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THE ROLE OF DIFFUSIONAL PROCESSES IN THE HETEROGENEOUS
DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR

by

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Submitted In Partial Fulfillment of Requirements

For The Degree of Bachelor of Science



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May 19, 1950

Professor Joseph S. Newell
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Dear Sir,

The thesis entitled "The Role of Diffusional Processes In The Heterogeneous Decomposition of Hydrogen Peroxide Vapor" is hereby submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

Respectfully submitted,

Stanley R. Meeken

CONTENTS

I. SUMMARY	1
II. INTRODUCTION	4
III. EXPERIMENTAL PROCEDURE	11
Construction of Apparatus	
Limitations of Apparatus	
Operation of Apparatus	
Calculation of Data	
Reproducibility of Data	
IV. THEORETICAL ANALYSIS	22
V. RESULTS AND DISCUSSION OF RESULTS	29
Decomposition Data	
Temperature Data	
Analysis of Data	
Comparison of Data With Predicted Values	
Conclusions	
Recommendations	
VI. CONCLUSIONS	47
VII. RECOMMENDATIONS	49
VIII. APPENDIX	51
Analytical Procedures	
Derivation of Diffusion Rate Equation	
Sample Calculations of Data	
Calculation of Profiles Along Catalyst Tube	
Axial Heat Flow In Catalyst Tube Wall	
Summary of Data And Calculated Values	
Location of Original Data	
Nomenclature	
Literature Citations	

FIGURES

	<u>Page</u>
Figure 1. Pressurized Boiler For The Vaporization of Hydrogen Peroxide-Water Solutions.	12
2. Apparatus For The Measurement of The Decomposition of Hydrogen Peroxide Vapor In A Catalyst Tube.	13
3. Predicted Length of 0.25 in. Catalyst Tube Required For A Fractional Decomposition of Initially Undecomposed Hydrogen Peroxide Vapor: Reaction Diffusion Controlled.	26
4. Vapor Phase Decomposition In A 0.25 in. Silver Catalyst Tube.	31
5. Temperature of Catalyst Surface: Distribution Along 0.25 in. Silver Catalyst Tube For Various Entering Peroxide Concentrations.	34
6. Temperature Profile For Run 19.52.	40
7. Interrelationship Between Heat And Mass Transfer Potentials, Runs 19 - 24.	40

TABLES

	<u>Page</u>
Table I. Chronology of Runs Made.	29
II. Summary of Runs Made.	29
III. Effect of Variations of Decomposition In Boiling On Peroxide Decomposition In The Catalyst Tube.	30
IV. Effect of Entrance Temperature On Peroxide Vapor Decomposition.	32
V. Comparison of Runs Made With 20% Peroxide.	38
VI. Observed And Calculated Bulk Temperatures Leaving Catalyst Tube.	39
VII. Effect of Flow Rate On Peroxide Decomposition.	42
VIII. Comparison of Data With Values Predicted By Mass Transfer Equation.	43

TABLES (Cont.)

	<u>Page</u>
Table A - I. Adiabatic Decomposition Temperatures For Various Fractions Peroxide Decomposed, 5% Hydrogen Peroxide Vapor.	59
A-II. Values of The Constants In The Equation $T = at + b$ For Various Initial Concentrations of Peroxide.	60
A-III. Atomic Volumes	61
A-IV. Summary of Values For The Diffusion Constant.	63
A-V. Mean Diffusivity For The System Peroxide-Air.	64
A-VI. Prandtl Numbers At Various Concentrations And Fractions Decomposed of Hydrogen Peroxide Mixtures.	64
A-VII. Actual And Predicted Heat Transfer.	77
A-VIII. Effect of Temperature Difference on Predicted And Actual Heat Transfer.	77

I. SUMMARY.

The rate of the surface-catalyzed decomposition of hydrogen peroxide vapor to form water and oxygen may be controlled either by the catalytic reaction rate or by the diffusion rate of peroxide from the bulk to the surface. The mechanism controlling will be determined by the catalytic activity of the surface and by the partial pressure and temperature of the peroxide. It is the purpose of this investigation to study the diffusional-controlled reaction, and to obtain data on the decomposition rate for comparison with values predicted from mass-transfer theory.

Vapor mixtures of hydrogen peroxide, water, and oxygen from partial decomposition in the process of vaporization, have been passed in a flow system through an insulated, cylindrical catalyst tube. Vaporization was accomplished with a recently developed thermal boiler, representing an improvement over catalyst bed vaporizers previously employed. The initial peroxide concentration ranged from 5 to 35% by weight; operation was at a total pressure of one atmosphere, with flow rates corresponding to tube Reynolds numbers from 4000 to 5000. The catalyst tube employed was of silver, 0.25 in. diameter, and 24 in. in length. Data were obtained on the decomposition occurring in the tube, and on the surface temperature of the catalyst tube.

A design equation has been derived from mass-transfer considerations, ignoring, however, the effect of large temperature gradients on mass transfer under a concentration gradient. This approximate relation allows a prediction to be made of the tube length required for a given degree of decomposition attained in an adiabatic, diffusional-controlled reaction, and the values so predicted have been compared with the

experimental data.

The results of this investigation have shown that the reaction is indeed controlled by diffusion rate under the conditions studied. The catalyst tube lengths predicted by the theoretical expression for the decomposition, however, are 33% below the actual tube length employed. This deviation of experiment from theory may be due in part to the approximations made in the derivation, and in part to the failure to consider mass transfer under a thermal gradient.

The entrance temperature of the stream was observed to have small effect on the amount of decomposition obtained in the diffusion-controlled reaction, provided partial condensation is avoided. The presence of condensate in the entering stream in amounts as little as 2% of the total stream decreased the final bulk temperature by 40 °F., and increased the percent peroxide not decomposed leaving the catalyst tube from a level of 15% to 30%. The decomposition obtained has been found to be dependent on three factors: the partial pressure of the entering peroxide, the total weight flow rate, and the molal flow rate of the entering peroxide.

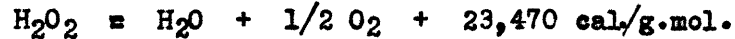
The surface temperature of the catalyst was found to be higher than the bulk stream temperature at all points. The catalyst temperature went through a maximum a short distance from the upstream end of the tube, and decreased along the tube in the direction of flow. The partial pressure of peroxide and the temperature of the bulk stream were found to determine the catalyst temperature, and a value of h/k for this system has been calculated.

Recommendations have been made for further study, both experimental and theoretical. The range of variables must be extended to include Reynolds numbers above 10,000, and an examination should be made of

the effect of catalyst tube length and catalyst activity on the decomposition attained and on the surface temperature of the catalyst. Several improvements in the apparatus are needed: fluctuations in the amount of decomposition occurring in the boiler should be reduced, and more effective insulation should be employed, or means provided for quantitative determination of the magnitude and distribution of the heat loss from the catalyst tube. The theoretical analysis should be examined in greater detail: the proper temperature function for integration of the diffusion equation across the film and along the tube is not completely established, the method of evaluation of the "effective film thickness" is not satisfactory, and the role of thermal diffusion should be investigated more fully.

II. INTRODUCTION.

The decomposition of hydrogen peroxide,



is an important potential source of energy for propulsion units requiring a high ratio of power output to weight, since it provides a convenient supply of high pressure, high temperature steam and oxygen. In addition, the vapor mixture produced from the decomposition can be employed to burn additional fuel, resulting in a gas phase of very high pressure and temperature capable of expansion in a suitable engine. Although the decomposition is readily catalyzed, hydrogen peroxide is quite stable in concentrated form, and it is available in moderate quantities at rather low cost.

Work along these lines was begun by investigators in Germany during World War II, and research has been continued in the United States. However, it has been found impractical to attempt precise design of decomposition chambers without further knowledge of the basic mechanisms of the reaction itself. In addition to providing the basis of chamber design, an increased knowledge of the reaction would assist in the design of vacuum distillation units for peroxide, and would contribute to the development of a direct synthesis of peroxide from the elements. Consequently, an extensive program of basic study has been inaugurated, principally by the military research offices. The present investigation is a part of that overall program.

The rate of a reaction between a gas phase and a surface active in the reaction may be controlled by the rate of one of five steps in the overall reaction mechanism,

1. Diffusion of the gas from the bulk stream through the laminar film

surrounding the surface,

2. Adsorption of the gas from the film onto the surface,
3. Chemical reaction between the adsorbed gas and the surface,
4. Desorption of the reaction products from the surface, and,
5. Diffusion of the reaction products from the surface to the bulk stream.

The diffusion of the reactants and the diffusion of the products are interrelated, and only the diffusion rate of the overall system need be considered. In catalytic reactions, it is convenient to combine Steps 2, 3, and 4 into an overall "chemical reaction" rate.

The catalytic decomposition of hydrogen peroxide vapor, therefore, may be controlled in rate by either the rate of diffusion or by the activity of the catalyst employed. For example, the rate of chemical reaction increases much more rapidly with increasing temperature than does the rate of diffusion. If the temperature level of the decomposition is increased, a point will be reached where the rate of chemical reaction (catalysis) is greater than the rate of diffusion, and hence the observed decomposition rate will be that of the diffusion. Similarly, if the level is decreased, the reaction rate may become less than the diffusion rate, and control by reaction rate will exist.

Previous investigations have shown that this transition from reaction to diffusion control of the rate of decomposition in the vapor phase occurs within the range of conditions of interest for decomposition chambers.

Isbin (7), (8) has reported a diffusional-controlled reaction in a study conducted with 50 - 83% peroxide at 500 p.s.i.g. in a small scale, adiabatic decomposition chamber. Peroxide, as liquid, was passed under

pressure through a bed composed of catalyst screens. Since the heat of decomposition liberated by partial reaction of strong liquid peroxide is sufficient to vaporize the stream, much of the decomposition in this system occurred in the vapor phase. Data were obtained on the effect on the fraction peroxide decomposed of the flow rate, dimensions of the bed, catalyst activity, peroxide concentration, and amount of throughput. It was possible to correlate the data (9) in a number of empirical equations.

The data of Isbin indicated that diffusion was the rate controlling mechanism for 83% peroxide, and that control gradually shifted to reaction rate as the concentration was reduced to 50%, under the conditions existing in the chamber. The presence of such a transition is shown by the following considerations.

1. The fraction peroxide decomposed was found to vary with a fractional power of the flow rate, the exponent being 0.4 for 83%, and increasing to 1 at 50% peroxide. It is possible to predict from theoretical diffusion and chemical reaction rate expressions that a diffusional-controlled decomposition would vary as a fractional power of the flow rate, while chemical-controlled decomposition would be directly proportional to the first power of the flow rate. Control by diffusion at the high temperatures corresponding to the adiabatic decomposition of 83% peroxide is indicated, control gradually shifting to chemical reaction rate with decreasing concentration, and hence temperature level.

2. Activities of different catalysts, which varied widely at lower temperatures, were found to become uniform as the temperature level was increased. Since reaction rates increase more rapidly with temperature than do diffusion rates, control by diffusion at high temperatures is

again indicated.

3. In runs made with solutions containing negative catalysts, the effective screen catalyst activity was relatively constant for a time, later undergoing a sharp break and slow decline. These data suggest that the initial decomposition was reaction controlled until poisoning reduced the chemical rate below the diffusion rate.

It was not possible to compare the rate data obtained with the values to be predicted from a theoretical mass transfer or chemical rate expression because of the complexity of the geometry of a screen bed chamber. For this reason, a quantitative delimitation of the transitional region from reaction control to diffusion control could not be made.

Wentworth (17), (18) later studied the decomposition of a vapor mixture passing through a cylindrical catalyst tube. Derivation of a theoretical rate for this geometry can readily be made, and it was proposed to compare the actual decomposition obtained with that predicted from a diffusion rate expression. The investigation was carried out at a total pressure of 500 p.s.i.g. with 83% peroxide in order to compare the data obtained with those of Isbin. The peroxide solution under pressure was passed through a catalyst screen bed sufficient in length to vaporize the stream by heat liberated in the partial decomposition. The vapor mixture of peroxide and decomposition products was then passed through a tube whose walls were an active catalyst. Samples were removed from points along the tube to determine the peroxide remaining in the stream. However, considerable difficulty was experienced with entrainment resulting from the vigorous reaction in the screen bed "boiler", in the form of liquid droplets of peroxide solution, even though the temperature in the catalyst tube was far above the liquid-vapor equilibrium temperature.

The sampling technique did not allow for homogeneous sampling of a two phase stream, and the desired results could not be obtained. It was possible, nevertheless, to conclude on a semi-quantitative basis that diffusion was controlling under the conditions of the experiment.

At the time of the investigation of Wentworth, there was no way of obtaining peroxide vapor for a flow system by direct thermal vaporization, all attempts resulting in serious decomposition or explosion. Recently, however, a direct thermal boiler has been developed for peroxide solutions which will produce a steady supply of vapor with small decomposition and with little danger of explosion at moderate concentrations. The present study represents a continuation of the work begun by Wentworth, employing the newly developed boiler to replace the catalyst screen "boiler".

The object of this investigation was to examine the decomposition of hydrogen peroxide vapor, from a suitable boiler, when passed through a cylindrical catalyst tube, with the purpose of obtaining data for comparison with the values predicted from the theoretical diffusion expressions. Due to the limitations imposed by the apparatus available, the major variable was the initial concentration of the peroxide, ranging from 5 weight percent to an upper limit of 35%, slightly below the explosive limit of the vapor. Operation was at a total pressure slightly greater than atmospheric, and the flow rate through the catalyst tube was held relatively constant at $1.3 \text{ gm./}(\text{cm.}^2)(\text{sec.})$ during the runs, corresponding to a Reynolds number of 4000 - 5000 in the tube. The catalyst tubes employed were of silver, 24 inches long, 0.25 in. i.d., 0.26 in. o.d., and wrapped with pyrex glass wool insulation to approach adiabatic decomposition conditions.

The physical picture presented by this arrangement is quite complex, involving multicomponent counter-diffusion of peroxide, water, and oxygen across a laminar film, together with simultaneous heat transfer from the catalyst surface to the bulk stream. A differential equation may be written to represent the diffusion in this system,

$$y_1 y_2 (v_1 - v_2) = -D_{12} \text{ grad } y + \frac{D_T}{T} \text{ grad } T \quad (1)$$

where, y_1, y_2 - Mol fractions of components 1 and 2
 v_1, v_2 - Convection velocities of components 1 and 2
 T - Temperature
 D_{12} - Molecular diffusivity of component 1 through 2
 D_T - Thermal diffusivity.

It is seen that the first term of the right represents the molecular transport under the influence of a concentration gradient, while the second term, the transport under a temperature gradient (thermal diffusion). Unfortunately, limited data are available on the values of thermal diffusivities, and these are principally for systems of isotopes where thermal diffusion is employed as a means of separation. Indeed, little is known quantitatively of simultaneous heat and mass transfer in systems with a large temperature gradient; most of the data and correlations available are based on systems found in drying, absorption, and psychrometry with temperature differences of the order of only 20 °F. It is only in certain chemical reacting systems, such as in the present case and in combustion, that temperature differences of several hundred degrees are found in mass transfer.

Since thermal diffusivity of this system is not known, a simplified approach to the problem must be made. An equation has been derived neglecting the thermal diffusion which has been employed to predict the

tube length required for a given degree of decomposition for comparison with the experimental data.

However, the use of any theoretical diffusion expression is predicated on the assumption that diffusion is rate controlling in this system, a fact that must be established from the experimental data.

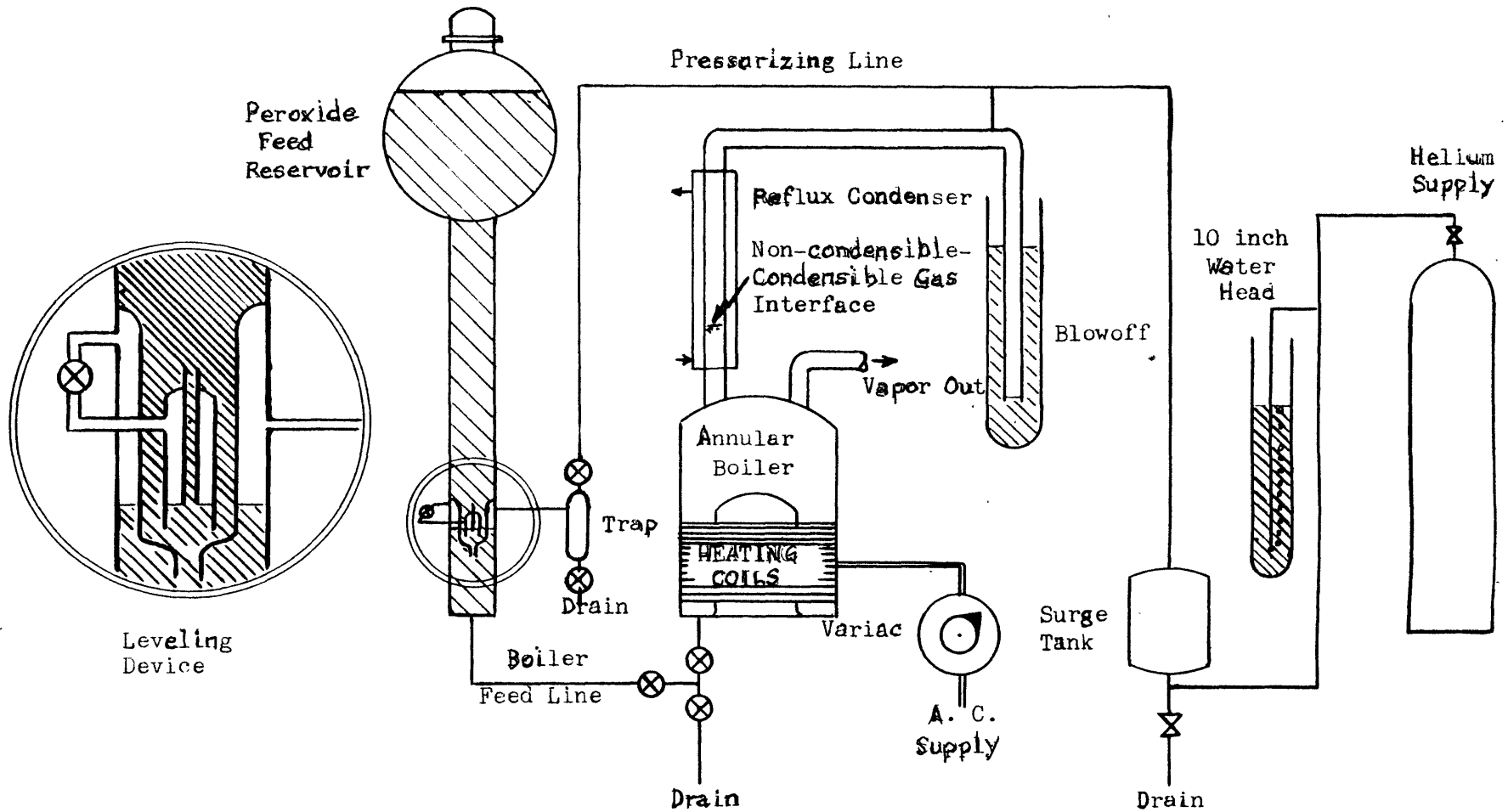
III. EXPERIMENTAL PROCEDURE.

