition in the tube between the sampling tubes, leading to a negative difference between the values of per cent not decomposed for the upstream and downstream sampling tubes. The differences between the downstream sampler and exit stream values in the short catalyst chamber are predominately positive, as would be expected if the sampling procedure gave correct data. Since it has been assumed that the presence of liquid produces a lower figure for the per cent not decomposed, it is not clear why these positive differences are so large, considering the short length of catalyst chamber between the downstream sampler and the place of cooling the exit stream.

In the 26 inch catalyst chamber the longer travel of the stream before reaching the sampling tubes provides a time for evaporation and mixing of liquid droplets. The use of the baffle encourages this process also. These conditions should have the effect of producing a more uniform stream at the level of the sampling tubes. The differences between the values of per cent not decomposed for the upstream and downstream sampling tubes in these runs are positive, indicating that homogeneity of the stream has been improved to the point where evaporation rate lags decomposition rate. The degree of decomposition in the vapor phase at this greater distance from the screen bed causes the differences between the values of per cent not decomposed for the samplers and exit stream to become predominately negative and more pronouncedly so with the downstream sampler-exit stream values.

Although these anomalies in the results are fairly well explained by the assumption of the persistence of liquid in the stream, an experiment was conducted to provide more direct evidence. A short length of 1/8 inch o.d., 0.061 inch i.d. tubing such as used for sampling tubes was filed half-round for a distance of 1/4 inch from one end leaving a trough with 0.032 inch wide edges. An aluminum wire of 0.035 diameter was led through the tube to the trough at the end and isolated from the tube wall by a

glass sleeve and packing of "Insalute" cement. This insulated wire, filed flat, could not make electrical contact with the edges of the trough thus providing a conductivity testing device. A dry cell, small resistance, and an ammeter were attached in series with the wire and the tube wall. After being placed in a muffle the current passed was observed to drop from 15 microamperes to zero as the temperature rose to 430°F, indicating that the thoroughly dry assembly was non-conducting. The assembly was also tested by clamping it over a Bunsen burner and dropping water and 83% hydrogen peroxide on the end. Contact of the water with the heated tube produced a current of 3.6 milliamperes, while the hydrogen peroxide allowed 0.05 milliamperes to pass.

The conductivity tester was then mounted in the catalyst chamber in a hole provided for a sampling tap 22.5 inches below the screen bed for run 393. During the course of the run, the current passed rose from 0.2 to 1.3 milliamperes. At the end of the run the current dropped steadily, reading .1 milliampere after a minute and finally 9 microamperes when readings were stopped. The temperature in the catalyst chamber at the point where the conductivity tester was inserted was about 450°C so that a steady supply of liquid must have been brought to this point in order for the tester to pass the current

noted.

The combination of the data obtained with the sampling tubes and the exit stream do not provide sufficient data to calculate either the amount of liquid in the stream or the distribution of hydrogen peroxide between liquid and vapor as taken by the sampling tube. It appears, however, that the sampling tubes do not withdraw only vapor. In run 390, if the value of per cent not decomposed recorded for the exit stream is assumed to exist at the downstream sampler, it is found that the sampler withdrew about 1% of the oxygen and 0.4% of the hydrogen peroxide at that point. If it is supposed that only gas is withdrawn it can be shown that the liquid passing by would be about 10 weight per cent hydrogen peroxide. When it is considered that the droplets must become more concentrated in hydrogen peroxide as they pass through the catalyst tube, this low figure does not seem likely, indicating that a part of the hydrogen peroxide must have been withdrawn as liquid.

#### Comparison of Predicted and Experimental Results

Since the results obtained with the sampling tubes are untrustworthy as a measure of the decomposition occurring in the catalyst chamber, the decomposition as measured by the differences between the per cent not

decomposed calculated from Isbin's work for the number of screens and flow rate used and the per cent not decomposed recorded in the exit stream have been compared with the performance calculated for a diffusion-controlled decomposition rate. This procedure is open to objection because of the fact that the per cent not decomposed predicted by Isbin's work (Fig. 1) may not be exactly reproduced. The activity of the catalyst bed often varies several per cent during a run, but the differences give an estimate of the order of magnitude of the actual performance as compared with the calculated performance.

Figures 5 and 6 present the results of calculated performance of a diffusion rate limited decomposition tube. The derivation of these figures is presented in the Appendix. Briefly, they are based on the assumption of diffusion of hydrogen peroxide vapor to the wall of a tube through a stagnant film of its products of decomposition at the adiabatic decomposition temperature corresponding to the degree of decomposition at the position in the tube. Diffusion in the bulk of the stream is not considered, nor are the plots applicable to positions in the tube near the screen bed where eddy diffusivity is of major importance.

Table IV presents a comparison of the actual performance of the catalyst tube as calculated by the difference

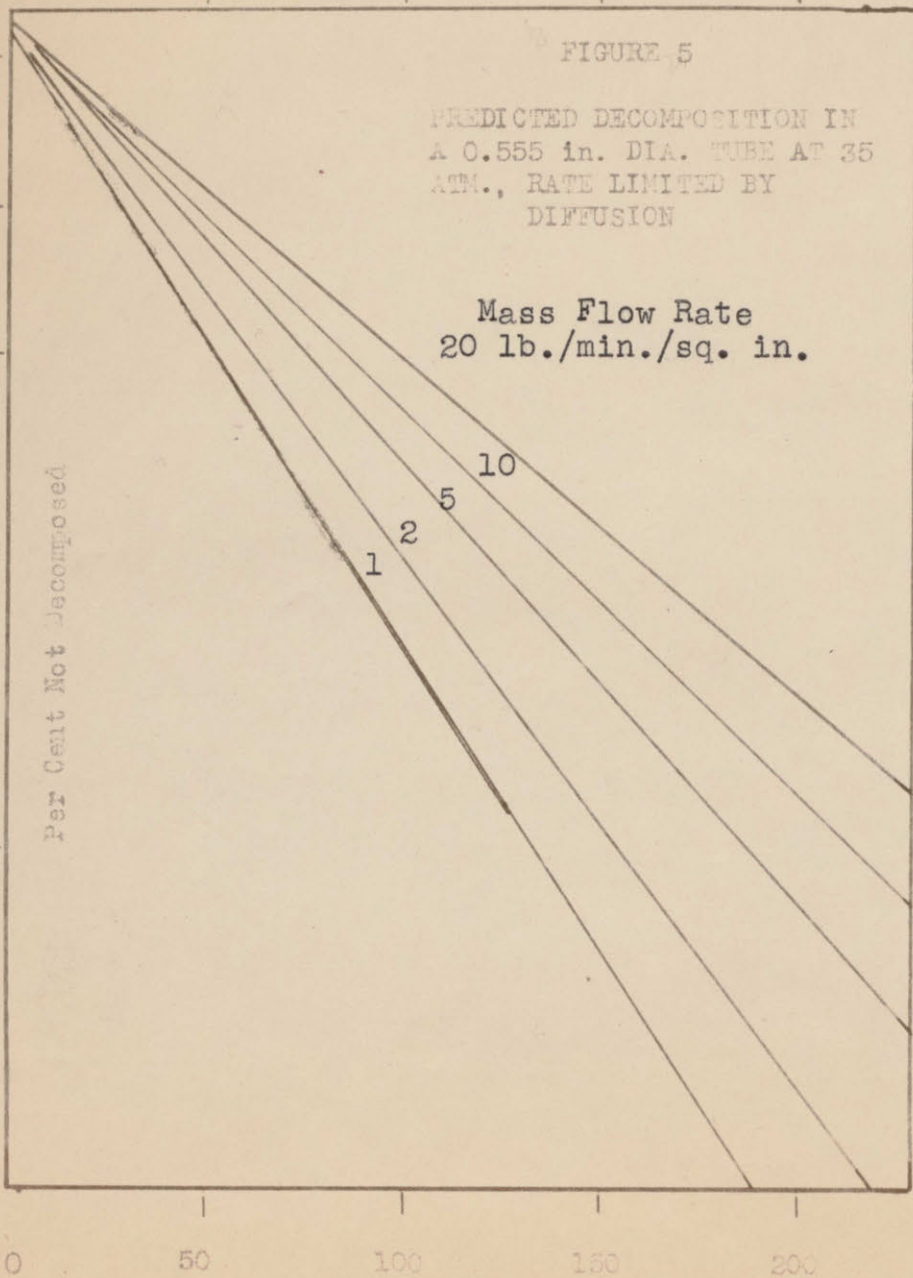
FIGURE 5

PREDICTED DECOMPOSITION IN  
A 0.555 in. DIA. TUBE AT 35  
ATM., RATE LIMITED BY  
DIFFUSION

Mass Flow Rate  
20 lb./min./sq. in.

Per Cent Not Decomposed

10  
5  
2  
1



Inches of 0.555 in. dia. Tube

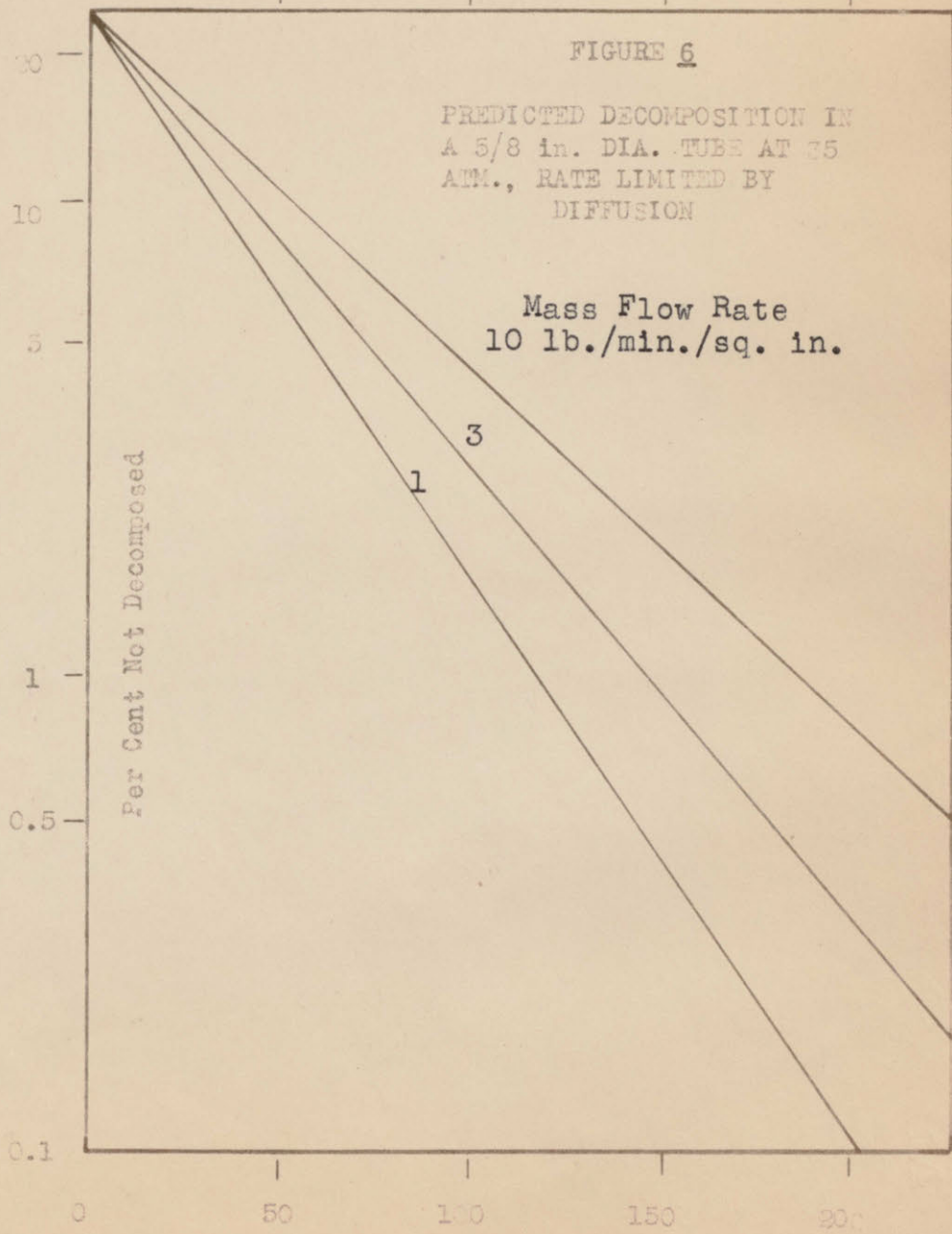
FIGURE 6

PREDICTED DECOMPOSITION IN  
A 5/8 in. DIA. TUBE AT 35  
ATM., RATE LIMITED BY  
DIFFUSION

Mass Flow Rate  
10 lb./min./sq. in.

Per Cent Not Decomposed

3  
1



Inches of 5/8 in. dia. Tube

between the per cent not decomposed calculated to exist at the end of the screen bed and the per cent not decomposed in the exit stream with the performance predicted from Figs. 5 and 6.

It can be seen that the actual performance of the catalyst tubes is in all cases greater than that predicted by Figs. 5 and 6. There are several reasons for this. In the portion of the tube immediately below the screens where the film has not been established at the wall, eddy diffusivity is of major importance and is greater in magnitude than the molecular diffusivity used in calculating Figs. 5 and 6. The presence of liquid droplets requires that the vapor be superheated relative to the equilibrium temperature for the entire stream. This greater temperature enhances the diffusivity. Continual evaporation of hydrogen peroxide from droplets tends to enrich the hydrogen peroxide concentration in the vapor, thus increasing the gradient for diffusion.