Construction of Apparatus. The equipment employed is shown in Fig. 1 and Fig. 2. The liquid feed is introduced from the feed reservoir to the boiler and the vapor produced is passed through the reaction tube. Both the feed levelling device and the boiler are maintained under a pressure of 10 inches of water by helium connected from a supply cylinder through a 5 gallon surge tank. Provision is made for analyses of the vapor stream before and after the catalyst tube, both through collection of liquid samples and through measurement of the non-condensable gas rate by a wet test meter. Thermometers and thermocouples are installed at various points to determine the temperature profile. The discussion of the equipment is logically divisible into two sections: the vaporization and the decomposition apparatuses.

Preliminary studies in the vaporization of peroxide solutions indicated that best operation was obtained with (a) a deep pool of liquid and (b) small residence time in the boiler to reduce the amount of decomposition of the boiling peroxide. Both of these requirements are met in the annular boiler shown in Fig. 1.

Considerable difficulty was experienced at first with pressure surging in the apparatus. Boilers of this type, when fed through a levelling device open to the atmosphere, operate satisfactorily when at atmospheric pressure. However, when coupled to an apparatus in which there exists a pressure drop due to the vapor flow, the boiler must of necessity be at greater than atmospheric pressure, and hence there is a pressure difference between the feed levelling device and the boiler. Any change in this fluid-flow pressure drop due to readjustment of stopcocks in the line or variation in the vapor rate will change the

FIGURE 1'
 PRESSURIZED BOILER FOR THE VAPORIZATION OF
 HYDROGEN PEROXIDE - WATER SOLUTIONS

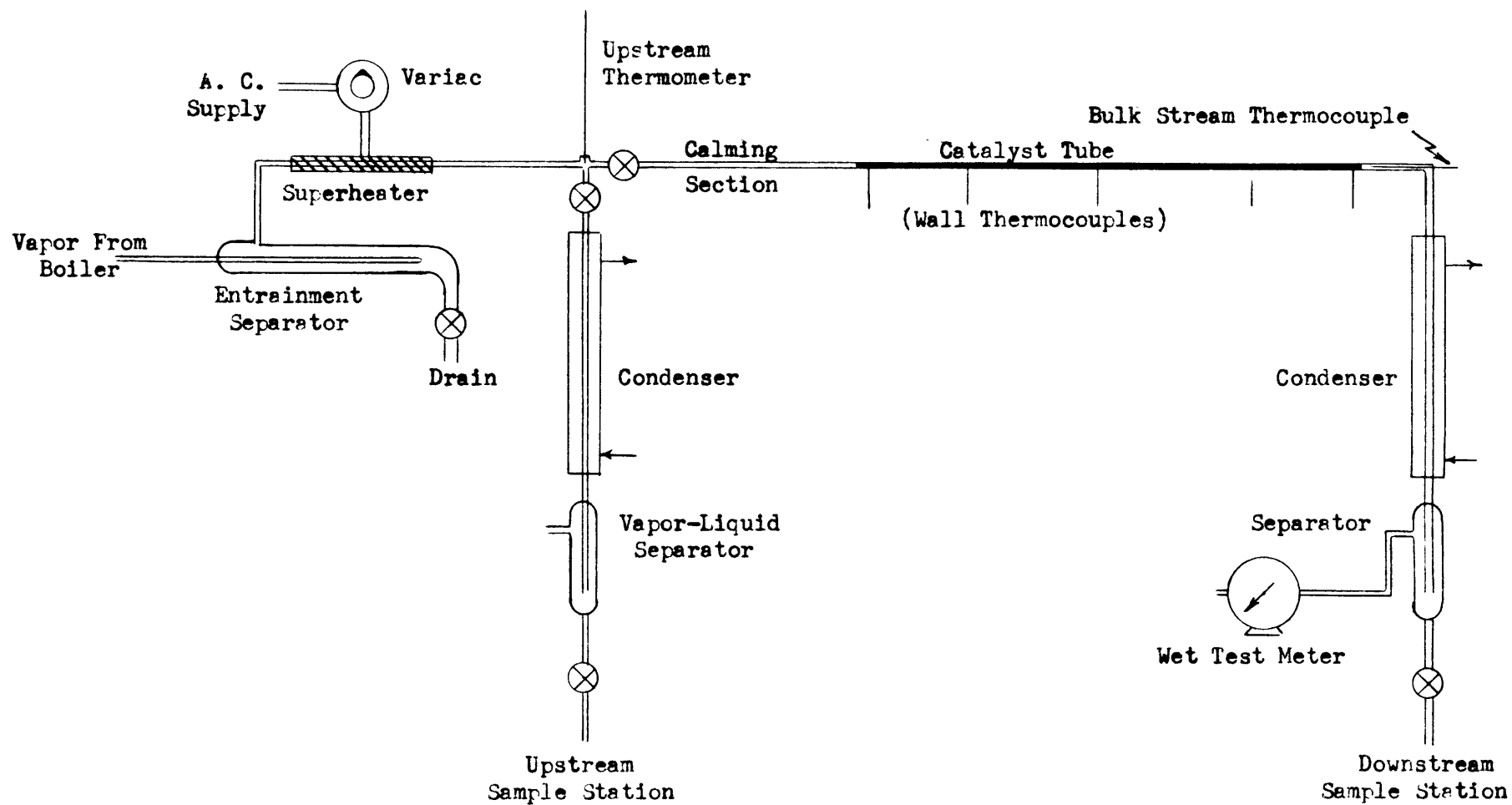


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Figure 2.

APPARATUS FOR THE MEASUREMENT OF THE DECOMPOSITION OF
HYDROGEN PEROXIDE VAPOR IN A CATALYST TUBE

(Shown Without Insulation)



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pressure difference between the boiler and the feed reservoir, changing the level in the boiler, either backing concentrated boiler liquid into the feed line or introducing a large amount of cold feed into the boiler. In addition, if the cold feed is introduced in rather large amounts, as from a Mariotte bottle, the boiling rate will be reduced periodically, the vapor rate and consequently the pressure drop will decrease, and more cold feed will be admitted to the boiler. Eventually, the heat supplied to the boiler will reestablish the boiling rate, and the cycle will be repeated. It is apparent that this type of vaporization will not produce vapor of constant concentration or rate.

The problem may be solved by (a) maintaining the feed levelling device and the boiler at the same pressure, and (b), introducing the feed in small amounts. Since the boiler vapors are condensable (except for the oxygen present through decomposition), the boiler and the levelling device must be connected through an intermediate gas. In the present apparatus, helium, chosen because it is both inert and lighter than the vapors, is connected to the boiler vapors through a non-condensable-condensable gas interface in a reflux condenser, and to the free space above the levelling device. The helium is maintained under a slight pressure to allow for the pressure drop through the reaction apparatus. In operation, this arrangement allows for the variation in pressure drop through changes in the amount of reflux flowing back to the boiler, and the vapors delivered are at a relatively steady concentration and rate of flow. The levelling device employed is shown in insert in Fig. 1, and is designed to deliver a small and almost constant flow of feed to the boiler.

The boiler was 80 mm. o.d., 65 mm. i.d., 150 mm. high and was heated

by a 2000 watt heating coil controlled by a Variac voltage regulator. The boiler had a capacity of about 350 ml., the reservoir holding 3 liters of feed solution. A large duct attached through the reflux condenser from the boiler to a water head slightly greater than that of the helium pressure provided a blow-off for the vapors in case of violent decomposition in the boiler. The boiler assembly (Fig. 1) was placed behind a 1/4 inch steel plate shield to offer additional protection to personnel.

The vapors from the boiler were passed (Fig. 2) through an entrainment separator and through a superheater, controlled by a Variac, to prevent condensation before the catalyst tube. Both were added between Runs 29 and 39, not being employed on the earlier runs. After the superheater, part of the vapor stream was split off and passed through a condenser for analysis at the upstream station. Provision was also made for determination of the temperature of the stream at this point. After passing through a 50 diameter calming section, the stream was introduced into the 1/4 inch diameter silver catalyst tube, and the effluent passed through a condenser. The liquid was removed for analysis, the non-condensable oxygen rate being determined by a wet test meter reading. The entire apparatus from the boiler to the condensers was insulated to a 3 inch diameter with pyrex glass wool, and wrapped with aluminum foil. Except for the silver catalyst tube, construction was entirely of pyrex glass, ground glass ball joints being employed to connect units.

The problem of joining the silver catalyst tube to the glass sections was never completely solved. The ends of the tubes were held butt-to-butt with a short length of Teflon tubing, the assembly being sealed

with a mixture of glass wool and partially polymerized silicone resin. This arrangement was subject to two types of failure. The silicone, while bonding to the glass and silver, did not adhere to the Teflon and the joint developed a leak in Runs 25 -29. In addition, in a run made with concentrated peroxide, where the temperature level was high, the Teflon decomposed, swelled, and crushed the silver tube.

Copper-constantan thermocouples were silver-soldered to the catalyst tube wall at five positions: 1, 3, 10, 16, and 22 inches from the upstream end; in addition, a thermocouple probe was inserted in the bulk stream below and parallel to the catalyst tube. By an arrangement of switches, successive thermocouple circuits could be connected to either a millivoltmeter or to a potentiometer circuit.

Limitations of The Apparatus. The apparatus as described imposed several limitations on the range of variables that could be investigated. The most important of these was the limitation of the boiling rate to a maximum of 27 cc./min. (tube Reynolds number of about 4000) imposed by the size of the boiler. It is doubtful if full turbulent flow existed at this flow rate.

Since the catalyst tube was silver, the concentration of peroxide was limited to below about 35% to prevent catalyst burnout. However, the lower explosive limits of peroxide vapor are believed to be about 40%.

The decomposition was designed to be adiabatic, no provision being made for the addition or removal of heat from the catalyst tube. However, the heat losses through the insulation proved to be greater than expected, approximately 20% of the heat of decomposition being lost through the insulation in some runs. In the runs made without the entrainment

separator and superheater, additional heat was consumed in the re-evaporation of the condensate, at the expense of the sensible heat of the vapor stream.

Operation of Apparatus. The feed reservoir and levelling device were charged with peroxide of the desired concentration, the peroxide being introduced through the top of the reservoir after the pressurizing and boiler feed valves were closed. The boiler was then filled through the reflux condenser with the concentration of peroxide in equilibrium with a vapor of the same strength as the feed to permit a more rapid attainment of steady-state boiling. The levels in the feed levelling device and in the boiler were equalized by opening the pressurizing and feed valves, and the feed line was then drained separately to replace with feed liquid any boiler liquid that might have backed into the line. The power was then turned on in small increments, and the system pressurized with helium when the reflux rate became appreciable. The vapor stream was split between the upstream and downstream stations to put 60-70% of the total flow through the catalyst tube. When steady-state operation had been attained, as evidenced by the constancy of the thermocouple readings along the catalyst tube, the actual run was begun. An hour to an hour and a half was usually required for establishment of the steady-state.

During the run liquid samples were taken every minute, being collected in the separators for 55 seconds, 5 seconds being allotted for drainage of the liquid into sample beakers. The oxygen rate was determined by observation of the wet test meter during the periods when the separator cock was closed. At the conclusion of the run, the samples were titrated for peroxide content with standardized potassium permanganate (Appendix).

A minimum of three observers were required for the operation of the equipment, their duties being as follows,

1. One observer to operate the upstream sample station: noting the time and calling to the downstream station operator the times to open and close the separator stopcock for collection of liquid, collecting the liquid samples at the upstream station, recording the upstream temperature once a minute, and checking on the operation of the boiler;
2. One observer to operate the downstream station: collecting liquid samples, and reading the wet test meter once a minute;
3. One observer to operate the thermocouple station, reading, as rapidly as possible, the voltages of six thermocouples. A pproximately six minutes were required for a complete set of readings, including restandardisation of the potentiometer circuit.

At the conclusion of the run, about ten samples being taken at each station, the apparatus was shut down and drained.

Calculation of Data. The data obtained from a run included volumes and peroxide content of the liquid samples, the wet test meter readings, the temperatures at the upstream thermometer, and the thermocouple readings along the catalyst tube and at the exit bulk stream. From the analytical data, the fractional decomposition of the peroxide as a result of passing through the catalyst tube may be calculated for each of the minutes. If the system were at true steady-state operation, the fractional decomposition should be the same for each of the minutes. A small fluctuation was noted, although the variation in the fraction decomposed at the upstream station was usually greater than that of the downstream station, and was cyclic in nature. The calculation of the data, while not complex, is lengthy, and hence has been developed in the Appendix as a sample calculation of a run. The data are also presented in summarized form in the Appendix.

During the process of vaporization, the peroxide-water solution has a tendency to concentrate or dilute in the boiler, i.e., the strength of the generated vapor is not the same as the feed liquid although steady-state operation has apparently been attained in the catalyst tube. A water balance written on the system will close within $\pm 10\%$ for most of the minutes. For this reason it is convenient to define and calculate a "pseudo-feed", the strength of the feed corresponding to the stream actually collected at the stations. In this manner it is possible to compensate for errors in the water balance when employing the data for further calculations.

Reproducibility of Data. An error analysis is given in the Appendix discussing the precision of the measurements taken, the analysis indicating a 5% error possible in the data. It is the purpose of this section to discuss the errors introduced by the apparatus and techniques employed.

The factors affecting the reproducibility of the data are enumerated and discussed below.

1. Regulation of feed rate.
2. Regulation of vapor rate.
3. Regulation of heat input.
4. Reproducibility of wet test meter readings.
5. Maintenance of adiabatic conditions.
6. Decomposition in the boiler.
7. Decomposition in the tubes leading to the catalyst tube, in the condensers leading to the sample points, and in samples before titration.
8. Accuracy of thermocouple readings.
9. Entrainment or partial condensation in the lines before the catalyst tube.

1. The feed rate is controlled by the constant levelling device. The purpose of the small bulb inside of the supply reservoir, Fig. 1, is to permit relatively steady flow of liquid, eliminating large fluctuations in boiler level. Therefore, the feed rate may be considered constant well within the accuracy of the other data.

2. The regulation of the rate of vaporization has been covered above, and has been shown to be a major problem in the generation of peroxide vapor in an apparatus of this type. With the present pressurized system it is believed that the problem has been eliminated.

3. The heat input to the boiler and to the superheater may be closely controlled by the voltage regulators described. However, no provision was made for the determination of the entrance temperature of the vapor to the silver tube when superheating was employed; the results indicate that the entrance temperature is not critical in this system.

4. Since the boiler is pressurized with helium through a reflux condenser, the possibility exists that helium may be present in the bulk stream and be measured by the wet test meter as oxygen. However, since the interface is well up in the reflux condenser, since the flow of vapor in the condenser is against any flow of helium, and since helium is considerably lighter than the vapor, this error is negligible.

5. The heat losses from this system are appreciable despite the insulation, and represent a source of error if the system is considered as true adiabatic decomposition. However, allowance may be made in the calculations for the heat loss.

6. Any decomposition occurring in the boiler will furnish heat for the vaporization rather than increasing the sensible heat of the vapor. A variation of the boiler decomposition, therefore, will not affect the temperature of the stream but only the concentration of peroxide in it. A cyclic variation in the strength of the vapors generated was observed, and although not large, presents an opportunity for improvement. The downstream samples were relatively constant despite this variation in the stream entering the catalyst tube.

7. Decomposition in the glass tubing leading to the catalyst tube will be indicated by an upstream temperature higher than the boiling temperature recorded in the literature (1). This decomposition, however, is small under the conditions of these runs since glass with clean, smooth surfaces is very inactive as a catalyst for peroxide vapors. No appreciable difference in boiling temperatures was observed during the experiment. The decomposition in the condensers, separators, and in the sample beakers is negligible in the absence of dust, dirt, or other contamination.

8. The thermocouple readings are believed to be accurate to within at least 10 °F., considerable attention having been given to the construction of the thermocouple installations and to the cold junction employed. Although, because of the time required, it was not possible to read the temperatures every minute to correspond with the other sampling techniques, the temperatures were not sensitive to the minute-to-minute variations in the bulk stream, and are representative of the runs as a whole. Since the thickness of the tube walls was only 0.01 inch, the axial heat flux is very small, and each segment of the catalyst surface is essentially insulated from its neighbors. Consequently, the thermocouple temperatures represent point conditions on the surface.

9. The presence of condensate in the stream entering the catalyst tube will reduce the sensible heat of the stream through re-evaporation, and possibly will interfere with the mass transfer pattern normally present. This situation was present in the early runs, Runs 19-29, before the addition of the entrainment separator and superheater.

IV. THEORETICAL ANALYSIS.

The fundamental equation for this system has already been given in the Introduction as,

$$v_1 v_2 (v_1 - v_2) = - D_{12} \text{ grad } y + \frac{D_T}{T} \text{ grad } T, \quad (1)$$

representing the sums of molecular transport under a concentration gradient and under a temperature gradient. The evaluation of this expression for the present case is not possible because the value of the thermal diffusivity for peroxide systems is not known. However, it is of interest to compare the experimental data with an approximate equation based solely on mass transfer considerations.

If it may be assumed that a temperature gradient does not affect mass transfer under a concentration gradient, the last term of Eqn. (1) may be discarded, and attention focused on diffusion under concentration gradient alone. The rate of transport of peroxide across the stagnant film in multi-component, counter-diffusion at any length of the catalyst tube may be written,

$$N = \frac{D \pi}{R T P_f} \frac{\Delta P}{x} \quad (2)$$

where,

- N - Rate of diffusion of peroxide, g.-mols/(cm.²)(sec.),
- D - Diffusivity of the peroxide in this system, cm.²/sec.,
- π - Total pressure, atm.,
- R - Gas constant,
- T - Temperature, °K, a mean across the film,
- x - Effective film thickness, cm.,
- ΔP - Partial pressure difference of peroxide across the film,
- P_f - Film pressure factor, logarithmic mean across the film of the term $(\pi + \delta P_{H_2O_2})$, where δ is the increase in total number of moles per mole of peroxide reacted.