The greater decomposition obtained is not so much greater as to make it likely that control of the decomposition by reaction rate is responsible for the increase. The results with the silver runs are not significantly different from the runs with the stainless steel to make it appear that the material of the wall affects the decomposition rate. It is concluded from this comparison that diffusion is indeed the controlling feature of hydrogen peroxide decomposition at high temperature.



TABLE IV

COMPARISON OF ACTUAL AND PREDICTED PERFORMANCE OF CATALYST CHAMBER

<u>Run No.</u>	<u>Mass Flow Rate lb./min./sq.in.</u>	<u>No. of Screens</u>	<u>Calculated % Not Decomp. from Fig. 1</u>	<u>Exit Stream % Not Decomp.</u>	<u>Difference D - E</u>	<u>Predicted Diff. from Figs. III &amp; IV</u>	<u>Length of tube in.</u>
371	3.1	10	12.7	4.0	8.7	2.1	7-3/8
372	3.1	10	12.7	3.4	9.3	2.1	7-3/8
383	3.1	10	12.7	3.2	9.5	5.3	25-3/8
373	3.1	8	12.7	7.2	14.0	3.2	7-3/8
374	3.1	8	12.7	8.0	13.2	3.2	7-3/8
375	3.1	8	12.7	5.5	15.7	3.2	7-3/8
376	3.1	8	12.7	5.7	15.5	3.2	7-3/8
377	3.1	8	12.7	6.7	14.5	3.2	7-3/8
378	3.1	8	12.7	6.0	15.2	3.2	7-3/8
379	3.1	8	12.7	4.9	16.3	3.2	7-3/8
380	3.1	8	12.7	5.7	15.5	9.0	25-3/8
381	3.1	8	12.7	8.0	13.2	9.0	25-3/8
382	3.1	8	12.7	4.0	17.2	9.0	25-3/8
384	3.1	8	12.7	4.6	16.6	9.0	25-3/8
385	3.1	8	21.2	4.7	16.5	9.0	25-3/8
386	3.1	8	21.2	2.3	18.9	9.0	25-3/8
387	3.1	6	34.8	4.1	29.7	13.7	25-3/8
388	3.1	6	34.8	5.0	29.8	13.7	25-3/8

(Cont'd on next page)

TABLE IV (Cont'd)

<u>Run No.</u>	<u>Mass Flow Rate</u> lb./min./sq.in.	<u>No. of Screens</u>	<u>Calculated % Not Decomp. from Fig. 1</u>	<u>Exit Stream % Not Decomp.</u>	<u>Difference D - E</u>	<u>Predicted Diff. from Figs. III &amp; IV</u>	<u>Length of tube in.</u>
395	4.2	10	15.2	0.7	14.5	6.2	25-3/8
S397	5.3	10	15.2	0.25	15.0	6.5	25-3/8
S400	5.3	8	23.5	2.0	21.5	10.5	25-3/8
S401	5.3	8	23.5	0.01	23.5	10.5	25-3/8
391	8.0	10	21.5	4.9	16.6	7.7	25-3/8
390	8.0	8	26.3	9.9	16.4	9.4	25-3/8
393	8.0	8	26.3	9.5	16.8	9.4	25-3/8
S398	10.2	10	21.5	10.0	11.5	8.7	25-3/8
S402	10.2	8	26.3	8.1	18.2	11.5	25-3/8
394	11.8	16	11.8	0.9 - 4.7	10.9 - 7.1	4.1	25-3/8
396	11.8	16	11.8	4.5	7.3	4.1	25-3/8
392	11.8	11	24.0	2.5 - 10.0	21.5 - 14.0	8.2	25-3/8
S399	12.5	16	11.0	2.2	8.8	10.1	25-3/8

Note: Run numbers prefaced by S denote a 0.555 in. diameter silver lined catalyst chamber. All other runs were made with a 5/8 in. diameter stainless steel tube. Mass flow rates tabulated are those existing in the tube.

## V. CONCLUSIONS

The results of this study show that the stream of hydrogen peroxide and products of decomposition issuing from a catalyst screen bed are not in thermal equilibrium. Furthermore, hydrogen peroxide exists in the liquid phase in downstream portions of the catalyst chamber where sufficient heat of decomposition has been evolved and temperature is sufficiently high to vaporize completely this liquid under equilibrium conditions. This fact makes representative sampling of the stream a difficult procedure, and the sampling technique used in this study did not produce reliable results.

Consideration of the results obtained by comparing the decomposition in a tube with the decomposition calculated on the basis of a simple diffusional process operating at the conditions in the tube has shown the actual decomposition to exceed the calculated decomposition. The difference is not large enough to make it appear that the decomposition is controlled by reaction rate, and it is concluded that diffusion of hydrogen peroxide to the catalyst surface is the controlling feature of the decomposition.

## VI. RECOMMENDATIONS

A study of the flow of hydrogen peroxide through a catalyst screen bed in a glass tube at atmospheric pressure is recommended as a means of obtaining visual evidence of the nature of the flow pattern issuing from the screens. Information obtained from this experiment would give a measure of the persistence of liquid spray and make it possible to choose the best orientation of sampling tubes in a catalyst chamber.

Another research group at M.I.T. has developed an apparatus for vaporization of concentrated hydrogen peroxide by boiling. This apparatus was developed for studies of homogeneous vapor phase decomposition and is safe and reliable in operation. By using such an apparatus to supply hot, concentrated hydrogen peroxide vapor to a catalyst tube the difficulties encountered with liquid droplets in this work might be avoided. It is recommended that an apparatus be constructed for the production and supply of hydrogen peroxide vapor by direct vaporization at reasonable rates to a catalyst tube where sampling measurements such as developed in this work might be made.

The conclusions of this group studying homogeneous vapor phase decomposition should be considered for its

possible contribution to the decomposition in a catalyst bed or tube. It may be necessary to make some allowance for this factor in the calculation of diffusion rates.

The results of this study make it clear that the designer and experimenter with catalysts for hydrogen peroxide decomposition should keep in mind the importance of preventing channeling in the catalyst bed. Provision consistent with pressure drop requirements should be made to reduce to a minimum the amount of liquid droplets persisting in the stream, since the space efficiency of the bed is reduced by the presence of such liquid.

APPENDIX

Details of Apparatus Reference should be made to Figs. 3 and 4, diagrams of the apparatus, in following the present discussion. In order to minimize decomposition of hydrogen peroxide in the system stainless steel was used as a material of construction throughout. Where gaskets or packing were necessary plastic material such as Koroseal or Teflon was used. Aluminum washers were used to seal the catalyst chamber and aluminum rupture discs were used.

Two tanks are provided for hydrogen peroxide supply, one of 2 gallon capacity, and the other of 5 gallon capacity. These tanks are provided with relief valves to guard against excessive pressure build-up in case of decomposition of the hydrogen peroxide stored in them. A manually operated valve is located at the bottom of the tank for the release of pressure at the end of a run. Connections are made from these tanks to a bank of four, 220 cu. ft., 2000 psig nitrogen tanks through two regulator valves in series.

The hydrogen peroxide flows under the influence of the nitrogen pressure to the system, the flow being regulated by a needle valve placed before each of two rotameters. A valve system makes it possible to choose the rotameter to be used in a particular run. The small rotameter

measures rates of flow from 0.2 to 1 lb. per min. and the large rotameter covers the range from 0.6 to 7 lb. per min. A check valve has been placed downstream from the rotameters to prevent backflow to the supply tanks of the stream which might contain catalyst particles.

The rotameter supplies hydrogen peroxide to the top of the catalyst chamber. At this point there is a line leading to an indicating, Bourdon type pressure gauge and to a continuous recording gauge for the upstream pressure. The catalyst chamber has been described in the Procedure. Quench fluid is supplied from an overhead tank containing about 2 liters at a pressure of 60 psig to the sampling tubes leading from the catalyst chamber. The flow of quench fluid is regulated by needle valves in the lines leading to the sampling lines.

At the bottom of the catalyst chamber is situated a tee from which a line to the safety disc, a quench fluid addition line, and a pressure normalizing line to the quench fluid tank can be led. The safety disc is an aluminum washer designed to rupture at 800 psig and held in place on a shoulder by a simple screwed fitting. The quench fluid<sup>line</sup> leads to a 3 liter capacity tank situated about 3 ft. above the bottom of the catalyst chamber. By equalizing the pressure above the fluid in the tank with



a gas line from the point at which the quench fluid is added to the hydrogen peroxide stream, a gravity flow of quench fluid is obtained. A tap from this pressure equalizing line leads to an indicating gauge and a recording gauge for downstream pressure. The latter gauge became defective soon after the beginning of this work and was not used thereafter.

Just downstream from the catalyst chamber is a needle valve for the regulation of the pressure in the catalyst chamber. This valve is cooled by a stream of water playing on the outside of it and on the section of tubing just below it. A drain pan below the valve and tubing collects the spray and sends it to waste.

From this point the stream passes through a cooling coil containing 20 ft. of 1/2 in. stainless steel tubing inside a 1 in. copper tubing jacket through which tap water may be passed. At the end of this coil the stream enters a gas-liquid separator. In this separator the stream containing gas and condensed vapor is thrown downwards against a conical shield which effectively separates the liquid from the gas. The gas is allowed to escape to the atmosphere through a bed of Berl saddles provided to clean up the last traces of hydrogen peroxide which may not have been condensed. The liquid is passed to a sampling station.

This equipment is set up behind a barrier constructed of 1/4 in. steel plates, with only the nitrogen tanks, handles of control valves, and recording instruments outside the barrier. Transparent plastic windows allow an operator to watch the rotameters, and a mirror is suspended at an angle above the apparatus so that the functioning of the equipment may be observed outside of the barrier.

Preliminary Work A large number of runs was made to perfect a sampling technique which would permit reliable sampling of the stream in the catalyst chamber. The problem to be met consisted of removing a part of the hot stream without allowing further decomposition of hydrogen peroxide to occur in the sampling apparatus. Sampling tubes for insertion into the catalyst chamber were prepared by peaning-over the end of a short piece of 1/8 in. stainless steel tubing and drilling a hole in the very end. At first this hole was made with a No. 60 drill, about 0.013 in. diameter. Later, the size of the hole was reduced by press-fitting a short length of stainless steel hypodermic tubing of 0.008 in. i.d. into the hole drilled in the tubing. Little trouble was experienced in keeping these small holes open and clear of debris. In order to make a pressure tight seal around the opening through which the sampling tube was inserted into the catalyst chamber, a collar was fitted tight around the sampling tube and the

collar pressed by a nut against a shoulder around the hole leading into the catalyst chamber. The sampling tube passed through the center of the nut and discharged into a section of 1/4 in. stainless steel tubing leading to the sampling station.

In the earlier runs the 1/4 in. tubing passed, unjacketed for about six inches to the entrance of a coil of twenty feet of 1/4 in. tubing surrounded by a water jacket. This arrangement allowed a relatively long part of the line to remain quite hot, the only cooling in this six inch section being done by the addition of stannate solution. A shield was put around this section later, and the tubing sprayed with water, but this was a cumbersome arrangement. By discarding the coil and jacketing the tubing with one foot of 1/2 in. tubing welded to the sealing nut a very effective cooling was obtained. In this arrangement the incoming cooling water line and the stannate addition line were fitted as close to the sealing nut as possible. The final arrangement provided a sonic orifice with consequent rapid travel of the vapor through about one inch of tube, catalyst chamber wall, and sealing nut before reaching cooled tubing and meeting quench fluid stream. No rise in temperature of the tubing after the water jacket could be noted during a run.

The effectiveness of various quench solutions was

tested by allowing a run to proceed without addition of quench fluid for a time and turning on the quench fluid stream for the balance of the run. By comparing the per cent not decomposed registered before and after the addition of quench fluid, a measure of its effectiveness was obtained. An 8% phosphoric acid solution had been used satisfactorily by Isbin (4) as a quench fluid in his work but with serious corrosion of the apparatus. A number of substitutes for this solution were tested and the results are summarized in Table AV where the increase in the value of per cent not decomposed observed after the addition of a particular reagent is tabulated.

Table AV  
COMPARISON OF THE EFFECTIVENESS OF  
VARIOUS QUENCH FLUIDS

<u>Run No.</u>	<u>Quench Fluid</u>	<u>% Not Decomposed Before &amp; After Addition of Quench</u>	<u>Difference</u>
352	8% H <sub>3</sub> PO <sub>4</sub>	7.5 - 8.5	1.0
355	8% H <sub>3</sub> PO <sub>4</sub>	13.0 - 15.0	2.0
356	8% H <sub>3</sub> PO <sub>4</sub>	7.0 - 9.5	4.5 <sup>2.5 ?</sup>
352	Water	9.0 - 11.0	2.0
353	Water	7.5 - 9.0	1.5
354	Water	5.0 - 6.0	1.0
357	2% H <sub>3</sub> PO <sub>4</sub> in sat Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	7.5 - 8.5	1.0
358	2% H <sub>3</sub> PO <sub>4</sub> in sat Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	6.0 - 7.5	1.5
359	1.7 N HNO <sub>3</sub>	3.5 - 4.5	1.0
362	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O, 1.8 g/l	5.0 - 7.0	2.0
361	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O, 1.2 g/l	6.0 - 8.5	2.5
360	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O, 0.6 g/l	6.5 - 9.0	2.5
363	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O, 0.3 g/l	5.0 - 7.5	2.5
364	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O, 0.3 g/l	6.0 - 8.5	2.5
365	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O, 0.3 g/l	4.5 - 6.5	2.0
366	Na <sub>2</sub> SnO <sub>3</sub> ·3H <sub>2</sub> O, 0.3 g/l	5.5 - 9.0	3.5

The results of this work show that the solution of sodium stannate is an effective quenching agent. It was used in all runs after no. 366.