In order that this equation may be integrated along the catalyst tube for an integral reactor, the following assumptions have been made:

1. That the process is adiabatic, both with respect to the surroundings and to adjacent differential tube elements;
2. That there is no axial diffusion along the tube;
3. That the bulk stream is well mixed;
4. That the partial pressure of the peroxide at the surface is zero;
5. That there is no homogeneous reaction in the gas phase, i.e., all of the decomposition occurs on the surface;
6. That the diffusivity for this complex system may be found as a mean of the diffusivities of several, separate, equivalent, binary systems, the binary diffusivities in turn being obtained from empirical correlations of Gilliland (3);
7. That the effective film thickness may be considered constant along the tube, or that a mean value may be employed, and furthermore, that this film thickness may be evaluated from previous mass-transfer correlations;
8. That the temperature function required may be approximated by the adiabatic decomposition temperature of the bulk stream along the tube.

Consider a mixture of 1 mole of peroxide and W moles of water entering the boiler undecomposed, as feed, and let the fraction of the peroxide entering the catalyst tube that has decomposed in boiling be f_1 and the fraction decomposed leaving the catalyst tube be f_2 . Since the partial pressure and the adiabatic decomposition temperature may be expressed in terms of f , and since the rate N is the rate per unit diffusional area or per unit (tube circumference) \times (tube length), Eqn. (2) may be integrated to give an expression for the tube length required for a given decomposition of peroxide. The details of the derivation and the evaluation of the constants are given in the Appendix; the final form of the equation may be written as:

$$Z = \frac{R m_0}{K \pi (d/x)} \left[\frac{2W + 3}{\sqrt{a + b}} \Delta \tanh^{-1} \sqrt{\frac{af + b}{a + b}} - \frac{1}{2a} \Delta \sqrt{af + b} \right]_{f_1}^{f_2} \quad (3)$$

$$W = (34/18) \frac{100 - C^*}{C^*} \quad (3a)$$

$$a = 0.0382 (C^*)^2 + 15.05 (C^*) \quad (3b)$$

$$b = T_0 - a f_1 \quad (3c)$$

where,

- C* - Pseudo-feed, weight percent peroxide in the feed calculated on a basis of the downstream samples.
 d/x - Ratio of tube diameter to effective film thickness.
 f - Fraction decomposed of peroxide entering as feed; f_1 entering catalyst tube, f_2 leaving.
 K - Diffusivity constant, 4.45×10^{-5} .
 m_0 - Rate of peroxide feed (at $f = 0$), gm.-moles/sec.
 R - Gas constant, $82.06 \text{ (cm.}^3\text{)(atm.)}/\text{(g.-mol.)(}^\circ\text{K.)}$.
 T_0 - Temperature of vapor stream entering catalyst tube, $^\circ\text{K}$.
 W - molal ratio of water to peroxide in the feed (at $f = 0$).
 Z - Axial length of catalyst tube, cm.

and,

- π - Ratio of circumference to diameter, 3.14159-

Equation (3) may be employed to predict the tube length for a given rate of peroxide flow (m_0), concentration (c), and limits of decomposition (f), provided the term d/x may be evaluated. Since the equation has been derived on the basic assumption that there is no effect on mass transfer by a large temperature difference, various correlations of d/x based on data from wetted-wall absorption towers might be employed as approximations. Sherwood (15) presents two such relations which are useful. One is based on data from absorption towers, the other on heat transfer data inside tubes, correlated by McAdams (11):

$$d/x = 0.023 N_{Re}^{0.83} N_{Sc}^{0.44} \quad (4a)$$

$$d/x = 0.023 N_{Re}^{0.8} N_{Pr}^{0.4} \quad (4b)$$

- where, N_{Re} - Reynolds number, $(d)(G)/(\mu)$
 N_{Sc} - Schmidt number, $(\mu)/(\rho)(D)$
 N_{Pr} - Prandtl number, $(c_p)(\mu)/(k)$;

- d - tube diameter
 G - flow per unit time per unit area
 D - Diffusivity
 c_p - Molal heat capacity at constant pressure
 k - Thermal conductivity
 μ - Viscosity
 ρ - Density

Equation (4b) has been used in conjunction with Eqn. (3) to prepare a plot of the fractions NOT decomposed ($1 - f$) vs. the catalyst tube length,

for the special conditions of peroxide entering undecomposed ($f_1 = 0$) at a flow rate of $1.17 \text{ gms./}(cm.^2)(sec.)$, for concentrations of 1, 10, 20, and 30% entering peroxide (Fig. 3).

Although it is not apparent from the equation itself, it may be seen from Fig. 3 that the logarithm of the percent not decomposed is virtually linear in the catalyst tube length, a fact shown experimentally by Isbin (9). Inspection of Equations (3) and (4) will show that the theoretical length required is independent of total pressure and of tube diameter as such, the latter appearing in various dimensionless moduli.

The accuracy of this equation will depend on the validity of the assumptions made in the derivation. Granting the basic assumption of pure mass transfer under a concentration gradient, the other assumptions may be justified as follows:

1. The decomposition may be made adiabatic with respect to the surroundings by insulation of proper quality; by employing a catalyst tube of sufficiently small wall thickness, the heat transfer by conduction from one wall segment to adjacent segments may be reduced to negligible proportions. It may be shown (cf. Appendix) that with a wall thickness of 0.01 inch under the temperature gradient along the wall existing in this experiment the heat flow along the tube is only 0.062% of the increase in sensible heat of the vapor stream passing through the tube.

2. Axial diffusion of peroxide in the bulk stream under the pressure gradient established in the tube by decomposition may be shown to be negligible with the flow rate employed in this study.

3. The assumption of a well-mixed bulk stream requires turbulent flow in the catalyst tube.

4. If the decomposition rate is indeed controlled by the diffusion

FIGURE 3

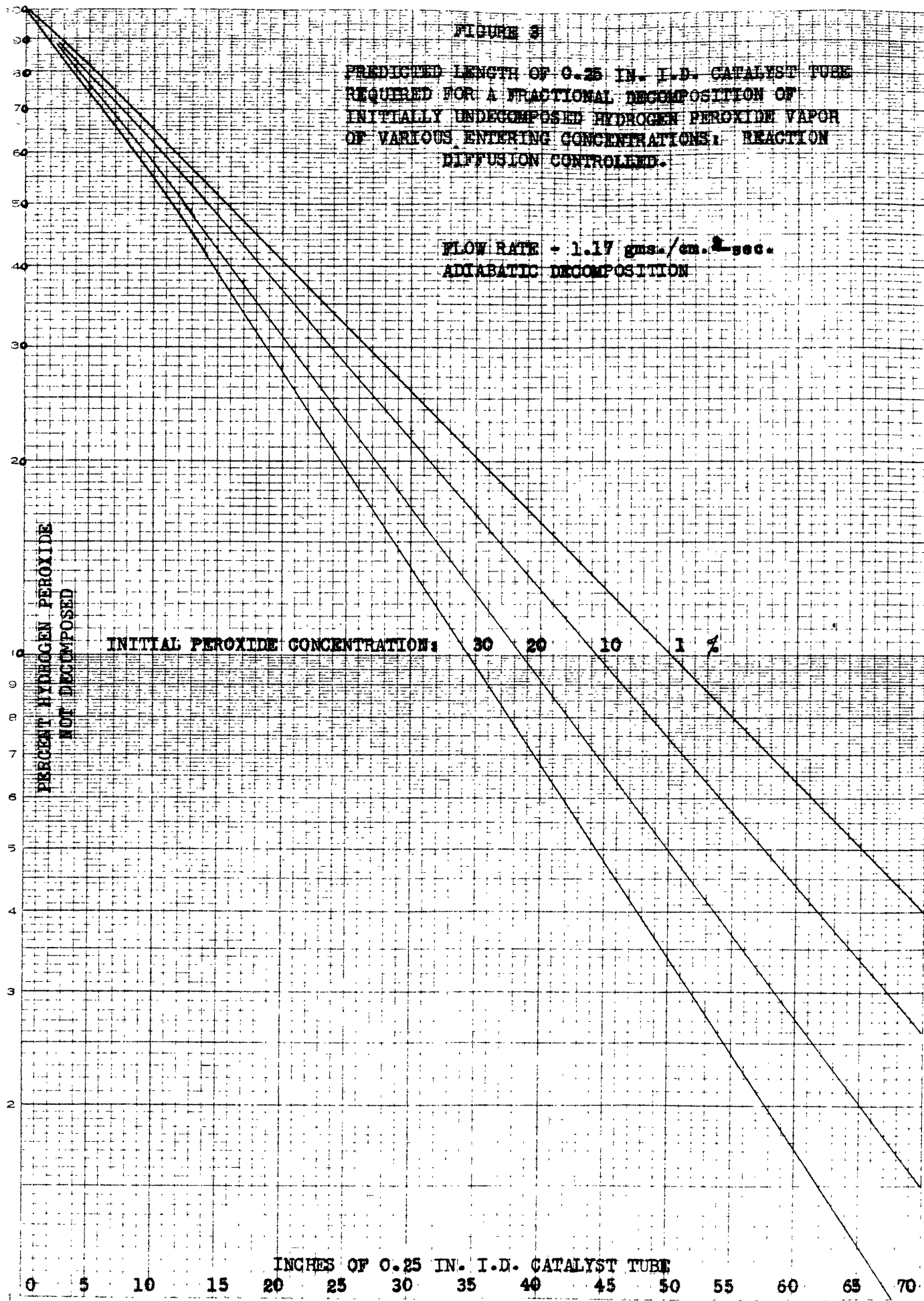
PREDICTED LENGTH OF 0.25 IN. I.D. CATALYST TUBE
REQUIRED FOR A FRACTIONAL DECOMPOSITION OF
INITIALLY UNDECOMPOSED HYDROGEN PEROXIDE VAPOR
OF VARIOUS ENTERING CONCENTRATIONS: REACTION
DIFFUSION CONTROLLED.

FLOW RATE = 1.17 gms./cm.²-sec.
ADIABATIC DECOMPOSITION

PERCENT HYDROGEN PEROXIDE
NOT DECOMPOSED

INITIAL PEROXIDE CONCENTRATION: 30 20 10 1%

INCHES OF 0.25 IN. I.D. CATALYST TUBE



rate, it is implied that the chemical reaction rate is many times greater than the diffusion rate, and the partial pressure of peroxide on the surface of the catalyst will approach zero in the limit.

5. Homogeneous reaction is believed to be small under the conditions existing in the catalyst tube (7), (9), (18).

6. The method employed for evaluation of the mass transfer diffusivity for this system is discussed at length in the Appendix. When the method developed is used to predict the diffusivity of peroxide vapor in air, the agreement with the experimental data of McMurtrie (12) is within 4%.

7. The determination of the effective film thickness is subject to considerable error; the only procedure available is the use of correlations based on wetted-wall absorption tower data, Eqn. (4a), heat transfer inside tubes, Eqn. (4b), or the j_D factor of Chilton (1a). These correlations in mass transfer with small temperature gradients are in error by as much as 20% when used for such systems; the error introduced by use of these correlations in the present system with a large temperature gradient is difficult to estimate. However, since the basic assumption of this derivation was that mass transfer was unaffected by a temperature gradient, and since no other data are available, the use of these correlations is partially justified. The role of eddy diffusion (16) need not be considered in this system since the "effective" film thickness is by definition the total resistance to mass transfer.

8. The use of the adiabatic temperature function is not correct; Eqn. (2) is the result of an integration across the laminar film, and hence the temperature function should more properly be the mean film

temperature. Further work is required for determination of the proper temperature expression for this equation.

The accuracy of the final equation for the diffusion-controlled region can be determined only by direct comparison with the experimental data: it is difficult to assign numerical values to the errors cited above.

V. RESULTS AND DISCUSSION OF RESULTS

A summary of the runs made is given in Tables I and II. A word of explanation about the nomenclature of the runs is perhaps desirable: since samples were taken at one minute intervals during a given run, it is important to refer not only to the run number but also to the representative minute upon which calculations have been based. Hence, the terminology "Run 19.52" has been established to refer to the data taken during minute 52 (from an arbitrary starting time) in run 19.

TABLE I.

CHRONOLOGY OF RUNS MADE

<u>RUN NUMBERS</u>	<u>NOTES</u>
1 - 18	Preliminary runs made during design of boiler (under D. I. C. 6552, September to December, 1949).
19 - 24	Runs made without superheating the vapor entering the catalyst tube; presence of condensate in the stream suspected.
25 - 29	A leak was discovered at the upstream joint of the catalyst tube to the glass tube after Run 29; the temperature data indicated leak was developing during these runs.
30 - 38	Runs made after reconstruction of apparatus to check joint, adiabaticity, and amount of boiler decomposition.
39 - 40	Runs made with superheated vapor entering tube.
41	Run made with 35% peroxide feed. Apparatus failure due to excessive temperature level; collapse of silver tube.

TABLE II.

SUMMARY OF RUNS MADE.

Feed concentration in weight percent
Flow rate in grams/square centimeter/second.

<u>RUN NO.</u>	<u>FEED CONG.</u>	<u>FLOW RATE</u>	<u>RUN NO.</u>	<u>FEED CONG.</u>	<u>FLOW RATE</u>
19	18.6	1.29	25A	10.1	1.43
20	20.17	1.33	25B	10.1	0.527
21	20.3	1.33	26	5.10	1.40
22	14.9	1.31	27	9.69	1.35
23	20.80	1.45	28	14.75	1.39
24	20.84	1.45	29	19.73	1.37
<u>RUN NO.</u>	<u>FEED CONG.</u>	<u>FLOW RATE</u>			
39	20.30	1.40			
40	10.44	1.07			
41	35.25	0.945			

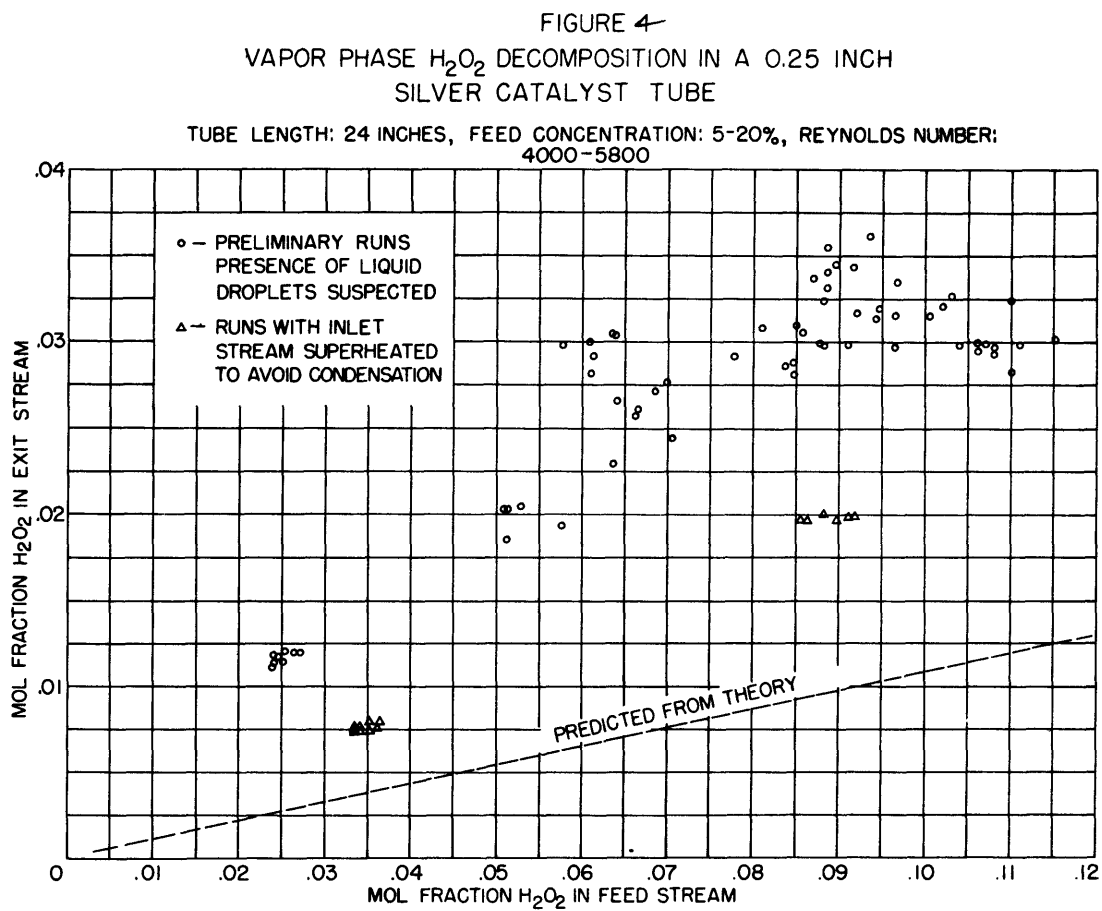
The data obtained are summarized in Figures 4 and 5, and tabulated in the Appendix.

Decomposition Data. Figure 4 presents a plot of the mole fraction peroxide in the stream leaving the catalyst tube vs. the mole fraction entering the tube, for each minute of Runs 19 - 24, 39 - 40; the other runs have been omitted for the reasons outlined in Table I. Although a convenient method of presenting decomposition data from a number of runs made at virtually the same total flow rate, this type of correlation does not show the effect of boiler decomposition (f_1). While the total weight flow rate and entering mole fractions may be identical for two data points, the amount of decomposition in the boiler determines the ratio of water to oxygen in the stream, and hence the molar flow rates of peroxide entering need not be identical. Consequently, a series of constant inlet peroxide mole fractions at constant weight flow rate need not attain the same level of exit decomposition, because of variations in decomposition in boiling. The vertical spread, or "irreproducibility," of the data points of Fig. 4 is due primarily to this cause. The magnitude of the effect may be seen by inspection of Table III, where the data of two runs are compared.

TABLE III.

EFFECT OF VARIATIONS OF DECOMPOSITION
IN BOILING ON DECOMPOSITION IN THE CATALYST TUBE.

RUN NUMBER	<u>19.51</u>	<u>20.47</u>
Mole fraction H_2O_2 entering tube	0.0641	0.0645
Total flow rate, gm./cm. ² /sec.	1.27	1.30
Fraction not decomposed entering tube	0.682	0.849
Pseudo-feed, weight percent	16.6	13.4
Mole fraction leaving tube	0.0266	0.0304
Peroxide flow rate(feed), g-mol./sec.	0.00187	0.00157



Comparison of the experimental data with the theoretical relationship derived in the preceding section should be made on the basis of a correlation similar to Fig. 3; however, Fig. 4 provides a more convenient representation of a large amount of data, and the effect of variations in boiler decomposition is not excessive.