Errors and Reproducibility of Results The discussion of the results has brought out the fact that the stream of hydrogen peroxide in the catalyst chamber contains liquid droplets. This makes the results of the sampling technique unreliable. Other factors which may affect the precision of the results are listed and discussed below:

1. Determination of input hydrogen peroxide concentration
2. Control of hydrogen peroxide flow rate
3. Titration of liquid samples for hydrogen peroxide content
4. Pressure variations
5. Homogeneity of samples withdrawn
6. Quantity of stream withdrawn in samplers
7. Quenching and cooling of sample
8. Timing volume of oxygen flow through wet test meter
9. Maintenance of adiabatic conditions
10. Possible homogeneous vapor phase decomposition.

1. The method used for determination of hydrogen peroxide content, titration with permanganate, is a standard one and has been shown to be quite accurate by Huckaba and Keyes (3). The hydrogen peroxide supplies

used were derived by dilution of 90% hydrogen peroxide solution made by the Buffalo Electro-Chemical Company with distilled water to 83%. Successive lots did not vary more than  $\pm 0.5\%$  from 83%.

2. The rotameters were calibrated with water and a density correction for the heavier hydrogen peroxide solutions applied to this calibration. At low flow rates there was a tendency for the rotameter float to vibrate because of pressure surges in the catalyst chamber. By careful attention the operator of the flow rate control valve could maintain the float at an average level of the flow rate desired. This vibration was not of sufficient magnitude to seriously affect the constancy of flow rate.

3. The calculation of the per cent not decomposed in the sample streams depends on a ratio of oxygen to hydrogen peroxide. It has been estimated that an error of 1 cc. in the quantity of ca. 0.2 N permanganate used to titrate these samples will result in about 2.5% error in the per cent not decomposed. This is a wide margin.

4. The work of Isbin (4) has shown the influence of pressure on the decomposition in a catalyst screen bed to be small. Pressure variations affect the quantity of material flowing through the sampling orifice, and, if variations occur while the oxygen flow through the wet test

meter is being read, an error will be introduced. Catalyst chamber pressure was usually maintained within 20 psi of 500 psig and the oxygen rate readings generally were steady or varied in a regular way.

5. As discussed before, non-homogeneity of the samples withdrawn is the most serious error in the work.

6. The fraction of the stream withdrawn by the sampling orifice was never more than 5% of the bulk stream and with the 0.008 inch diameter orifice averaged around 2%. This is certainly not enough to affect the precision of the results of determination of per cent not decomposed in the exit stream.

7. The development of the cooling and quenching technique has been discussed before. It is believed that the procedure adopted protects the samples taken from decomposition in the sampling tubes.

8. It has been estimated that an error of 0.2 sec. in the timing of the oxygen rate through the wet test meter will result in an error of about 0.5% in the per cent not decomposed. The stop watch used can be read to 0.1 sec.

9. By assuming the 100% adiabatic decomposition temperature of 83% hydrogen peroxide to exist at all points in the 6 inch catalyst chamber the heat loss to the surroundings was estimated to be about 10% of the heat of

decomposition at a mass flow rate of 3.5 lb. per min. per sq. in. Since conditions do not approach this extreme, heat losses are smaller and the catalyst chamber can be considered to be virtually adiabatic. The 26 inch catalyst chamber was wrapped with a 1/2 inch layer of asbestos tape to minimize heat losses.

10. It is quite possible that homogeneous thermal decomposition plays a part in the high temperature vapor phase decomposition of hydrogen peroxide. There are no data which would make possible the estimation of the extent to which it proceeds. Some of the increase in decomposition over that predicted by diffusion theory noted in the results may be due to homogeneous thermal decomposition.

Calculation of the Rate of Diffusion in a Tube Sherwood (8)

presents an equation for the diffusion of one gas through a second stagnant gas. For the present case it may be written:

$$N = \frac{dn_{H_2O_2}/d\theta}{dA} = \frac{DP}{RTx} \frac{(p_{H_2O_2 \text{ bulk}} - p_{H_2O_2 \text{ surf}})}{p_{BM}} \quad (1)$$

where

N = diffusion rate, lb. mols/min./ft<sup>2</sup>  
 D = diffusivity, ft<sup>2</sup>/min.  
 P = pressure, atmospheres  
 T = temperature, degrees Kelvin  
 R = gas constant, ft<sup>3</sup> atm./lb.mol/°K.  
 x = film thickness, ft.



$P_{H_2O_2 \text{ bulk}}$  = partial pressure of hydrogen peroxide  
 in bulk of stream  
 $P_{H_2O_2 \text{ surf}}$  = partial pressure of hydrogen peroxide  
 at catalyst surface  
 PBM = mean partial pressure of stagnant gas.

This equation is not strictly applicable to the present case since there is multicomponent counter-diffusion of products of decomposition away from the catalyst surface, but a more rigorous treatment as suggested by Hougen and Watson (2) was found to give virtually the same results.

In order to evaluate the diffusion rate of hydrogen peroxide vapor to a catalyst surface it will be assumed that adiabatic conditions with slug flow and complete mixing within the slug are maintained. The terms in equation (1) can then be evaluated in terms of  $f$ , the fraction of the original hydrogen peroxide remaining undecomposed at any time in a process. Sufficient heat of reaction is liberated by the adiabatic decomposition of 83% hydrogen peroxide to completely vaporize the hydrogen peroxide and products of decomposition when the fraction decomposed has reached 0.765. The diffusion rate will be evaluated in this vapor phase region where the fraction decomposed varies from 0.765 to 1.0.

The diffusivity,  $D$ , may be calculated from Gilliland's empirical equation (1):

$$D = 0.0043 \frac{T^{3/2}}{P(V_A^{1/3} + V_B^{1/3})} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (2)$$

where

$$\begin{aligned}
 D &= \text{diffusivity, cm}^2/\text{sec.} \\
 T &= \text{temperature, } ^\circ\text{K.} \\
 M_A, M_B &= \text{molecular weights of gases A and B} \\
 P &= \text{absolute pressure, atmospheres} \\
 V_A, V_B &= \text{molecular volumes of A and B}
 \end{aligned}$$

As  $f$  varies from .765 to 1.0 the average molecular weight of the products of decomposition varies from 21.2 to 21.75. An average value of 21.62 was taken for  $M_B$ . The molecular volumes are given in Sherwood (8).

For 83% hydrogen peroxide diffusing through the products of its decomposition at 35 atm., equation (2) becomes

$$D = 1.215 \times 10^{-6} T^{3/2} \quad (3)$$

The diffusivity for hydrogen peroxide predicted by equation (2) at room temperature has been obtained in experiments by McMurtrie and Keyes (7).

This may be expressed in terms of  $f$  through an equation from Isbin (4) for the temperature attained by the adiabatic decomposition of 83% hydrogen peroxide initially at room temperature

$$T = 1405f - 557 \quad (4)$$

The partial pressure of hydrogen peroxide at the catalyst surface is taken to be zero. Operation at 35 atmospheres is assumed. The partial pressures of the

stream components can then be calculated as,

$$p = \frac{35n}{\sum n}$$

where  $n$  = mols of any component.

If 1 lb. of 83% hydrogen peroxide is taken as a basis, there will be initially 0.0244 lb. mols of hydrogen peroxide and 0.00945 lb. mols of water. By stoichiometry, the partial pressures of each component after a given degree of decomposition will be

$$p_{\text{H}_2\text{O}_2} = \frac{0.845(1 - f)}{0.03385 + 0.0122 f} \quad (5)$$

$$p_{\text{O}_2} = \frac{0.427f}{0.03385 + 0.0122f} \quad (6)$$

$$p_{\text{H}_2\text{O}} = \frac{0.3305 + 0.845f}{0.03385 + 0.0122f} \quad (7)$$

Since the ratio of total pressure to mean pressure of stagnant gas is nearly one in the range  $f = 0.765$  to 1.0, the arithmetic mean of the partial pressure of the stagnant gas will be used instead of the logarithmic mean.

$$\text{PBM} = \frac{35 + p_{\text{H}_2\text{O}_2} + p_{\text{O}_2}}{2} \quad (8)$$

The thickness of the gas film for diffusion is assumed to be the same as that for heat transmission. McAdams (6) shows that this film thickness can be expressed as a function of tube diameter, Reynolds number, and Prandtl number.

$$x = \frac{\text{tube dia.}}{0.023 \text{ Re}^{0.8} \text{ Pr}^{0.4}} \quad (9)$$

where  $x$  = film thickness, ft.

The Prandtl number is taken constant at 0.903, and for a tube of 0.555 in. diameter the film thickness becomes

$$x = \frac{2.255}{\text{Re}^{0.8}} \quad (10)$$

Substitution of these expression into equation (1) yields an expression for  $N$  in terms of  $f$  and  $\text{Re}$ :

$$N = \frac{0.942 \times 10^{-6} (1405f - 557)^{\frac{1}{2}} \text{Re}^{0.8} (1 - f)}{(0.887 + f)} \quad (11)$$

If an expression for  $n'$ , the lb. mols of hydrogen peroxide per min. flowing past a given point in the catalyst tube is made in terms of  $f$ , equation (11) can be integrated for the length of tube,  $L$ , necessary to attain a given degree of decomposition.

$$f = \frac{n_0' - n'}{n_0'} \quad (12)$$

where subscript 0 refers to entrance conditions.

In terms of the mass flow rate,  $G$ , and the cross section area of tube,  $S$ ,

$$n' = 0.0244GS(1 - f) \quad (13)$$

Now, 
$$N = \frac{dn/d\theta}{dA} = \frac{dn'}{dA} = \phi(n')$$

where  $\phi(n')$  is the expression resulting from equations (11) and (13).

By integrating

$$\int_{0.765n_0'}^{n'} \frac{dn'}{\phi(n')} = \int dA = \int_0^L \pi(\text{dia.})dL$$

we find that

$$L = 3.03 \times 10^5 \frac{n_0'}{\text{Re}^{0.8}} \sqrt{1 - 1.657 \frac{n'}{n_0'}} - 9.48 \frac{n_0'}{\text{Re}^{0.8}} \times 10^5 \tanh^{-1} \sqrt{1 - 1.657 \frac{n'}{n_0'}} + 7.59 \times 10^5 \frac{n_0'}{\text{Re}^{0.8}} \quad (14)$$

$L$  being expressed in feet of 0.555 in. diameter tube.

Equation (14) has been used to plot Fig. 5. A similar equation was developed for a 5/8 in. diameter tube

and used to plot Fig. 6. The difference between the two plots is small.

The diffusion rate of hydrogen peroxide in a tube as calculated by equation (11) is accurate only to the extent that flow conditions in the tube make the use of equation (9) for the estimation of film thickness accurate. Equation (9) probably affords a good estimate of film thickness in turbulent flow in round, straight pipes at a point sufficiently removed from obstructions and changes in direction<sup>of</sup> flow. Equation (11) also depends upon the assumption of zero hydrogen peroxide concentration at the catalyst surface and uniform hydrogen peroxide concentration in the bulk of the stream at any particular level in the tube. If diffusion rate is the controlling factor in the rate of decomposition, the assumption of zero hydrogen peroxide concentration at the catalyst surface is justified. Sherwood and Woertz (9) have shown that a significant part of the resistance to diffusion may occur in the core or bulk of a flowing stream. Some of the discrepancy between the true rate and a rate calculated by consideration of diffusion in the bulk of stream may be overcome by the fact that the film thickness calculated from equation (9) in an "effective" film thickness derived from experimental results.

As mentioned in the Discussion of Results, the measurement of the decomposition in the tube by the difference in per cent not decomposed between that in the exit stream and that calculated to exist at the end of the screen bed is not strictly comparable to the difference predicted by Figs. 5 and 6 because the measurement is taken over a length of tube in which diffusion is not altogether controlled by a film resistance. In the portion of the tube immediately downstream from the screen bed the film at the tube wall has not been established and eddy diffusivity in the bulk of the stream is rate-controlling. Towle, Sherwood, and Seder (10) studied the effect of a screen grid upon turbulence and showed that the eddy diffusivity downstream from a screen approached the value obtained without a screen as the distance from the screen increased.

It is believed that the true diffusion rate in this portion of the tube where turbulence conditions are changing is greater than that predicted by equation (11) and this belief is borne out by the comparison made in Table IV.

#### Sample Calculation from Experimental Data

The following data were collected for a sampling tube at some time during a run:

Volume of liquid sample collected in 1 min.: 40.5 ml.

Volume of 0.2048 N  $\text{KMnO}_4$  needed for above: 8.3 ml/ml.

Oxygen rate: 1 liter in 7.5 sec.

Oxygen measured at  $23.6^\circ\text{C}$

Barometer: 30.27 in. Hg.