The theoretical line given in the plot represents the values predicted for the conditions of the runs from the mass transfer equation, Eqn. (3). Although shown by a line, the points are actually somewhat scattered, as explained above. The runs have been divided into two groups, Runs 19-24 (circles), in which the entering stream was not superheated, and Runs 39 - 40 (triangles), in which superheating was employed. (Because of the leak, Runs 25 - 29 have not been shown; Run 41 has been omitted because of the catalyst failure). It will be noted that the data of runs in which superheating was used lie much closer to the values predicted from Eqn. (3). In order to show that this effect was not due solely to superheating alone, two runs were made at different degrees of superheat; the results are outlined in Table IV.

TABLE IV.

EFFECT OF ENTRANCE TEMPERATURE ON VAPOR DECOMPOSITION.

<u>RUN NO.</u>	<u>FLOW RATE</u>	<u>FRACT. NOT DECOMP. ENTERING CAT. TUBE</u>	<u>UPSTREAM TEMPERATURE</u>	<u>FRACT. NOT DECOMP. LEAVING CAT. TUBE.</u>
40. 58	1.06	0.620	310 °F	0.1405
40.100	0.99	0.624	422	0.1409

The values obtained by increasing the superheat by 112 °F. were well within the minute-to-minute variations of the initial run; it is concluded that superheating itself is not responsible for the increased decomposition shown in Fig. 4 for Runs 39 - 40. (The very low temperature coefficient of the reaction is also indicative of diffusion control.) If

condensate was present in Runs 19-24, where there was no superheating, two effects on the amount of decomposition occurring may be predicted, depending on the amount of condensate present: (a) the evaporation of droplets in the vapor stream would cool the stream, lowering the diffusion rate to the surface, or (b), part of the catalyst surface would be masked from mass transfer by drops of condensate evaporating on the surface. In either case, decomposition would be reduced by the presence of condensate. Since the heat loss from the section of tubing leading to the catalyst tube is constant (the condensation temperature of different concentrations of vapors not varying widely), the data of these runs correlate on this type of plot despite the presence of condensate. The divergence from theory of Runs 39-40 will be discussed below.

Temperature Data. The temperature profiles along the catalyst tube, together with the measured exit bulk stream temperature, are shown in Fig. 5. The plot is presented in three sections for clarity, the runs being separated according to whether they were characterized by (a) condensate, (b) leak, or (c) superheating. The observations to be made from these data are best tabulated before discussion.

1. The catalyst surface temperature is considerably higher than even the final bulk stream temperature, initial temperature differences, wall to bulk, being the order of 200 - 400 °F.

2. The catalyst temperature decreases along the tube in the majority of the runs; in runs where a leak was present, the temperature increases with length.

3. The catalyst wall temperature goes through a maximum a short distance from the upstream end, both in the runs with condensate, and in runs with superheating.

Figure 5: TEMPERATURE DISTRIBUTION ALONG 0.25 IN. I.D. SILVER CATALYST TUBE AND EXIT TEMPERATURE OF BULK STREAM FOR VARIOUS ENTERING PEROXIDE CONCENTRATIONS, FLOW 1.4 gm./cm.²-sec.

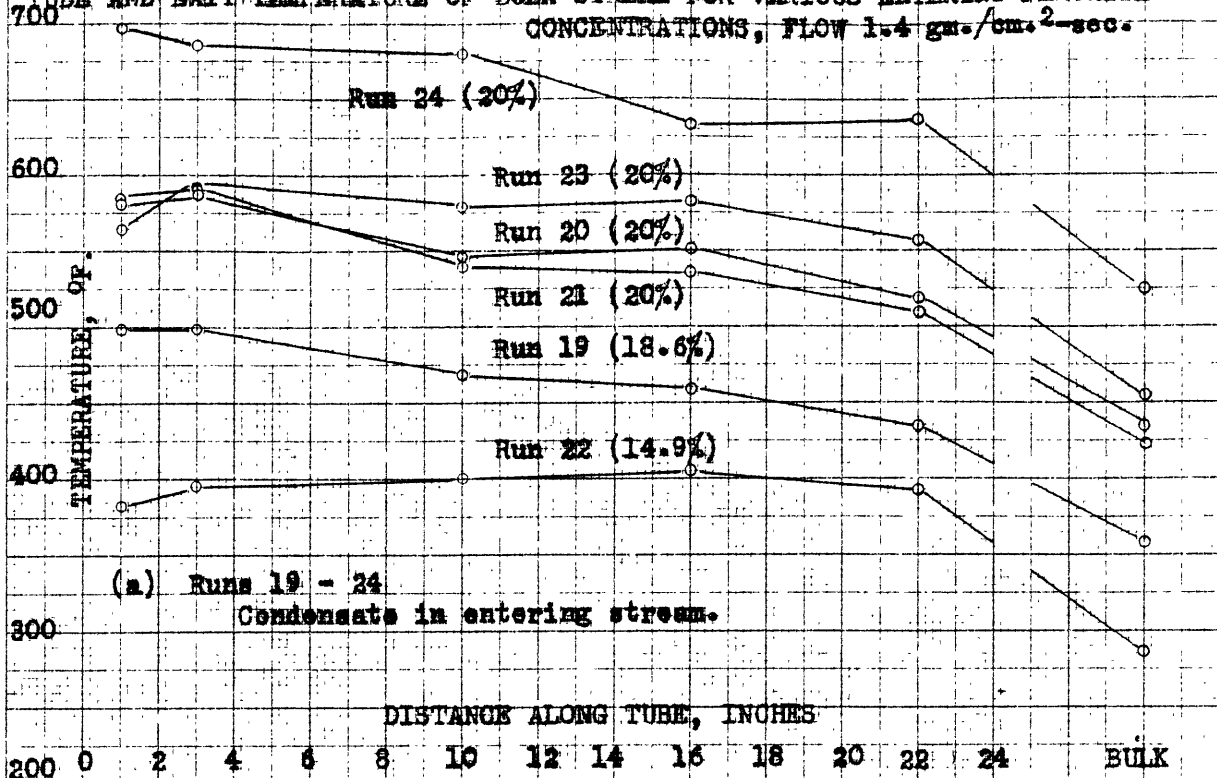
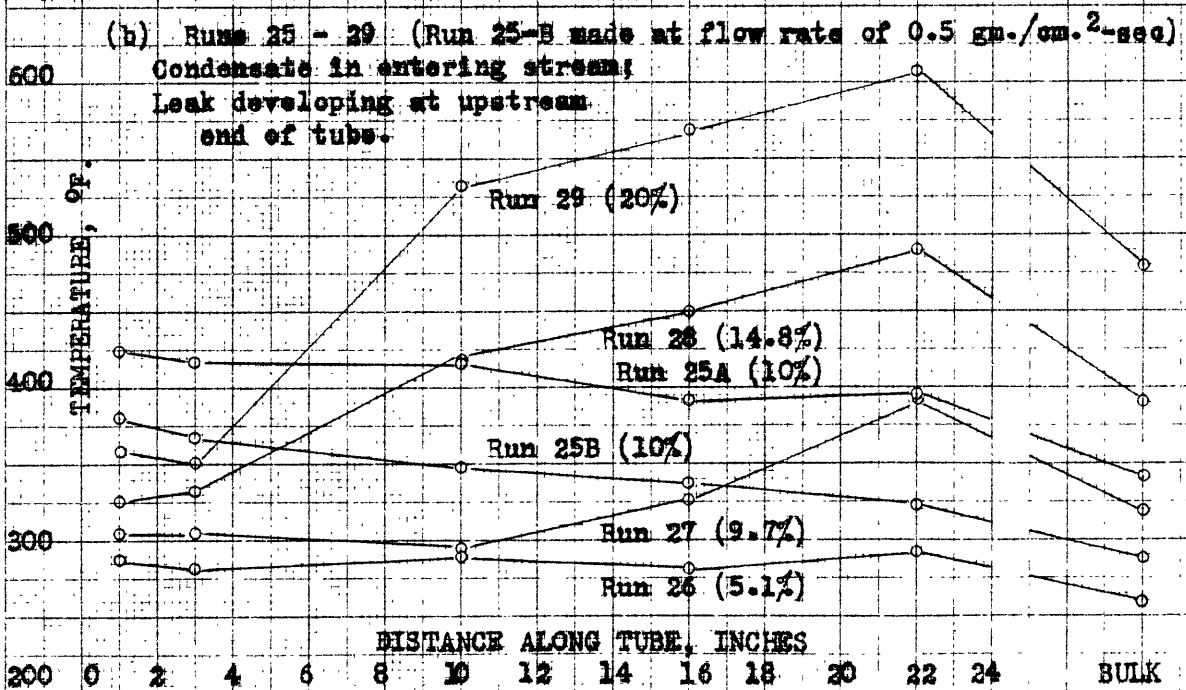


Figure 5: TEMPERATURE DISTRIBUTION ALONG 0.25 IN. I.D. SILVER CATALYST TUBE AND EXIT TEMPERATURE OF BULK STREAM FOR VARIOUS ENTERING PEROXIDE CONCENTRATIONS, FLOW 1.4 gm./cm.²-sec.



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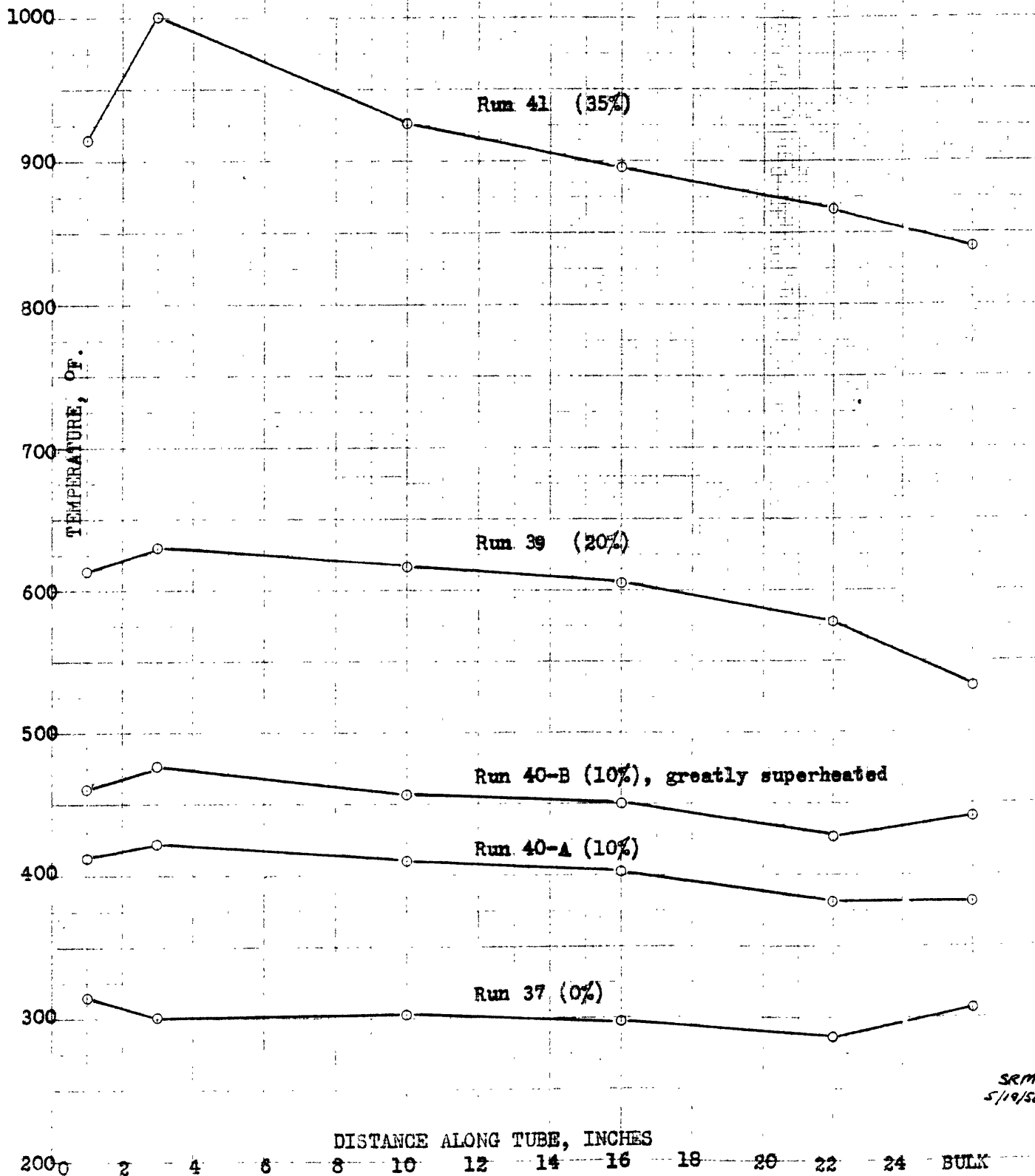
FIGURE 5.

TEMPERATURE DISTRIBUTION ALONG 0.25 In. I.D. SILVER CATALYST
TUBE AND EXIT TEMPERATURE OF BULK STREAM
Flow - 1.4 gm./cm.²-sec.

(o) Runs 39 - 41

Vapor superheated to prevent condensation before tube.

Run 37 made with superheated steam for comparison.



SRM
5/19/50

4. Increasing the superheat (i.e., the entrance temperature of the stream) merely increases the temperature level of the surface, Runs 40-A, 40-B.

5. The data are reproducible, as shown by the series of 20% runs.

6. The effect of condensate is to lower the temperature level.

Although it might be expected that the catalyst temperature would increase along the tube as the bulk stream became warmer through decomposition, a heat balance will show the data to be consistent. In an adiabatic decomposition the heat liberated by the decomposition on the surface must be transferred to the bulk from the catalyst surface,

$$h A_H \Delta T = k_G A_D (H_r) \Delta P \quad (5)$$

where, h - Local coefficient of heat transfer,
 k_G - Local coefficient of mass transfer,
 A - Catalyst surface area, A_H for heat transfer, A_D for mass transfer (reaction),
 H_r - Heat of reaction,
 ΔT - Temperature difference, wall to bulk,
 ΔP - Partial pressure difference of peroxide, bulk to wall.

By rearrangement,

$$(T_W - T_B) = \frac{k_G (H_r)}{h} \frac{A_D}{A_H} (P_B) \quad (5a)$$

where the subscripts W and B represent the catalyst wall and bulk stream conditions respectively (the partial pressure of peroxide on the surface being zero).

From Eqn. (5a) it is seen that in the upstream section of the catalyst tube, where the partial pressure of peroxide is high, there must be a large temperature difference from the wall to the bulk to sustain the required heat flux. However, as the stream is depleted of peroxide, the temperature difference will decrease along the tube. Whether the catalyst temperature will decrease with length will depend on the profile of the bulk stream

temperature (and any heat loss through the insulation). When the leak developed at the upstream end of the catalyst tube, the escaping vapors condensed, wetting the insulation and greatly increasing the heat loss from the upper end of the tube. Apparently this change in the operating conditions was responsible for the reversal of the surface temperature profile.

The existence of a maximum in the temperature profiles is probably due to the existence of a transitional of a transitional tube-length required for establishment of the full mass transfer pattern, similar to the transitional length long recognized in fluid mechanics. If the mass transfer is not fully developed at the beginning of the catalyst tube, then from Eqn. (5a) it is apparent that the temperature difference required will be less.

The effect of entrance temperature on the temperature profile of the catalyst surface is shown by comparison of Runs 40-A and 40-B (Table IV). Although Run 40-B had not reached complete thermal equilibrium when the sample was taken, as indicated by the fact that the exit bulk stream is at a slightly higher temperature than the catalyst surface, it may be surmised that the effect of superheat is merely to increase the temperature of the surface at all points.

The reproducibility of the data and the effect of the amount of boiler decomposition on the temperature profile are shown admirably by the profiles for the 20% runs, Runs 20, 21, 23, 24, and 39. Table V contains the operating characteristics of these runs. In the runs made without superheating the entrance stream, Runs 20, 21, 23, 24, the temperature level of the catalyst surface is seen to depend markedly on the amount of boiler decomposition, i.e., on the mole fraction of the entering peroxide.

TABLE V.
COMPARISON OF RUNS MADE WITH 20% PEROXIDE

<u>RUN</u>	<u>FEED</u>	<u>FLOW RATE</u>	<u>RANGE OF FRACTIONS NOT DECOMPOSED ENTERING TUBE</u>	<u>TEMPERATURE LEVEL OF CATALYST TUBE</u>
20	20.1 %	1.33 g/cm ² sec	0.760 - 0.846	580 - 519 °F.
21	20.3	1.33	0.782 - 0.877	590 - 510
23	20.80	1.40	0.783 - 0.977	580- 557
24	20.84	1.45	0.944 - 1.-	690 - 637
39	20.30	1.40	0.765 - 0.870	620 - 577

Run 39, made with superheated vapor, corresponds in feed, flow rate, and fractions not decomposed with Run 21; yet, the catalyst temperature is both higher at the beginning of the tube and at a higher level along the tube. Since the amount of superheating in Runs 39-40 was based on calculations of heat loss through the insulation before the catalyst tube in steam runs (Run 37), the intent being to introduce just sufficient superheat to prevent condensation before the tube, the temperature of the vapor entering the catalyst tube in Run 39 should be relatively close to that of Run 21. In Run 40, 100 °F of superheat changed the surface temperature level by 50 °F. Since the superheat of Run 39 over Run 21 is only 66 °F, and the difference in surface temperature level is again the order of 50 °F., there is additional indication of the presence of condensate in Run 19 et seq. The greater initial increase in catalyst temperature 1 to 3 inches downstream in Run 39 as compared to Run 21 suggests that part (but not all) of this maxima effect may be attributed to the evaporation of condensate in this section of the tube.

Analysis of Runs. The magnitude of the heat losses in the system (i.e., the departure from adiabaticity) may be seen from Table VI, where the measured bulk temperatures leaving the catalyst tube are compared with the

TABLE VI.

OBSERVED AND CALCULATED BULK TEMPERATURES
LEAVING CATALYST TUBE.

<u>RUN</u>	<u>BULK</u>	<u>ADIAB.</u>	<u>Δ</u>	<u>RUN</u>	<u>BULK</u>	<u>ADIAB.*</u>	<u>Δ</u>
19	358 °F	444 °F	- 86 °F	39	532 °F	574 °F	- 42 °F
20	435	515	- 80	40(A)	381	380	0
21	424	509	- 85	41	840	1020	-180
22	287	396	-109				
23	455	525	- 70				
24	526	630	-104				

(*Assuming vapor enters tube at condensation temperature.)

temperatures calculated for an adiabatic system corresponding to the decompositions observed. In the runs made in the presence of condensate, apparently as much as one half of the total loss in sensible heat of the vapor is due to evaporation of condensate.

A temperature profile for Run 19.52 is given in Fig. 6, showing the catalyst surface temperature, adiabatic bulk temperature, and calculated bulk stream temperature corrected for heat loss, along the tube length. The calculations are based upon the assumption that the logarithm of the fraction not decomposed is linear in the length of tube, as discussed above in conjunction with the mass transfer equation and the data of Isbin. Knowing, then, the fractional decomposition at any point by interpolation, the adiabatic bulk temperature may be calculated and the bulk stream temperature calculated by assuming a heat loss distribution. The calculations are given in detail in the Appendix. The evaporation of condensate has been assumed to occur in the first section of the tube; the profile of the bulk stream contains a finite discontinuity for the first two inches to allow for this effect. The bulk stream profile obtained in this manner is much flatter than the adiabatic profile; indeed, it may be shown that for longer tubes the heat liberation by decomposition of 20% peroxide will barely compensate for the insulation heat loss.

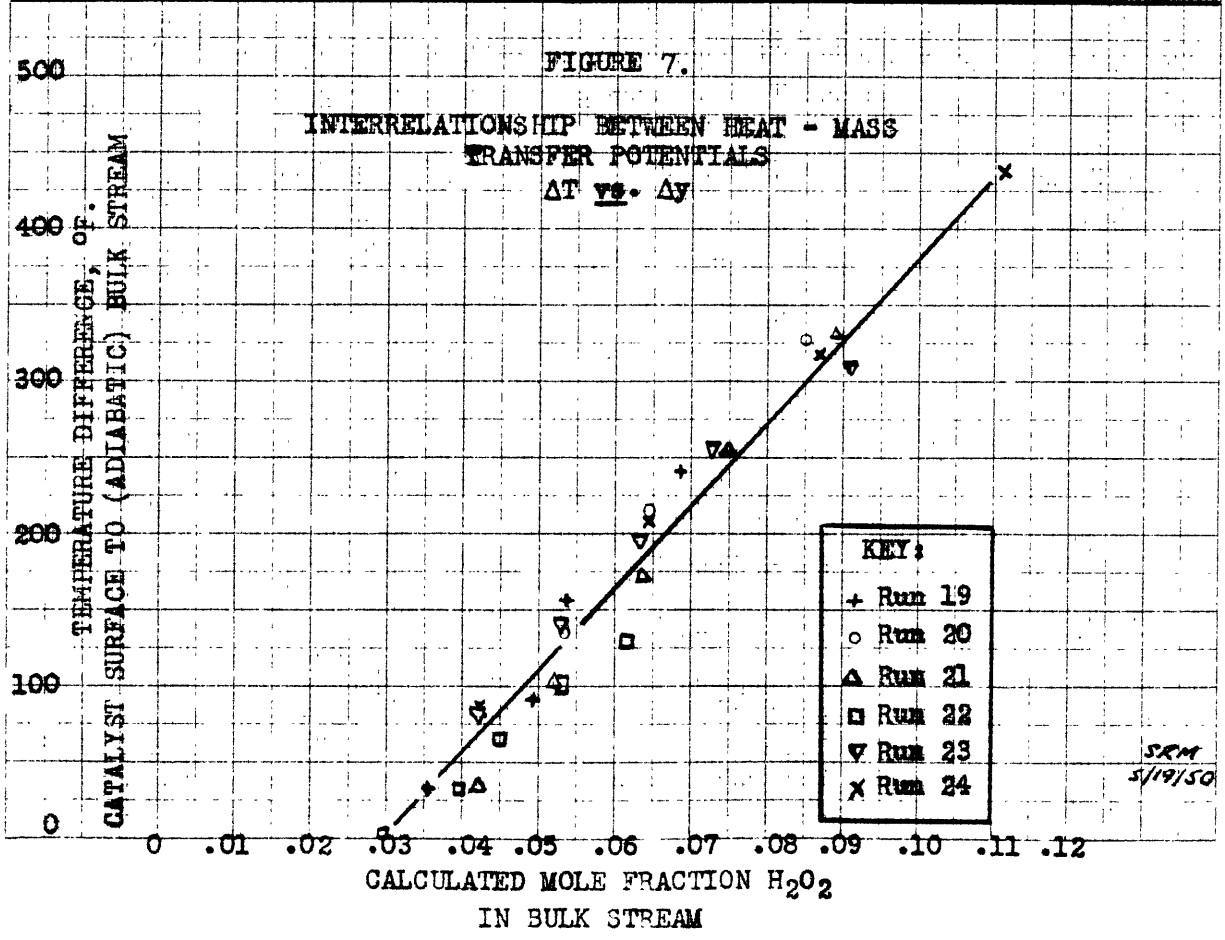
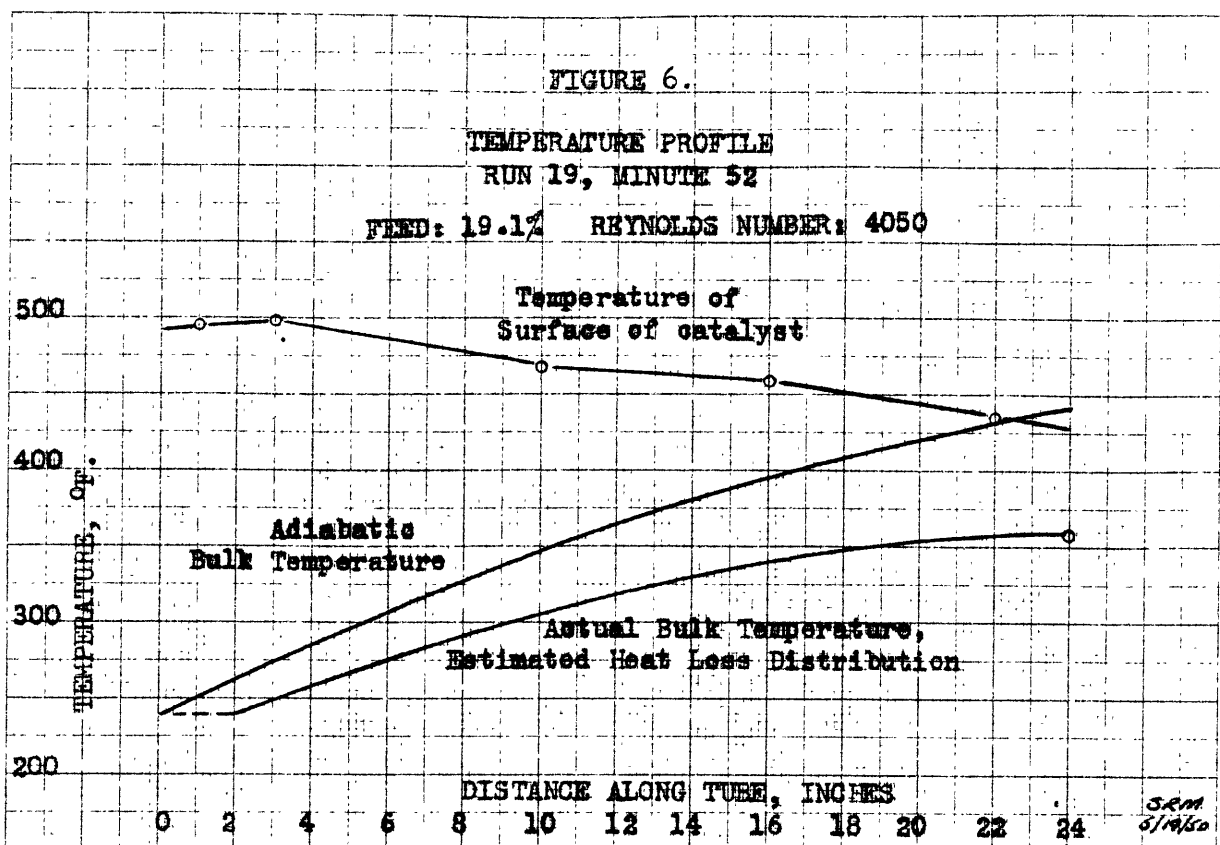


Figure 7 shows the temperature difference, wall to (adiabatic) bulk stream, plotted against the partial pressure difference of peroxide, bulk stream to wall, at several points along the tube for Runs 19-24. The calculation of the mole fraction distribution along the tube is readily made through the linear relationship mentioned above; however, the computation of the actual bulk stream temperature distribution is laborious. Therefore, although the actual bulk stream temperature should be used, the adiabatic temperatures have been employed. It will be noted that the data points are consistent, both within a run and among runs, and that a straight line may be drawn through the points without difficulty.

The significance of Fig. 7 may be shown by a modification of Eqn. (5) to allow for insulation heat loss (Q), neglecting the initial section of the tube where evaporation of condensate occurs,

$$\Delta T = \frac{k_G (H_r)}{h} \frac{A_D}{A_H} \Delta P - \frac{Q}{h A_H} \quad (6)$$

If some assumption is made as to the constancy of the heat losses, so that an h may be defined based on the difference between the catalyst surface and adiabatic bulk temperatures, then the slope of the best line through the data points will give the value of the slope term of Eqn. (6), and the intercept on the ΔT axis will be the temperature potential lost because of non-adiabatic decomposition. The k/h term may be evaluated from the plot as,

$$\frac{k_G (H_r)}{h} \frac{A_D}{A_H} = 5500 \text{ } ^\circ\text{F./atm.}$$

If the heat of decomposition is taken as 43,400 Btu./lb.-mol., and the entire surface is regarded as catalytic so that $A_D = A_H$, then,

$$h/kg = 7.9 \text{ (Btu./}^\circ\text{F.)}/(\text{lb. mol./atm.}),$$

where h is based on the adiabatic bulk temperature. Because of the limited data taken with superheated vapor, it was not considered desirable to repeat the procedure for Runs 39 - 40.

Comparison of Data With Predicted Values. Before employing the theoretical relation derived, it is first necessary to establish that diffusion is the rate controlling ~~step~~ in this system. Since the range of variables considered was limited, unquestionable confirmation of diffusion control is difficult; however, three considerations favor such a conclusion. First, the decomposition showed no marked temperature coefficient (Table IV), such as would be expected of a reaction-rate controlled decomposition. Secondly, the decomposition did not vary linearly with the flow rate (Table VII below), as is the case in a reaction rate system. Finally, the reproducibility of the data obtained is indicative of control other than by chemical reaction rate where the systems are strongly affected by the condition of the catalyst surface. It is not unreasonable on the basis of these limited data, then, to assume a diffusion mechanism controlling.

However, the principal difficulty lies not with determination of diffusion control, but rather with the determination of the presence of full turbulent flow in the catalyst tube, as required by an assumption made in the derivation.

TABLE VII.

EFFECT OF FLOW RATE ON DECOMPOSITION

<u>RUN NO.</u>	<u>FEED</u>	<u>FRACT. NOT DECOMP. ENTERING CAT. TUBE</u>	<u>FLOW RATE</u>	<u>FRACT. NOT DECOMP. LEAVING CAT. TUBE</u>
25.26	10.1%	0.864	1.32 g/cm ² sec	0.348
25.39	10.1	0.866	0.527	0.368

Only a slight increase in decomposition was observed when the flow rate was reduced by a half, indicating (a) diffusion control and (b) turbulent flow as compared to transitional flow. On this basis, turbulent flow would seem to exist in this system; however, the Reynolds numbers for the runs are the order of 4000 - 5000, bordering on the upper transitional or lower turbulent region (1a). It is doubtful if full turbulent flow existed at these flow rates.

If diffusion is accepted as rate-controlling, and if the flow is considered to be fully turbulent, then the tube lengths required for the decomposition noted may be readily calculated from the relations derived, Eqn. (3 et al) and Eqn. (4). Sample calculations are given in the Appendix. The values obtained are summarized in Table VIII.

TABLE VIII.

COMPARISON OF DATA WITH VALUES PREDICTED BY MASS
TRANSFER EQUATION, EQN. (3).

Actual Tube Length 24 inches.

<u>RUN NO.</u>	<u>PREDICTED TUBE LENGTH</u>	<u>RATIO: PREDICTED/ACTUAL</u>
19.51	9.72 inches	0.405
20.26	11.6	0.484
21.41	12.2	0.509
22.47	8.06	0.388
22.48	9.41	0.393
23.13	10.9	0.454
39.41	15.9	0.663
39.43	16.13	0.674
40.57	16.9	0.705

Some variation in minute-to-minute values for the runs is noted. As mentioned in conjunction with Fig. 4, the runs made with superheated streams entering the catalyst tube show better agreement with the predicted diffusion equation than do the runs made without the superheat. However,

the mass transfer equation remains in error by 33% for the runs made with superheated vapor, error due to both the method of evaluation of the effective film thickness and the temperature function. The divergence due to the effect on mass transfer of a temperature gradient cannot be estimated from these data.

Conclusions. On the basis of the discussion of the results obtained in this investigation, it is possible to draw several important conclusions regarding the heterogeneous decomposition of hydrogen peroxide vapor. However, it must be emphasized that the majority of the data are from runs made with two-phase streams: only three runs were made where there was no condensate in the vapor entering the catalyst tube.

Diffusion of peroxide from the bulk stream to the catalyst surface is the rate controlling mechanism under the conditions investigated. However, thermal diffusion may be important in reducing the rate of transport of peroxide vapor to the catalyst surface below that required by the partial pressure potential. The equation derived solely on the basis of mass transfer by a concentration gradient is a useful approximation, the error in the predicted tube length being the order of 33% below the actual.

The surface temperature of the catalyst tube is higher than the bulk stream at all points, decreases with increasing tube length in the absence of excessive, localized heat loss, goes through a maximum a short distance from the entrance to the tube, and is determined by the partial pressure of peroxide in the bulk stream and by the bulk stream temperature profile. The entrance temperature of the vapor to the catalyst tube appears to have only a small effect on the amount of decomposition obtained, even though it be raised by 112 °F. The presence of condensate

in amounts of the order of 2% of the entering stream decreased the exit bulk stream temperature by 40 °F., and increased the fraction not decomposed leaving the catalyst tube from a level of 0.15 to 0.30.

The amount of decomposition attainable is dependent not only on the mole fraction of peroxide entering the stream and on the total weight flow rate, but also on the extent of previous decomposition, as it determines the ratio of water to oxygen in the stream and hence the molal flow rate of peroxide entering the tube. It is unfortunate that the boiler employed in this investigation, while producing a vapor at a relatively steady flow rate, was still subject to a cyclic fluctuation in the amount of decomposition occurring in the vaporization of peroxide.

Recommendations. This work represents but a preliminary investigation with this type of equipment; consequently, the recommendations are extensive, both in the experimental program and in the theoretical aspects of the problem.

The variables to be examined must be more inclusive. Operation at higher flow rates, Reynolds numbers of 10,000 or greater, as well as consideration of flow rate as a variable, is essential. The length of catalyst tube should be examined as a variable, particularly in a "differential reactor" to evaluate the significance of the maximum observed in the catalyst surface temperature profile and of the transitional tube length postulated for mass transfer systems. Different catalyst surfaces should be employed besides silver, to delimit more effectively the region of diffusion control.

Improvements in the apparatus may be made. If possible, the cyclic fluctuation of boiler decomposition should be eliminated or reduced, since the boiler decomposition is an important (and uncontrollable)

variable. Heat losses from the catalyst tube should either be reduced by more effective insulation, or measured by suitably installed thermocouples. It is particularly important to provide some means of determining the entrance temperature of the stream when superheating is employed. Since the flow pattern would be disturbed by probes, the measurement must be made by determination of the heat loss along the calming section.

Further work is required in the theoretical analysis of this system, in the determination of the proper temperature function for the mean film temperature, and in the evaluation of the effective film thickness. The role of thermal diffusion must be investigated to a greater extent than has been possible at this time.

VI. CONCLUSIONS.

1. Diffusion is the rate-controlling mechanism in the (quasi-) adiabatic heterogeneous decomposition of hydrogen peroxide vapor on a cylindrical, silver catalyst tube at 1 atm. total pressure, in concentrations from 5 to 35% by weight, and at flow rates of $1.3 \text{ gm./}(\text{cm.}^2)(\text{sec.})$.

2. The equation derived solely on the basis of mass transfer as a result of a concentration gradient, without consideration of the effect of the large temperature gradient present in this system, is a useful though approximate theoretical relation, the predicted values being the order of 33% below the experimental.

3. The surface temperature of the catalyst tube (a) is higher than the bulk stream temperature at all points, (b) decreases with increasing tube length in the direction of flow, (c) goes through a maximum a short distance from the upstream end, perhaps because of a transitional tube length required to establish the transfer pattern, and (d), is determined by the partial pressure of the peroxide in the bulk stream and by the bulk stream temperature.

4. The entrance temperature of the vapor to the catalyst tube, although not studied widely, appeared to have small effect on the amount of decomposition obtained, even though it be increased by 112 °F.

5. The presence of condensate in the entering stream has a marked effect on both the decomposition level attained and on the temperature level of the catalyst surface and the bulk stream. The presence of condensate in amounts of the order of 2% of the entering stream decreased the bulk stream temperature by 40 °F., and increased the fraction peroxide not decomposed leaving the tube from a level of 0.15 to 0.30.

6. The amount of decomposition attainable is dependent not only on

the mole fraction of peroxide in the entering stream, but also on the amount of prior decomposition.

7. The boiler employed in this investigation, while producing a vapor at a relatively steady rate, was still subject to a cyclic fluctuation in the amount of decomposition occurring in the process of vaporization.

8. The method of insulating the apparatus was not satisfactory, nor was the determination of such heat loss reliable.

9. The type of silver-to-glass joint employed in this apparatus was not satisfactory.

VII. RECOMMENDATIONS.

1. The range of variables investigated must be extended:

- (a) Higher Reynolds numbers of the order of 10,000 are required to assure full turbulent flow in the catalyst tube;
- (b) The flow rate must be considered a variable;
- (c) The dimensions and material of the catalyst tube should be examined critically. The tube length should be varied to investigate the existence of a transitional length at the beginning of the tube, to establish the dependence of decomposition on the tube length for comparison with the theory developed, and to examine the decomposition in a "differential reactor". A study of the effectiveness of different active catalytic surfaces will serve to delimit the region of diffusional rate control.

2. Further work is necessary in the theoretical aspect of this decomposition:

- (a) The proper film temperature function for integration of the diffusion equation across the film and along the tube is not completely established;
- (b) The method of evaluation of the "effective film thickness" is not satisfactory;
- (c) The role of thermal diffusion in this decomposition mechanism should be investigated more fully, both theoretically, and by imposing an external heat source on the catalyst tube.

3. Improvements in the apparatus may be made:

- (a) Elimination or reduction of the fluctuations in boiler decomposition of peroxide will permit a closer correlation of the data obtained;
- (b) The insulation employed should be more effective in nature, or means should be employed to determine quantitatively the magnitude and distribution of the heat loss from the catalyst tube surface;

(c) Provision must be made for determination of the entrance temperature of the vapor stream when superheating is employed to prevent condensation in the calming section and lead tubes.