Entering hydrogen peroxide concentration: 83%

Wet test meter correction factor: 1.01

Rotameter reading: 1

In this sample then

$$\frac{\text{gm. moles } \text{H}_2\text{O}_2}{\text{min.}} = \frac{0.017 \text{ N } \text{KMnO}_4 \cdot \text{ml. } \text{KMnO}_4}{34 \text{ ml. sample}} \cdot \frac{\text{ml. sample}}{\text{min.}}$$

$$= 1.014 \times 10^{-4} \times 8.3 \times 40.5 = 0.0341$$

$$\frac{\text{gm. mols } \text{O}_2}{\text{min.}} = \text{vol. corr. to S.T.P.} \times \frac{1. \text{O}_2}{\text{min.}} \times \frac{1}{\frac{1. \text{O}_2}{\text{gm. mol, S.T.P.}}}$$

vapor pressure of water at  $23.6^\circ\text{C} = 0.85 \text{ in. Hg (5)}$

pressure of  $\text{O}_2 = 30.27 - 0.85 = 29.42$

$$\frac{\text{gm. mols } \text{O}_2}{\text{min.}} = \frac{29.42 \times 273 \times 1.01 \times 60}{29.92 \times 296.5 \times 22.4 \times 7.5} = 0.326$$

$$\text{fraction decomposed} = \frac{2 \times 0.326}{0.0341 + 2 \times 0.326} = 0.950$$

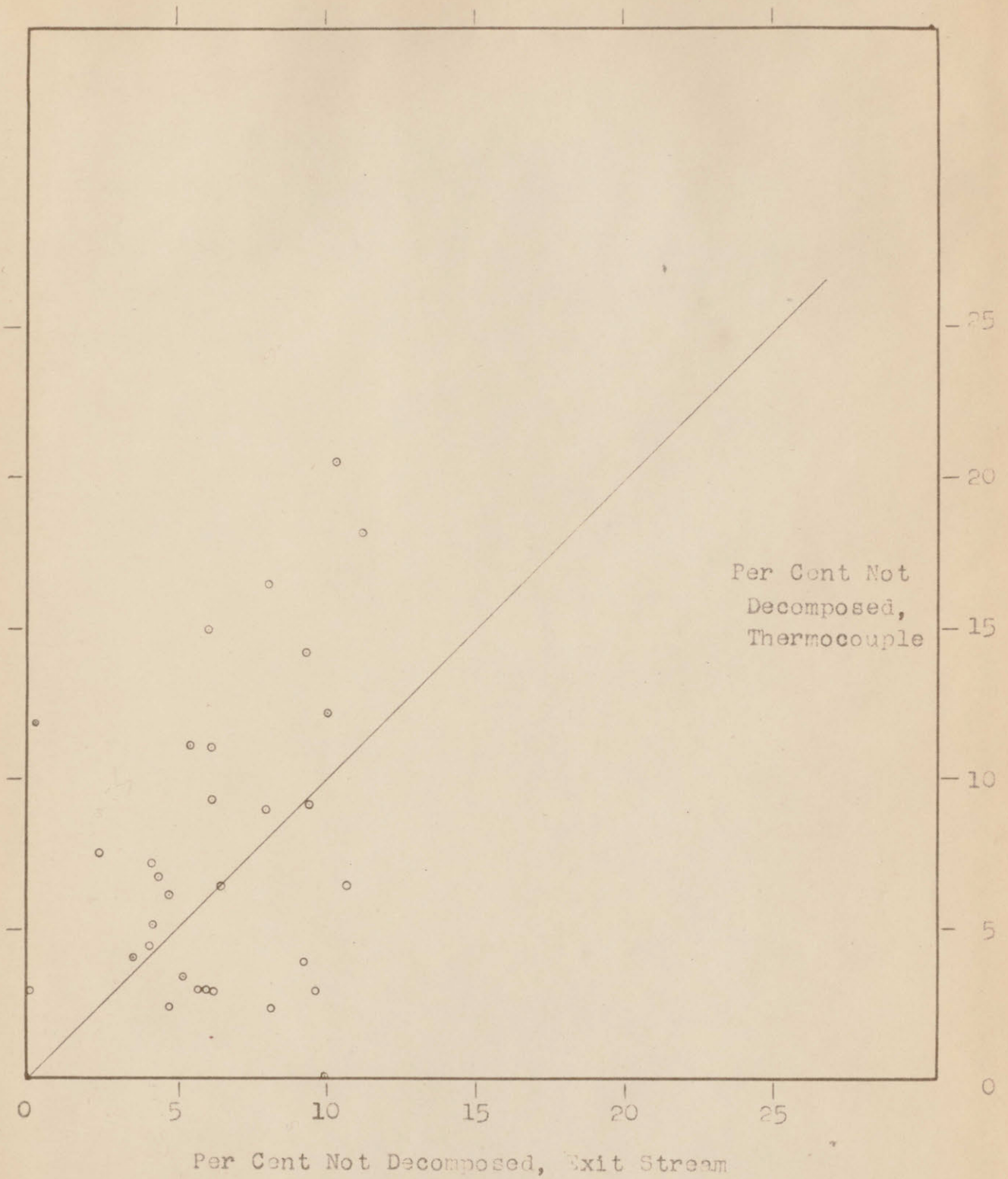


and expressed as per cent not decomposed is 5%.

Thermocouple Measurements A measurement of the temperature of the hydrogen peroxide stream in the catalyst chamber as recorded by a Chromel-Alumel thermocouple was made during most runs. As mentioned in the Introduction, this measurement is known to be undependable, but the record for each run was kept to form a guide to the conditions in the catalyst chamber adjacent to the downstream sampler. Since the values for the sampler are unreliable a rough comparison of the thermocouple data with the exit stream data will be made. In Fig. A7 the values of per cent not decomposed for the exit stream and those corresponding to the adiabatic decomposition temperature registered by the thermocouple are plotted against each other. Correspondence between the two values is indicated by points lying on the  $45^\circ$  line through the origin. Since the stainless steel thermocouple well was located about 3 inches upstream from the point where cooling and quenching of the exit stream occurred, the thermocouple values should be somewhat greater than the exit stream values. Keeping in mind the difference in position of the two measuring points it can be seen that the thermocouple tends to read a temperature corresponding to a greater degree of decomposition than is actually the case.

FIGURE A7

COMPARISON OF PER CENT NOT DECOMPOSED AS  
MEASURED BY THERMOCOUPLE AND TITRATION OF STREAM



This behavior bears out the experience of Isbin (4).

Compilation of Data Table AVI is an extract of the calculated data and notes for all runs made. The original data sheets, pressure and temperature records, and calculations are in the keeping of the hydrogen peroxide project at M.I.T. under the Office of Naval Research, contract no. N50RI-78, Task Order XIX.