APPENDIX

ANALYTICAL PROCEDURESDetermination of Hydrogen Peroxide (5), (14),

The quantity of peroxide contained in the liquid samples is determined by titration with standard potassium permanganate. A portion of the sample, usually 1 cc., is added to 20 cc. of hot 1/20 N sulfuric acid. The hot mixture is titrated to the pink endpoint with ca. 0.2 N potassium permanganate.

Standardization of Potassium Permanganate (2).

About 0.3 gram of sodium oxalate (dried at 105 °C) is added to a 600 ml. beaker. 250 ml. of diluted sulfuric acid (5 ml. acid to 95 ml water), previously boiled for 10 to 15 minutes and cooled, are added. The potassium permanganate is added at a rate of 25 to 35 ml./min. while stirring slowly. After the initial pink color has disappeared, the solution is heated to 55 to 60 °C, and the titration completed.

The excess of permanganate required to impart color to the solution is determined by adding permanganate to the same volume of diluted sulfuric acid at 55 to 60 °C. This correction usually amounts to 0.03 to 0.05 ml.

DERIVATION OF THE GENERAL EQUATION FOR REACTION RATE
CONTROLLED BY DIFFUSIONAL PROCESSES

If the decomposition rate is controlled by diffusional processes, the rate of reaction will be determined by the diffusion of hydrogen peroxide from the bulk stream to the surface of the catalyst tube through the stagnant film. Since the reaction is irreversible, and since the equilibrium lies far towards the formation of water and oxygen, the possibility of diffusion rate control by the reaction products may be discarded, and attention focused on the diffusion of the peroxide alone.

This section will be sub-divided into two parts: the general derivation of the diffusion equation, and the evaluation of the factors in that equation.

I. Derivation of Diffusion Equation.

A feed mixture of hydrogen peroxide and water is fed to the boiler, where it is vaporized, the vapors being passed through a length of unpacked, cylindrical tube. Some decomposition of the peroxide occurs before the catalyst tube, the peroxide partially decomposing in the process of vaporization, or possibly on the walls of the glass tubing leading to the catalyst tube. This latter effect is believed to be small, and it will be assumed that all of the decomposition taking place before the catalyst tube occurs in the boiler, and, in addition, that the heat liberated by this decomposition furnishes heat of vaporization for the boiling liquid, rather than raising the sensible heat of the generated vapor. It will also be assumed in this derivation that,

- a. The bulk stream is well mixed at all points in the tube (turbulent flow),

- b. The decomposition is adiabatic, and
- c. No decomposition occurs in the bulk stream without catalysis.

The feed entering the boiler may be considered to consist of 1 mole of peroxide (basis) and W moles of water per mole of peroxide, the feed rate being m_0 moles of peroxide per second. The boiling temperature, and hence the initial temperature of the vapors, is T_b °K, and the fraction decomposed of the peroxide entering the system occurring in the boiler is f_1 . The vapors enter the catalyst tube at temperature T_0 , which may be equal to or greater than T_b , depending on the amount of superheating. The peroxide at a length of catalyst tube Z cm. from the upstream end has undergone a total fractional decomposition f and is at an adiabatic decomposition temperature T . A complete table of nomenclature will be found at the end of this section.

It is desired to derive an equation relating f and Z for various entering concentrations of peroxide.

The diffusional processes involved here are those of multicomponent diffusion through a laminar film, the peroxide diffusing towards the interface countercurrent to the water and oxygen liberated by the decomposition diffusing towards the bulk stream. In addition, there is a heat flux from the interface to the bulk stream. The interaction on mass transfer by simultaneous heat transfer will be neglected, since little is known of this effect.

A rigorous solution for this system of multicomponent diffusion has been developed by Gilliland (15) in the form of two simultaneous equations. A more convenient relation is presented by Hougen and Watson (4), based on the simplifying assumption that in a complex system of diffusing gases, the diffusional gradient established for any component A is equal to the sum of the gradients which would result from the separate diffusion

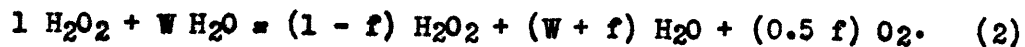
of A with each of the other components in separate binary systems in which the concentrations and rates are the same as in the complex system. By direct comparison of the equation derived on this basis with the more rigorous method of Gilliland, Hougen and Watson demonstrate that this assumption is justified. The equation so derived will be used for the system under consideration,

$$(N_A)_Z = \frac{D_{Am} \pi (P_{A1} - P_{A2})}{R T x P_f} \quad (1)$$

$$P_f = \frac{(\pi + \delta_A P_{A1}) - (\pi + \delta_A P_{A2})}{\ln_e \frac{(\pi + \delta_A P_{A1})}{(\pi + \delta_A P_{A2})}} \quad (1a)$$

- where,
- D_{Am} - Mean diffusivity of component A (H_2O_2) in the system of diffusing components A + B + C + ..., $cm^2/sec.$
 - $(N_A)_Z$ - Diffusional rate of component A at point Z, moles/ cm^2 -sec.
 - P_A - Partial pressure of component A; P_1 at bulk-film interface, P_2 at film-surface interface, atm.
 - R - Gas constant, $82.06 \text{ cm}^3\text{-atm/mole-}^\circ\text{K}.$
 - T - Temperature, $^\circ\text{K}.$
 - x - Effective film thickness, cm.
 - π - Total pressure, atm.
 - δ_A - Change in total number of moles per mole of A reacted.

At any point in the tube, the composition of the stream, on the basis of 1 mole of peroxide entering in the feed, will be,



Substituting into the defining relation for δ ,

$$\delta_{H_2O_2} = + 1/2$$

and from Eqn. (1a), the defining equation for P_f , considering that P_{A2} will be zero if diffusion is the rate controlling step,

$$P_f = \frac{1}{\ln \frac{1 + 0.5 f + W}{f + 2 W + 2}} \quad (3)$$

However, the logarithmic mean may be replaced by the arithmetic mean if the logarithmic group ratio is unity. The range of concentrations is from 1 to 40 weight percent, or values of W from 2.8 to 190, and f may vary from 0 to 1.0; the maximum value of $(2W + 3)/(f + 2W + 2)$ is 1.13. Consequently, P_f may be written as,

$$P_f = \frac{(\pi + 1/2 P_{A1}) + (\pi + 1/2 P_{A2})}{2} = \pi + 1/4 P_{A1} \quad (4)$$

The diffusivity for a binary system of A diffusing through a stagnant film of B is given by an empirical equation of Gilliland (3), based on correlation of experimental data and the kinetic theory,

$$D_{AB} = \frac{0.0043 T^{3/2}}{\pi (V_A^{1/3} + V_B^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (5)$$

where, M - Molecular weight
 V - "Molecular volume", values given in the reference.

In order to simplify the notation, define

$$K_{AB} = \frac{0.0043 \sqrt{1/M_A + 1/M_B}}{(V_A^{1/3} + V_B^{1/3})^2}, \quad (6)$$

or, in terms of Eqn. (5),

$$D_{AB} = \frac{K_{AB} T^{3/2}}{\pi} \quad (7)$$

Continuing with the assumption that diffusion in a complex system may be represented by the sum of diffusions in separate, equivalent binary systems, Hougden and Watson recommend that a weighted average of the binary diffusivities be used for the overall coefficient D_{Am} ,

$$(1 - y_A) D_{Am} = \sum y_n D_{A-n} \quad (8)$$

where, D_{Am} - Diffusion coefficient of A in the complex system,
 D_{A-n} - Diffusion coefficient of A in a binary system of A and the n-th component,
 y_n - Average mole fraction across the film of the inert component in the binary system of A and n.

C. R. Wilke has recommended the use of a harmonic mean (20),

$$D_{Am} = \frac{1 - y_A}{\sum \frac{y_n}{D_{A-n}}} \quad (9)$$

Both averages give virtually the same values for D_{Am} for this system; Eqn. (8) will be employed. In any case,

$$D_{Am} = \frac{K_m T^{3/2}}{\pi} \quad (10)$$

Combining Eqns. (1), (2), (4), and (10),

$$(N_A)_Z = \frac{4 K T^{1/2}}{R x} \frac{1 - f}{f + 4W + 5} \quad (11)$$

By defining the following symbols, and noting that N_A represents the moles of peroxide transported across the film per unit time per unit area, N_A may be expressed in terms of the fraction decomposed, f ,

- n - Moles of peroxide diffusing per unit time, at point Z,
- m - Moles of peroxide flowing in bulk stream per unit time, at point Z,
- m_0 - Moles of peroxide entering at $f = 0$ per unit time.

By definition,

$$f = \frac{m_0 - m}{m_0} \quad (12)$$

and by a material balance on peroxide at point Z,

$$dn = - dm \quad (13)$$

Eqn. (12) may be differentiated to give,

$$m_0 df = - dm \quad (12a)$$

By definition,

$$(N_A)_Z = \frac{dn}{dA} \quad (14)$$

where A is the area of diffusion; assuming the entire tube surface is active, $A = (\pi d) dZ$, d being the diameter of the tube. Combining Eqns. (14), (12a), (13), and the area expression,

$$(N_A)_Z = \frac{m_0}{\pi d} \frac{df}{dZ} \quad (15)$$

Combining Eqns. (11) and (15), and separating the variables,

$$\frac{4 K \pi d}{R m_0 x} dz = \frac{1}{T^{1/2}} \frac{f + 4W + 5}{(1 - f)} df \quad (16)$$

It will be shown below that the temperature may be expressed as a linear function of the fraction decomposed,

$$T = a f + b, \quad (17)$$

and the dimensionless ratio d/x will be considered constant over the tube length for lack of accurate data. The differential equation may now be integrated between the limits $0 < z < Z$ and $f_1 < f < f_2$, f_2 being the fraction decomposed at the end of the catalyst tube. The resultant expression is the theoretical diffusion equation for this system,

$$Z = \frac{R m_0}{K \pi (d/x)} \left[\frac{2W + 3}{\sqrt{a + b}} \Delta \tanh^{-1} \sqrt{\frac{a f + b}{a + b}} - \frac{1}{2a} \Delta \sqrt{a f + b} \right]_{f_1}^{f_2} \quad (18)$$

The factors K , d/x , a and b , and W are to be evaluated.

II. Evaluation of Factors.

A. Feed Concentration.

The molal ratio of water to peroxide in the feed, W , may be expressed in terms of the weight percent peroxide,

$$W = \frac{34}{18} \frac{100 - C^*}{C^*}, \quad (19)$$

where C^* is the weight percent peroxide in the pseudo-feed.

B. Adiabatic Temperature As A Function of Fractional Decomposition.

In order to perform the integration of Eqn. (16), it is necessary to express the temperature in terms of one of the variables.

It is desired to calculate the adiabatic decomposition temperature corresponding to various fractions decomposed for various concentrations

By plotting t vs. f , it is found that T is very nearly linear in f ; the values of the intercepts and slopes of the linear plots for various concentrations of peroxide are summarized in Table A-2,

Table A-2
Values of The Constants In The
Equation $T = af + b$ For Various
Initial Concentrations of H_2O_2

<u>Weight Percent H_2O_2</u>	<u>a -$^{\circ}K$</u>	<u>b -$^{\circ}K$</u>
0*	0	373
1*	15	373
5	76	373
10*	155	374
20*	318	376
30*	483	378

Plotting a against the concentration, C^* , it is found that a is second order in C^* ,

$$a = 0.0382 (C^*)^2 + 15.05 (C^*) \quad (21)$$

In the system under consideration, some decomposition occurs in the boiler, where the heat of reaction does not increase the sensible heat of the vapor. Hence, Eqn. (31) must be corrected so that $T = T_0$ when $f = f_1$. On the basis of the derivation, b is T_0 when $f = 0$, and thus the final temperature function may be written

$$T = a f + b \quad (22)$$

$$a = 0.0382 (C^*)^2 + 15.05 (C^*) \quad (22a)$$

$$b = T_0 - a f_1 \quad (22b)$$

where T_0 should be approximately the boiling temperature, since that was the basis of the enthalpy calculations. Small error will be introduced by slight changes in the entrance temperature.

B. Determination of Diffusion Coefficients.

Gilliland presents (3) the following data in conjunction with his equation for estimating diffusion coefficients, Eqn. (5),

*Calculated by Wentworth (19).

Table A-3Atomic Volumes, Eqn. (5)

<u>Element</u>	<u>Atomic Volume</u>
Hydrogen	3.7
Oxygen	12.0
Nitrogen	15.6

The atomic volumes are additive for compounds,

Table A-3a"Atomic Volumes"

<u>Component</u>	<u>Atomic Volume</u>	<u>Molecular Weight</u>
H ₂ O ₂	22.2	34
H ₂ O	14.8	18
O ₂	14.8	32
N ₂	31.2	28

Upon substituting the values of Table A-3a into the basic equation, Eqn. (5), and evaluating K from Eqn. (6), the following values for the diffusivities in the binary systems are obtained:

Table A-4

<u>Binary System</u>	<u>$K = (D\pi)/(T^{3/2})$</u>
H ₂ O ₂ in H ₂ O	4.52×10^{-5}
H ₂ O ₂ in O ₂	3.81
H ₂ O ₂ in N ₂	3.09

Eqn. (8) will now be evaluated over the range of the variables.

Basis: 1 mole H₂O₂ , W moles H₂O/ mole H₂O₂ .

<u>Component</u>	<u>Moles in Bulk Stream</u>	<u>Moles at Surface</u>
H ₂ O ₂	1 - f	0
H ₂ O	W + f	W + f
O ₂	0.5 f	0.5 f
Total Moles	$1 + 0.5 f + W$	$1.5 f + W$

<u>Component</u>	<u>Mole Fraction In Bulk Stream</u> $1 - f$	<u>Mole Fraction At Surface</u>	<u>Mole Fraction Film Average</u> $1 - f$
H_2O_2	$1 + 0.5f + W$	0	$f + 2W + 2$
H_2O	$1 + 0.5f + W$	$1.5f + W$	$\frac{(f + W)(2f + 2W + 1)}{(1.5f + W)(f + 2W + 2)}$
O_2	$1 + 0.5f + W$	$1.5f + W$	$\frac{(0.5f)(2f + 2W + 1)}{(1.5f + W)(f + 2W + 2)}$

Substituting these average mole fractions across the film of the components into Eqn. (8), substituting the values of the binary system diffusivities from Table A-4, and simplifying results in the following expression for the mean diffusion constant for the system in terms of the water-peroxide ratio and the fraction decomposed,

$$K_m = \frac{12.84 f + 9.04 W}{3 f + 2 W} \quad (23)$$

The term W may be expressed in terms of the concentration through Eqn. (19),

$$K_m = \frac{6.42 f + 8.54 \frac{(100 - C^*)}{C^*}}{1.50 f + 1.89 \frac{(100 - C^*)}{C^*}} \quad (23a)$$

Eqn. (23a) has been evaluated for the range

$$\begin{aligned} f &= 0 \text{ to } f = 1 \\ C^* &= 1 \text{ to } C^* = 40\%, \end{aligned}$$

and the results are summarized in Table A-4.

It is interesting to compare the values obtained by use of Eqn. (23a), based on the average of Eqn. (8), with those obtained using the method of Wentworth (19), in which an average value of M_D is substituted directly in Eqn. (5). The average molecular weight of the non-diffusing components will first be calculated.

<u>Component</u>	<u>Moles</u>	<u>Grams</u>	<u>Average Molecular Weight With Respect to Component</u>
H ₂ O	f + W	18f + 18W	34 f + 18 W
O ₂	0.5f	16f	-----
	<u>1.5f + W</u>	<u>34f + 18W</u>	1.5f + W

<u>Fraction Decomposed</u>	<u>Average Molecular Weight With Respect To Component</u>	<u>Average Molecular Weight Component and Decomposition</u>	
0	18		
	18W + 34	36 W + 61	
1	-----	M _{bav.} = -----	(24)
	W + 1.5	2 W + 3	

or, incorporating Eqn. (19),

$$M_{Bav.} = \frac{61 + 68.1 \frac{(100 - C^*)}{C^*}}{3 + 3.78 \frac{(100 - C^*)}{C^*}} \quad (24a)$$

Evaluation of Eqn. (24a) for the range of concentrations from 1 to 40% and substitution into Eqn. (6), as for the binary systems, leads to a series of values which are included in Table A-4 for comparison.

Table A-4
Summary of Values of K_m

C*	Eqns. (6) And (24a)	K _m x 10 ⁵			Average
		f = 0	f = 0.5	f = 1.0	
1	4.52	4.52	4.51	4.52	4.52
20	4.42	4.52	4.50	4.48	4.50
40	4.31	4.52	4.46	4.43	4.47
Average	4.42		4.47		

The mean value of K will be taken as,

$$K_m = 4.45 \pm 3\% \quad (25)$$

In order to check the validity of the basic assumption of the applicability of Eqn.(5) to a peroxide system, the diffusion coefficient for a peroxide-air system has been calculated, both by Eqns. (6)-(24a) and by Eqn. (23a), and compared with the experimental value reported by

McMurtrie (12).

Table A-5
 D_m For The System Peroxide-Air
 60°C.

<u>Experimental</u>	<u>Eqs. (5)-(24a)</u>	<u>Eqn.(23a)</u>
0.191		
0.189	0.194	0.197
0.183		

D. Evaluation of The Mean Film Thickness.

Determination of the film thickness is based solely on correlations of previous data, taken mainly from absorption towers. Two relations are recommended by Sherwood (15),

$$d/x = 0.023 \left(\frac{d G}{\mu} \right)^{0.83} \left(\frac{\mu}{\rho D} \right)^{0.44} \quad (26)$$

$$d/x = 0.023 \left(\frac{d G}{\mu} \right)^{0.8} \left(\frac{C_p \mu}{k} \right)^{0.4} \quad (27)$$

The Prandtl Number for Eqn. (27) may be estimated from an equation of McAdams (11),

$$N_{PR} = \frac{4}{9 - \frac{5C_v}{C_p}} \quad (28)$$

This expression has been evaluated for the range of concentrations involved, using thermal data from Millard (13) and Becco (1). The results are summarized in Table A-6.

Table A-6

<u>Prandtl Numbers</u>		
C^*	$f = 0$	$f = 1$
1	0.779	0.767
30	0.779	0.776

A mean value of 0.774 will be taken for the Prandtl Number.

Values of the viscosity are required for use of either equation. However, no data are available on the viscosity of peroxide vapor, and hence, because of the diluteness of the mixtures (80 mole percent water), the viscosity of the mixture is taken as equal to that of water vapor (10).