TABLE A-VI  
COMPILATION OF DATA

Run No.	352	353	354	355	356	357	358	359	360	361	362
Mass Flow Rate lb./min./sq. in	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6
No. of Screens	10	6	10	10	10	10	10	10	10	10	10
Upstream sampler in. from screens	0	0	0	0	0	0	0	0	0	0	0
Downstream sampler in. from screens	none	none	none	none	none	none	none	none	6-1/4	none	none
<b>UPSTREAM SAMPLER</b>											
% Not Decomposed											
High value	46.0	63.5	15.0	9.0	7.5	86.5	8.0	3.5	8.7	14.3	11.1
Selected value <sup>1</sup>	--	--	13.0	4.5	6.5	--	4.5	3.5	5.0	7.5	7.5
Low value	7.0	33.0	8.5	3.7	6.0	6.2	4.5	2.5	4.2	5.0	5.5
<b>DOWNSTREAM SAMPLER</b>											
% Not Decomposed											
High Value									9.1		
Selected value									8.5		
Low value									0.5		
<b>EXIT STREAM</b>											
% Not Decomposed											
Selected value	8.5	9.0	6.0	9.5	8.0	8.0	7.5	4.5	9.0	10.0	7.0

Notes: 1 Selected values are taken at same time for each sample position.

TABLE A-VI (Cont'd)

Run No.	363	364 <sup>2</sup>	365	366	367	368	371	372	373	374	375
Mass Flow Rate lb./min./sq.in.	3.6	3.6	3.6	3.6	3.6	3.6	3.1	3.1	3.1	3.1	3.1
No. of Screens	10	10	10	10	10	10	10	10R <sup>3</sup>	8	8	8
Upstream Sampler in. from screens	0	0	0	0	0	0	0	0	0	0	0
Downstream Sampler in. from screens	none	none	none	none	none	none	6-1/4	6-1/4	6-1/4	6-1/4	6-1/4
<b>UPSTREAM SAMPLER</b>											
% Not Decomposed											
High value	10.0	36.5	15.0	56.5	62.1	--	6.8	7.8	9.0	11.0	12.3
Selected value	8.0	--	6.5	--	--	2.5	3.0	7.5	6.3	10.3	9.4
Low value	6.5	1.7	0.1	4.4	5.4	--	2.0	1.5	4.4	6.0	6.4
<b>DOWNSTREAM SAMPLER</b>											
% Not Decomposed											
High value							3.5	7.2	11.5	12.1	12.0
Selected value							2.8	6.8	10.5	12.0	11.0
Low value							1.8	1.6	9.0	3.5	7.8
<b>EXIT STREAM</b>											
% Not Decomposed											
Selected value	8.0	9.0	6.5	0-	--	4-10	4.0	3.4	7.2	8.0	5.5

Notes: <sup>2</sup> Water spray on sampling tube.  
<sup>3</sup> R indicates screens not changed between runs.

TABLE A-VI (Cont'd)

Run No.	376 <sup>4</sup>	377	378	S379 <sup>5</sup>	380	381 <sup>6</sup>	382	383	384	385 <sup>7</sup>	386
Mass Flow Rate lb./min./sq.in.	3.0	3.1	4.0	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1
No. of Screens	8R	8	8R	8	8	8R	8	10	8	8	8
Upstream sampler in. from screens	0	0	0	0	0	0	0	0	0	0	0
Downstream sampler in. from screens	6-1/4	6-1/4	6-1/4	6-1/4	24-1/4	24-1/4	0	0	0	24-1/4	24-1/4
UPSTREAM SAMPLER											
% Not Decomposed											
High value	15.6	14.0	12.5	10.0	60.1	18.3	69.0	5.5	14.5	- -	2.6
Selected value	15.1	12.0	12.0	9.0	55.0	1.8	- -	2.5	9.0	- -	2.3
Low value	12.3	10.0	10.5	7.8	1.4	0.9	8.0	1.4	11.0	- -	0.8
DOWNSTREAM SAMPLER											
% Not Decomposed											
High value	12.6	13.7	11.0	16.7	47.4	11.3	52.5	3.2	21.6	2.8	1.8
Selected value	12.5	12.5	8.2	8.5	35.0	4.8	- -	2.5	16.5	2.2	1.7
Low Value	11.5	11.5	7.7	8.0	29.5	2.8	4.1	2.1	15.5	2.2	1.3
EXIT STREAM											
% Not Decomposed											
Selected value	5.7	6.7	6.0	4.9	5.7	8.0	4.9	3.9	5.6	4.7	2.3

Notes: 4 Water jacket on sampling tube.  
 5 S indicates silver catalyst tube.  
 6 0.008 in. diameter sampling orifices used in subsequent runs.  
 7 Baffle used in all subsequent runs.

TABLE A-VI (Cont'd.)

Run No.	387	388	390	391	392	393 <sup>e</sup>	394	395
Mass Flow Rate lb./min./sq.in.	3.1	3.1	8.0	8.0	11.8	8.0	11.8	4.2
No. of Screens	6	6	8	10	11	8	16	10
Upstream sampler in. from screens	0	18	18	18	18	18	18	18
Downstream sampler in. from screens	24-1/4	24-1/4	24-1/4	24-1/4	24-1/4	24-1/4	24-1/4	24-1/4
UPSTREAM SAMPLER								
% Not Decomposed								
High value	5.1	13.0	10.3	6.2	9.7	10.1	--	2.9
Selected value	4.5	4.5	7.7	4.6	2.5	9.5	--	1.3
Low value	3.9	3.8	7.6	4.0	2.3	7.7	--	0.8
DOWNSTREAM SAMPLER								
% Not Decomposed								
High value	9.8	3.9	4.5	2.9	2.5	7.4	--	2.3
Selected value	2.0	2.5	4.5	1.8	2.0	5.3	--	0.5
Low value	1.7	2.2	4.4	1.7	1.3	5.3	--	0.5
EXIT STREAM								
% Not Decomposed								
Selected value	4.1	5.0	9.9	4.9	2.5-10	9.5	0.9-4.7	0.7

Notes: <sup>e</sup> Conductivity test made.

TABLE A-VI (Cont'd)

Run No.	396	S397	S398	S399	S400	S401	S402
Mass Flow Rate lb./min./sq. in.	11.8	5.3	10.2	12.5	5.3	5.3	10.2
No. of Screens	16	10	10	16	8	8	8
Upstream sampler in. from screens	18	18	18	18	18	18	18
Downstream samper in. from screens	24-1/4	24-1/4	24-1/4	24-1/4	24-1/4	24-1/4	24-1/4
<b>UPSTREAM SAMPLER</b>							
% Not Decomposed							
High value	4.8	2.3	0.9	6.2	4.3	2.9	8.7
Selected value	4.1	0.4	0.6	2.1	2.5	0.1	7.8
Low value	3.8	0.2	0.5	1.8	2.0	0.1	7.2
<b>DOWNSTREAM SAMPLER</b>							
% Not Decomposed							
High value	4.2	1.3	1.3	2.0	2.8	2.5	5.9
Selected value	2.2	0.3	0.3	1.2	1.7	0.01	4.7
Low value	2.2	0.2	0.2	1.1	1.1	0.01	4.4
<b>EXIT STREAM</b>							
% Not Decomposed							
Selected value	4.5	0.25	10.0	2.2	2.0	6.01	8.1



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