Properly, the term d/x should be included in the integral of Eqn. (16); the accuracy with which the film thickness may be predicted does not seem to warrant such refinement, and the use of a mean between the entrance and exit values will be employed.

E. Theoretical Diffusion Equation.

The final form of the theoretical equation for the case where the decomposition rate is controlled by the diffusion of the peroxide is,

$$Z = \frac{R m_0}{K \pi (d/x)} \left[\frac{2W + 3}{\sqrt{a + b}} \Delta \operatorname{tanh}^{-1} \sqrt{\frac{af + b}{a + b}} - \frac{1}{2a} \Delta \sqrt{af + b} \right]_{f_1}^{f_2} \quad (29)$$

$$W = 1.89 \frac{100 - C^*}{C^*} \quad (29a)$$

$$a = 0.0382 (C^*)^2 + 15.05 (C^*) \quad (29b)$$

$$b = T_0 - a f_1 \quad (29c)$$

where,

- C^* - Pseudo-feed, weight percent peroxide in the feed calculated on a basis of the downstream samples.
- d/x - Ratio of tube diameter to effective film thickness; predicted from Eqns. (26) or (27).
- f - Fraction decomposed of peroxide entering as feed; f_1 entering catalyst tube, f_2 leaving.
- K - Diffusivity constant, 4.45×10^{-5}
- m_0 - Rate of peroxide feed, gm.-moles/second.
- R - Gas constant, $82.06 \text{ cm}^3\text{-atm/g-mole-}^\circ\text{K}$.
- T_0 - Temperature of vapor stream entering catalyst tube, $^\circ\text{K}$.
- W - Molal ratio of water to peroxide in feed.
- Z - Length of catalyst tube, cm.
- π - Ratio of circumference to diameter, 3.14159-

SAMPLE CALCULATION OF DATA

The data obtained in Minute 41 of Run 39 are as follows:

Run 39:

Normality of KMnO_4 titrating solution	0.228 N.
Barometric pressure	29.84 in. Hg.
Feed: cc. KMnO_4 /cc. feed	56.2 cc./cc.

Minute 41:

Upstream Station

Volume of liquid collected in minute	4.4 cc.
KMnO_4 , cc./cc. sample	42.2 cc./cc.

Downstream Station

Volume of liquid collected in minute	18.0 cc.
KMnO_4 , cc./cc. sample	9.9 cc.

Gas Station

Wet test meter temperature	24.5 °C.
Gas rate	0.20 liters in 10.9 seconds

The following equations may be written,

$$\begin{aligned} \frac{\text{gms. H}_2\text{O}_2}{\text{cc. smple}} &= (\text{cc KMnO}_4)(N \text{ KMnO}_4) \left(\frac{1}{\text{cc smple}} \right) \left(\frac{\text{moles H}_2\text{O}_2}{\text{meq. H}_2\text{O}_2} \right) \left(\frac{\text{gms. H}_2\text{O}_2}{\text{mole H}_2\text{O}_2} \right) \\ &= \frac{\text{cc KMnO}_4}{\text{cc smple}} \times (N \text{ KMnO}_4) (1/2000) (34) \\ &= 0.0170 (\text{cc KMnO}_4/\text{cc smple})(N \text{ KMnO}_4) \end{aligned} \quad (30)$$

$$\text{Wt. \% H}_2\text{O}_2 = \frac{\text{gms. H}_2\text{O}_2}{\text{total gms}} = \frac{1}{P} (0.0170) \left(\frac{\text{cc KMnO}_4}{\text{cc smple}} \right) (N \text{ KMnO}_4) \quad (31)$$

The preceding equations may be employed to prepare the following table for the data:

STATION	VOLUME SAMPLE	$\frac{\text{cc KMnO}_4}{\text{cc smple}}$	$\frac{\text{cc} \times N}{\text{cc}}$	wt % H_2O_2	wt H_2O_2
Feed	---	56.2	12.80	20.3	---
Upstm	4.4	42.2	9.61	15.52	0.719 gms.
Dnstm	18.0	9.9	2.26	3.81	0.691

By dividing the grams of peroxide by weight fraction peroxide, the total weight of sample may be obtained, and the weight of water found by difference.

STATION	WT. H ₂ O ₂	TOTAL WT.	WT. H ₂ O
Upstm.	0.719 g.	4.63 g.	3.91 g.
Dnstm.	0.691	18.13	17.44

The peroxide equivalent to the oxygen rate is found by applying the following expression, noting that the vapor pressure of water at the wet test meter temperature is 0.91 in. Hg., and hence the partial pressure of oxygen is 29.84 - 0.91 in. Hg.

$$\frac{\text{g. H}_2\text{O}_2}{\text{minute}} \text{ equiv. to O}_2 = \frac{(\text{liters})}{(\text{second})} \frac{\text{sec. } 1}{\text{min. } 22.4} \frac{273}{298} \frac{29.84 - 0.91}{29.92} (2)(34)$$

$$= 161 \text{ (liters O}_2\text{/second)}$$

For Minute 41,

$$\frac{\text{g. H}_2\text{O}_2}{\text{minute}} \text{ equivalent to O}_2 = (161.4)(0.20/10.9) = 2.95 \text{ grams/minute}$$

$$\frac{\text{g. H}_2\text{O}}{\text{minute}} \text{ equivalent to O}_2 = (2.95)(18/34) = 1.56 \text{ grams/minute}$$

A water balance may be calculated to check the equilibrium conditions. From the known feed concentration and the oxygen rate, the water that should be in the liquid sample may be calculated, and compared with the water found by analysis.

The total peroxide will be (H₂O₂ in sample.) + (H₂O₂ equiv. to O₂)

$$\text{Total Peroxide} = 0.691 + 2.95 = 3.64 \text{ g./min.}$$

The water associated with this peroxide is,

$$\text{Assoc. water} = 3.64 (100 - 20.3)/(20.3) = 14.30 \text{ g./min.}$$

The water from decomposition, or water equivalent to oxygen, is,

$$\text{Decomp. water} = 1.56 \text{ g./min.,}$$

and the total water calculated is,

$$\text{Calc. total water} = 15.86 \text{ g./min.}$$

The water in the sample by analysis is,

$$\text{Actual total water} = 17.44 \text{ g./min.,}$$

or, the error in the water balance is,

$$\Delta \text{H}_2\text{O} = + 1.58 \text{ g./min.}, \text{ or } + 9\%.$$

This gain of water results from concentration of the feed in the boiler, the vapors generated not being the same strength as the feed liquid.

Due to this non-steady operation, it is convenient to define a "pseudo"-feed concentration, or the feed equivalent to the vapors actually evolved if no concentration or decomposition occurred in the process of vaporization.

$$C^* = \frac{3.64 (100)}{3.64 + (17.44 - 1.56)} = 18.61\%$$

The fraction NOT decomposed at the upstream station, F_1 , is given by the ratio of the peroxide in the sample taken to the total peroxide, or the peroxide in the pseudo-feed. However, calculations are to be based on the downstream data since no measurement of the upstream oxygen rate was made. The fraction NOT decomposed will be given by the ratio $(\text{H}_2\text{O}_2)_1/(\text{H}_2\text{O}_2)_0$, where the formula represents the weight in grams per minute, and the subscripts refer to the upstream and feed conditions, respectively. Since the reaction of one mole of peroxide forms one mole of water, the sum of the moles of water and peroxide must be fixed throughout the apparatus, and one may multiply the above ratio by the ratio of the sum of the moles of water and peroxide in the feed and in the upstream sample (the ratio being unity numerically), obtaining,

$$F_1 = \frac{1/18 (\text{H}_2\text{O})_0 + 1/34 (\text{H}_2\text{O}_2)_0}{1/18 (\text{H}_2\text{O})_1 + 1/34 (\text{H}_2\text{O}_2)_1} \times \frac{(\text{H}_2\text{O}_2)_1}{(\text{H}_2\text{O}_2)_0}$$

By rearrangement,

$$F_1 = \frac{(\text{H}_2\text{O}/\text{H}_2\text{O}_2)_0 + 0.53}{(\text{H}_2\text{O}/\text{H}_2\text{O}_2)_1 + 0.53} \quad (32)$$

Applying Eqn. (32) to the data at hand,

$$(H_2O/H_2O_2)_0 = (100 - 18.61)/(18.61) = 4.36$$

$$(H_2O/H_2O_2)_1 = (3.91)/(0.719) = 5.44$$

$$F_1 = (4.36 + 0.53)/(5.44 + 0.53) = 0.819$$

The fraction NOT decomposed at the downstream station, F_2 , is given by the ratio of peroxide in the liquid sample to the total peroxide, liquid peroxide plus peroxide equivalent to oxygen,

$$F_2 = (0.691)/(3.64) = 0.1900.$$

In terms of the fraction decomposed, f , the mole fraction peroxide is,

$$Y = \frac{2(1-f)}{2W+3+f},$$

on a basis of one mole of oxygen in the stream at total decomposition.

Transforming the equation into terms of the fraction NOT decomposed, values calculated above, the expression is obtained,

$$Y = \frac{2F}{2W+3-F} \quad (33)$$

where W , the molal ratio of water to peroxide, is the quantity previously termed $(H_2O/H_2O_2)_0$ multiplied by the ratio of molecular weights (34/18).

The mole fraction peroxide upstream is,

$$Y_1 = \frac{2(0.819)}{2(4.36)(34/18) + 3 - 0.819} = 0.0896,$$

and the mole fraction peroxide downstream,

$$Y_2 = \frac{2(0.1900)}{2(4.36)(34/18) + 3 - 0.1900} = 0.0197.$$

The values for Run 39.41 are then, recording in the manner followed in the Table of Data and Calculated Values at the end of this section,

<u>RUN</u>	<u>P₁</u>	<u>Z₁</u>	<u>P₂</u>	<u>Z₂</u>	<u>O₂</u>	<u>C*</u>	<u>F₁</u>	<u>F₂</u>
39.41	0.719	3.91	0.691	17.44	2.78	18.61	0.819	0.1900

The predicted tube length required for this degree of decomposition may now be calculated, employing Eqn. (29).

The term a is

$$a = (0.0382)(18.61)^2 + (15.05)(18.61) = 293$$

and, $af_1 = (293)(1 - 0.819) = 53.1$

$$af_2 = (293)(1 - 0.1900) = 237$$

From the Summary of Data, the upstream temperature is 306 °F; the assumption will be made that the superheat is lost through the insulation before the catalyst tube is reached. From Run 21 it is seen that the condensation temperature is 240 °F, or 389 °K. Consequently, $b^* = 389$. Subtracting the term af_1 to correct for boiler decomposition,

$$b = 336$$

$$a + b = 629$$

$$\sqrt{a + b} = 25.0$$

The final bulk temperature may be calculated as,

$$T_a = 237 + 336 = 577 \text{ °K} = 574 \text{ °F.}$$

The arithmetic average temperature of the bulk stream is 407 °F; the viscosity of water vapor at this temperature is (10) 1.60×10^{-4} gm./cm.sec. The total flow through the tube is $0.691 + 17.44 + 2.78$ or 20.9 gm./min; on the basis of a 1/4 inch tube, the Reynolds Number may be calculated as,

$$\begin{aligned} N_{Re} &= (1/4)(2.54)(20.9)/(\pi/4)(1/4 \times 2.54)^2(60)(1.60 \times 10^{-4}) \\ &= 4370 \end{aligned}$$

The d/x ratio becomes,

$$d/x = 0.023 (4370)^{0.8} (0.774)^{0.4} = 17.2$$

Evaluating the constants,

$$\frac{R m_0}{K \pi (d/x)} = \frac{(82.06) (3.61) / (60) (34)}{(4.45 \times 10^{-5}) (3.14) (17.2)} = 60.4$$

$$\frac{2W + 3}{\sqrt{a + b}} = \frac{(2)(4.36)(34/18) + 3}{25.0} = 0.780$$

Eqn. (29) then becomes,

$$Z = 60.4 \left[0.780 \Delta \tanh^{-1} \frac{\sqrt{293 f + 336}}{25.0} - \frac{1}{586} \Delta \sqrt{293 f + 336} \right] \begin{matrix} f_2 = 0.810 \\ f_1 = 0.181 \end{matrix}$$

Evaluating the function,

$$\begin{aligned} Z &= 40.4 \text{ cm.} \\ &= 15.9 \text{ inch.} \end{aligned}$$

The theoretical diffusion equation then predicts a catalyst tube length of 15.9 inches, compared to an actual length of 24 inches,

$$\Delta = 24/15.9 = 1.5.$$

CALCULATION OF PROFILES ALONG CATALYST TUBE

(Preparation of Figures VI, VII)

1. Adiabatic Bulk Stream Temperature Distribution.

The theoretical equation, Eqn. (A-29), and previous correlations of Isbin (7), (9) indicate that the fraction not decomposed is linear in the length of catalyst tube within a small error; the accuracy of this approach may be seen by inspection of Figure III. Knowing the fractions not decomposed at the upstream and downstream stations, one may find the fraction not decomposed at any intermediate tube length by linear interpolation, assuming the data follow this predicted relation. The adiabatic decomposition temperature at any length may then be found through use of Eqn. (A-22).

2. Distribution of Heat Losses Along Catalyst Tube.

Preliminary design calculations on the heat loss through the insulation indicated that the heat loss should be small; however, the disagreement between the adiabatic decomposition temperature and the final bulk temperature, even after improvements in the thermocouple technique, shows that the heat loss encountered is appreciable. Run 19.52 will be taken as illustrative.

The data of this run will be repeated here for convenience:

Entrance temperature	242 °F.
Exit temperature	340
First wall temperature	478
Last wall temperature	414

The heat loss from the upstream thermometer to the final bulk temperature position may be found by an enthalpy balance, datum 242 °F. Letting the total heat loss be Q , the enthalpy H , and the heat of decomposition ΔH_r ,

$$Q = H_1 - H_2 + \Delta H_r$$

The grams of peroxide decomposed in the tube in the minute will be difference between the peroxide entering the tube and leaving,

Data:

Fraction not decomposed upstream	0.763
Fraction not decomposed downstream	0.308
Peroxide collected downstream	1.14 gms./min.

The peroxide decomposed is,

$$\Delta m = 1.14 (0.763/0.308) - 1.14 = 1.68 \text{ gm./min.}$$

The heat of decomposition at 242 °F. is 710 cal./gm., and hence the heat release is,

$$\Delta H_p = (710)(1.68) = 1190 \text{ cal./min.}$$

The increase in heat content of the stream must now be computed. The required thermal data may be obtained from Ref. (1), (10), (13).

Component	Grams	C_p 340 °F	C_p 242 °F	C_p ave.	NC_p
H ₂ O ₂	1.14	0.309 cal/g°K	0.288 cal/g°K	0.30	0.342
H ₂ O	20.9	(1211.7)*	(1165.0)*		
O ₂	1.20	0.311	0.289	0.30	0.360
					0.702

(*- Enthalpies.)

$$\begin{aligned} H_2 &= (0.702)(340 - 242)(1.8) + (20.9)(1/1.8)(1211.7 - 1165.0) \\ &= 666 \text{ cal./min.} \end{aligned}$$

The heat balance is then,

$$Q = 1190 - 666 = 524 \text{ cal./min. heat loss.}$$

By assuming the following data,

Length, upstream thermometer to tube	18 in.
Diameter of glass tube	0.25 in.
Diameter of insulated glass tube	3 in.
Bulk temperature	242 °F.
Temperature, outside insulation	74 °F.
Thermal conductivity, glass wool	0.024 Btu./((hr.)(ft.²))($\frac{°F}{ft}$)

the heat loss in the section before the catalyst tube may be calculated as 58.5 cal./min.:

$$\text{Area}_1 = (3.14)(0.25)(18) = 10.2 \text{ in.}^2$$

$$A_2 = (3.14)(3)(18) = 170 \text{ in.}^2$$

$$A_{\text{mean}} = (170 - 10.2)/\ln(170/10.2) = 56.7 \text{ in.}^2$$

$$Q = k A_m \Delta T / \Delta x$$

$$= (0.024)(56.7)(1/12)(168/1.37)(1/60) = 58.5 \text{ cal./min.}$$

Since this heat loss will result in partial condensation of the stream, heat will be taken from the heat of decomposition to evaporate this condensate. Hence, the total heat loss from the bulk stream will be 2(58.5) or 117 cal./min. loss in sensible heat. The assumptions employed in the calculation limit this figure to an estimate, but more rigorous consideration does not seem warranted by the data.

(A calculation of interest is the amount of condensate. Taking a figure of 970 Btu./lb. for the heat of condensation, the condensate is,

$$(58.5) / \left(\frac{970}{1.8} \right) = 0.109 \text{ grams/minute out of 23.2 total.}$$

The following table may then be prepared for the tube heat losses,

Total heat loss	524 cal./min
Lost up to tube	58.5
Lost from tube	<u>465.5</u>
Lost in evaporation	58.5
Insulation losses of tube	<u>407 cal./min.</u>

This insulation loss is now to be distributed along the tube length. Assuming the outside of the insulation is at 78 °F. (later data indicate that it is probably higher), and that the heat transfer coefficient is independent of temperature, the equation may be written,

$$Q = h_o A \Delta T_m = h L \frac{478 - T_w}{\ln(400)/(T_w - 78)}$$

At L = 24 inches, T_w = 414 °F, or ΔT_m = 368 °F. Consequently,

$$h = (407)/(24)(368) = 0.0460 \text{ cal./min.-in.-}^\circ\text{F.}$$

$$\text{or, } Q = 0.0460 L \frac{478 - T_w}{\ln(400)/(T_w - 78)} .$$

The procedure is then to choose a tube length L , obtain T_w from the profile given in Figure V, and compute the heat lost through the insulation up to that point from the above equation. The losses are summarized below:

<u>Tube Length, inches</u>	<u>Insulation Heat Loss, cal./min.</u>
8	143
14	247
19	328
24	406

When plotted, these values of heat loss are not linear in tube length, although almost so. At 24 inches, a line through the origin would pass through a mean of the points to indicate 420, as compared to 406 read from the curve. If the insulation loss is closely linear in length, then it cannot be linear in the fraction not decomposed, for that is linear in e raised to the exponent tube length. Consequently, any correction of the adiabatic bulk temperature equation, Eqn. (A-22), for heat loss becomes a complex function of tube length and wall temperature. The computation may be made for this case as outlined below, noting that the heat capacity of the stream may be calculated as 7.34 cal./min.-°F. from previous data,

<u>L</u>	<u>T_{adiab}</u>	<u>Q_{insul}</u>	<u>ΣQ</u>	<u>ΔT</u>	<u>T_{bulk}</u>	<u>Notes</u>
0	242	0	58.5	0	242	Two-phase stream
3	272	53	170	23.2	249	Evap. of condensate
8	326	143	260	35.6	290	
14	380	247	364	49.7	330	
19	415	328	445	60.6	354	
24	432	406	523	71.4	360	

Figure VI presents a plot of T_{bulk} vs. L .

3. Comparison of Potentials, ΔY vs. ΔT

A plot of the mole fraction peroxide in the bulk stream vs. the temperature difference, catalyst surface to (adiabatic) bulk stream. In Section (1) of this discussion, a method of calculating the fraction not decomposed at intermediate tube lengths was developed. The corresponding mole fraction may then be calculated from Eqn. (A-33). The plot should more properly be based on the actual bulk temperature, but lack of accurate data on insulation surface temperatures makes this refinement unnecessary.

4. Comparison of Actual And Predicted Heat Transfer.

The heat actually transferred may be found by the amount of peroxide decomposed and the heat of reaction, as was done in Section (1) above, employing the intermediate fractions not decomposed as before.

The predicted heat transfer is computed by treating the catalyst tube as a heat exchanger,

$$Q = h A \Delta T_m \quad (34)$$

the heat transfer coefficient, h , being predicted from a relation of McAdams (11) already cited,

$$\frac{d}{x} = \frac{h d}{k} = 0.023 \left(\frac{d G}{\mu} \right)^{0.8} \left(\frac{C_p \mu}{k} \right)^{0.4}, \quad (27)$$

and discussed under the derivation of the theoretical equation.

The thermal conductivity may be eliminated from the term hd/k by dividing the expression by the product of the Reynolds and Prandtl Numbers,

$$\frac{h}{G C_p} = 0.023 (d G / \mu)^{-0.2} (G_p \mu / k)^{-0.6} \quad (27a)$$

The predicted heat transfer may then be calculated by computing the value of h , and substituting h , the heat transfer area corresponding to a given tube length, and the mean temperature difference into Eqn. (A-34). Since the bulk temperature corrected for heat loss was computed for Run 19.52 only, the difference between the wall temperature and the adiabatic bulk temperature is used as an approximation.

The calculation results are summarized below.

Table A-7:

ACTUAL AND PREDICTED HEAT TRANSFER, Btu./min.

RUN	(1) Tube length of 10 inches.		(2) Tube length of 16 inches	
	Q_{actual}	$Q_{\text{predicted}}$	Q_{actual}	$Q_{\text{predicted}}$
19	5.14	3.08	6.14	3.43
20	6.18	4.47	7.55	6.47
21	5.37	4.29	6.78	5.79
22	3.76	2.03	4.69	2.14
23	5.80	3.85	7.40	6.45
24	5.79	6.40	8.05	6.90

Table A-8:

EFFECT OF TEMPERATURE DIFFERENCE ON
PREDICTED AND ACTUAL HEAT TRANSFER.

<u>L</u>	<u>RUN</u>	<u>$(T_w - T_{\text{gas}})_{\text{ln mean}}$</u>	<u>RATIO: $Q_{\text{predicted}}/Q_{\text{actual}}$</u>
10 in.	19	162 °F.	0.600
	20	237	0.724
	21	224	0.800
	22	94.9	0.540
	23	188	0.664
	24	284	1.10
16	19	113	0.570
	20	214	0.857
	21	189	0.854
	22	69	0.456
	23	196	0.873
	24	201	0.856

ERROR ANALYSIS1. Experimental Data.

(a) Grams of peroxide per minute collected as liquid samples.

From Eqn. (A-30),

$$\frac{\text{gms. H}_2\text{O}_2}{\text{minute}} = 0.0170(\text{cc. KMnO}_4)(N \text{ KMnO}_4)(1/\text{cc sample})(\text{Volume sample}/\text{min.})$$

By differentiating the function, dividing by the function, and approximating differentials by a finite error, the error expression becomes,

$$\Delta m/m = \Delta(\text{cc KMnO}_4)/(\text{cc KMnO}_4) + \Delta(N)/(N) + \Delta(1/\text{cc})/(1/\text{cc}) + \Delta V/V.$$

The data of Run 39.41 will be used as representative,

Upstream:	Downstream:
$\Delta(\text{cc KMnO}_4)/(\text{cc KMnO}_4) = 0.1/42.2 = 0.00237$	$= 0.1/10 = 0.01$
$\Delta(N)/(N) = 0.0005/0.228 = 0.00219$	$= 0.00219$
$\Delta(1/\text{cc})/(1/\text{cc}) = 0.005/1.00 = 0.00500$	$= 0.00500$
$\Delta(V)/(V) = 0.1/4.4 = 0.0227$	$= 0.1/18.0 = 0.00555$
	0.02274
	0.03216

The error in the grams of peroxide collected is 3.2% upstream and 2.2% downstream.

(b) Weight percent peroxide, Eqn. (31).

$$\begin{aligned} \Delta(\text{wt.}\%)/(\text{wt.}\%) &= \Delta(1/\rho)/(1/\rho) + \Delta(\text{cc KMnO}_4)/(\text{cc KMnO}_4) + \Delta(1/\text{cc})/(1/\text{cc}) \\ &\quad + \Delta(N)/(N). \\ &= 0.001 + 0.01 + 0.005 + 0.002 = \\ &= 0.018 \end{aligned}$$

(c) Weight of water.

$$\begin{aligned} \Delta(\text{total weight})/(\text{total weight}) &= \Delta(\text{H}_2\text{O}_2)/(\text{H}_2\text{O}_2) \pm \Delta(\text{wt.}\%)/(\text{wt.}\%) \\ &= 0.032 + 0.018 \\ &= 0.050 \end{aligned}$$

$$\frac{\Delta(\text{wt. H}_2\text{O})}{(\text{wt. H}_2\text{O})} = \frac{\Delta(\text{total wt.}) \pm \Delta(\text{wt. H}_2\text{O}_2)}{(\text{total wt.}) \pm (\text{wt. H}_2\text{O}_2)} = \frac{(0.050)(27) + 0.03}{27 - 1} = 0.052$$

(c) Gas Analysis.

The error from the wet test meter readings is approximately,

$$\frac{\Delta O_2}{O_2} = \frac{\Delta(\text{liters/sec})}{(\text{liters/sec.})} = \frac{\Delta(\text{liters})}{(\text{liters})} \pm \frac{\Delta(\text{seconds})}{(\text{seconds})} .$$

The wet test meter may be read to 0.01 l., and the stop watch error is approximately 0.2 second:

$$\Delta O_2/O_2 = 0.01/0.20 + 0.20/10.9 = 0.028.$$

(d) Summary.

The error in the experimental data has been shown to be -

Peroxide in liquid samples	3.2% upstm., 2.3% dwnstm.
Water in liquid samples	5.2%
Oxygen rate	2.8%

The accuracy of the titration of peroxide with permanganate from a chemical viewpoint need not be considered, since Huckaba and Keyes (5) have shown the chemical error to be 1 part in 5000.

The experimental data are accurate, then, from 3 to 5%, and are adequate for the present purpose. The major source of error in this work lies not in the measurement of data but rather in experimental difficulties with pressure surges and heat loss.

2. Theoretical Diffusion Equation, Eqn. (A-29).

Granting the correctness of the assumptions made in the derivation, the major source of error in the theoretical equation will be the evaluation of the term d/x . Both the Sherwood and McAdams equations are empirical in nature, representing the best curves through data points. These equations may be in error by as much as 30% under normal conditions, and the accuracy is questionable in the present case where a large temperature difference exists.

AXIAL HEAT TRANSFER IN CATALYST WALLS.

If there is heat transfer by conduction along the silver tube, then the decomposition will not be adiabatic at a given point. It is desired to calculate the magnitude of the heat conduction under conditions representative of conditions during a run.

Data:

Temperature potential along tube wall:	60 °F.
Thermal conductivity of silver (212°F)	238 Btu/(hr.)(ft ²)(°F/ft.)
Length of tube	2 ft.
Inside diameter of tube	0.25 in.
Wall thickness of tube	0.010 in.

$$\begin{aligned} \text{Area of heat flow} &= 1/4 \pi d_2^2 - 1/4 \pi d_1^2 = 1/4 \pi (d_2 + d_1)(d_2 - d_1) \\ &= \pi/4 (0.51/12)(0.01/12) \text{ ft.}^2 \end{aligned}$$

$$Q_{\text{tube}} = k A \Delta T / \Delta x = (238)(\pi/4)(0.51/12)(0.01/12)(60/2) = 0.2 \text{ Btu./hr.}$$

For comparison, the heat content of the gas stream may be estimated by assuming an entrance temperature of 212 °F., an exit temperature of 400 °F., and employ^{ing} the enthalpy of steam as an approximation:

$$\begin{aligned} h_{\text{H}_2\text{O}} \quad 400 \text{ °F} &= 1240 \text{ Btu./lb.} \\ h_{\text{H}_2\text{O}} \quad 212 \text{ °F} &= 1150 \\ \Delta h &= 90 \text{ Btu./lb.} \end{aligned}$$

If a representative flow rate of 27 gas./min. is taken,

$$Q_{\text{gas}} = (27 \times 60/454)(90) = 322 \text{ Btu./hr.}$$

The ratio of the heat conduction along the tube to the increase in heat content of the gas stream is,

$$Q_{\text{tube}} / Q_{\text{gas}} = 0.2/322 = 0.00062, \text{ or, } 0.062\%$$

Axial conduction of heat is therefore small.

SUMMARY OF DATA AND CALCULATED VALUESI. DECOMPOSITION DATA

The following symbols are employed:

- RUN - Data based on one minute samples taken during run.
 P - Peroxide collected in liquid samples, gms./minute; P_1 at upstream station, P_2 at downstream station.
 Z - Water collected in liquid samples, gms./minute; Z_1 at upstream station, Z_2 at downstream station.
 O_2 - Oxygen rate, gms./minute, as observed at downstream wet test meter.
 C* - Pseudo-feed, weight percent peroxide.
 F - Fraction NOT decomposed of peroxide in feed, F_1 upstream, F_2 downstream.

<u>RUN</u>	<u>FEED CONC</u>	<u>P₁</u>	<u>Z₁</u>	<u>P₂</u>	<u>Z₂</u>	<u>O₂</u>	<u>C*</u>	<u>F₁</u>	<u>F₂</u>
19.49	18.6	0.52	3.65	1.20	21.40	2.51	16.2	0.758	0.308
50		0.51	3.55	1.11	20.29	2.61	16.3	.720	.28.6
51		0.46	3.49	1.10	20.60	2.57	16.6	.682	.288
52		0.50	3.55	1.14	20.88	2.41	15.9	.763	.308
53		0.50	3.67	1.09	20.81	2.53	16.3	.721	.288
54		0.51	3.54	1.08	21.02	2.45	15.1	.823	.293
55		0.53	3.54	1.29	23.11	2.53	16.1	.964	.324
20.24	20.17	0.48	2.67	1.32	21.06	3.02	18.9	0.791	0.292
25		0.53	3.13	1.31	21.11	2.88	18.7	.760	.294
26		0.53	2.93	1.24	20.52	3.02	18.9	.785	.279
27		0.56	2.86	1.27	21.03	3.00	18.7	.846	.285
28		0.55	2.85	1.28	20.11	3.02	19.5	.814	.285
29		0.44	2.52	1.20	20.60	3.04	19.0	.767	.271
30		0.59	3.09	1.22	20.96	3.13	19.1	.826	.269
31		0.46	2.60	1.22	20.68	3.04	18.9	.779	.274
32		0.47	2.91	1.29	21.86	3.14	18.6	.731	.281
33		0.50	2.70	1.23	20.27	3.00	19.1	.800	.279
21.35	20.3	0.712	3.62	1.57	21.27	2.75	18.5	0.877	0.350
36		0.691	3.74	1.47	20.42	2.75	18.9	.816	.335
37		0.714	3.72	1.46	20.95	2.86	18.9	.844	.325
38		0.699	3.76	1.45	20.79	2.90	19.1	.807	.320
39		0.703	3.77	1.43	20.52	2.75	18.7	.834	.329
40		0.698	3.83	1.38	20.02	2.86	19.3	.782	.312
41		0.719	3.81	1.40	20.58	2.86	18.9	.814	.316
22.46	14.9	0.293	2.27	1.32	22.08	1.78	13.2	0.856	0.412
47		0.336	2.92	1.32	21.68	1.78	13.4	.849	.412
48		0.297	2.31	1.32	21.73	1.85	13.1	.860	.422
49		0.282	2.42	1.37	23.03	1.89	13.3	.775	.405
50		0.306	2.49	1.31	21.89	1.87	13.6	.792	.399
51		0.298	2.39	1.30	21.83	1.87	13.1	.835	.404
52		0.285	2.30	1.23	21.87	1.89	13.4	.810	.380

RUN	FEED		P ₁	Z ₁	P ₂	Z ₂	O ₂	C*	F ₁	F ₂	
	CONC										
23.07	20.80		1.00	4.62	1.46	22.14	3.09	18.9	0.939	0.309	
8			0.94	4.67	1.53	22.57	3.00	18.5	.904	.324	
9			0.95	4.67	1.44	22.36	2.86	17.7	.947	.321	
10			0.85	4.23	1.41	22.01	3.64	20.8	.783	.268	
11			0.89	4.61	1.46	22.44	3.00	18.3	.962	.314	
12			0.84	4.26	-	-	-	-	-	-	
13			0.98	4.95	1.44	22.26	2.94	18.1	.909	.317	
14			0.82	4.25	1.42	22.23	2.90	18.0	.890	.315	
15			0.95	4.55	1.48	22.42	3.04	18.5	.851	.314	
16			0.80	3.78	1.43	22.27	2.86	17.8	.977	.319	
24.57		20.84		1.10	4.75	1.36	22.54	3.41	19.4	0.944	0.272
58				1.06	4.69	1.34	22.16	3.35	19.5	0.950	.273
59				1.06	4.69	1.34	22.16	3.333	19.4	0.950	.274
60				1.10	4.67	1.39	23.01	3.28	18.7	1.02	.285
61				1.08	4.68	1.33	22.07	3.41	19.7	0.944	.269
62				1.16	4.73	1.35	22.15	3.30	19.3	1.02	.278
63			1.13	4.84	1.35	22.15	3.46	19.9	0.950	.269	
64			1.06	4.71	1.33	21.83	3.48	20.2	0.900	.264	
65			1.10	4.66	1.33	21.83	3.35	20.0	0.950	.267	
66			1.11	4.75	1.31	22.99	3.33	18.7	1.018	.270	
67			1.10	4.75	1.37	22.73	3.41	19.4	0.973	.274	
68			1.14	4.83	1.39	23.31	3.29	18.9	1.010	.279	
25.23(A)	10.1		0.442	4.32	0.994	24.8	1.67	10.34	0.889	0.360	
24			0.985	4.15	0.938	24.5	1.67	10.20	1.017	.346	
25			0.441	4.16	0.985	24.6	1.71	10.69	0.889	.349	
26			0.424	4.14	0.941	23.5	1.67	10.70	.864	.348	
27			0.436	4.23	0.890	24.3	1.67	10.18	.911	.333	
28			0.446	4.13	0.894	23.9	1.62	10.18	.956	.342	
25.38(B)		10.1		1.746	17.95	0.388	9.62	0.607	10.00	0.877	0.375
39			1.780	18.04	0.369	9.08	0.600	10.31	.866	.368	
40			1.631	15.60	0.452	10.00	0.613	10.30	.859	.409	
41			1.595	15.62	0.319	8.29	0.607	10.80	.850	.331	
42			1.790	18.12	0.578	13.09	0.584	8.70	1.031	.484 (?)	
43			1.804	18.10	0.424	9.88	0.641	10.39	0.870	.384	
26.21	5.10		0.296	6.27	0.589	26.6	0.825	5.29	0.848	0.403	
22			0.293	6.17	0.590	26.8	0.770	5.07	.915	.418	
23			0.277	5.97	0.557	25.7	0.744	5.08	.873	.413	
24			0.298	6.16	0.556	25.3	0.744	5.42	.896	.413	
25			0.297	6.28	0.575	25.4	0.752	5.39	.868	.420	
26			0.313	6.24	0.564	25.5	0.752	5.41	.927	.414	
27			0.288	6.07	0.559	25.3	0.785	5.29	.854	.401	
28			0.298	6.06	0.559	25.3	0.806	5.36	.870	.396	
29			0.294	6.36	0.585	25.6	0.775	5.30	.835	.415	
30			0.277	5.98	0.534	25.0	0.721	5.02	.881	.410	

RUN	FEED		P ₁	Z ₁	P ₂	Z ₂	O ₂	C*	F ₁	F ₂
	CONC									
27.41	9.69		0.74	7.05	1.11	23.94	1.37	9.63	0.951	0.432
42			0.69	7.18	1.09	23.49	1.37	10.05	.861	.426
43			0.66	7.08	1.10	23.70	1.44	10.30	.812	.418
44			0.71	6.87	1.12	23.22	1.37	10.20	.906	.419
45			0.71	7.16	1.07	23.87	1.35	9.77	.920	.428
46			0.71	7.07	1.13	23.79	1.39	10.20	.889	.437
47			0.68	6.97	1.09	23.49	1.41	10.20	.867	.422
48			0.72	7.05	1.09	23.49	1.37	10.08	.911	.427
49			0.70	7.17	1.11	23.79	1.46	10.38	.854	.417
50			0.72	7.05	1.08	23.82	1.41	10.08	.914	.418
28.25	14.75		0.535	3.62	1.734	23.5	1.88	14.2	0.925	0.466
26			0.625	3.87	1.712	23.4	1.94	14.5	.960	.455
27			0.597	3.74	1.760	23.3	1.90	14.5	.944	.466
28			0.550	3.63	1.700	22.9	1.95	14.7	.889	.451
29			0.539	3.53	1.751	23.3	1.91	14.5	.907	.464
30			0.601	3.90	1.748	23.5	1.96	14.6	.911	.456
31			0.624	3.79	1.696	23.2	1.94	14.5	.972	.451
32			0.564	3.63	1.760	23.2	1.91	14.6	.913	.464
29.10	19.73		0.828	3.74	2.200	23.0	2.71	19.1	0.945	0.434
11			0.892	4.10	2.265	23.8	2.69	18.7	.954	.444
12			0.899	3.79	2.001	21.4	2.72	19.8	.964	.408
13			0.803	3.86	2.090	22.1	2.79	19.8	.860	.413
14			0.785	3.67	2.335	24.4	2.71	18.6	.946	.448
15			0.805	3.91	1.930	20.8	2.80	20.3	.915	.394
39.39	20.30		0.816	4.25	0.712	17.98	2.94	19.05	0.836	0.1859
40			0.795	4.16	0.712	17.98	2.78	18.21	.870	.1945
41			0.719	3.91	0.691	17.44	2.78	18.61	.819	.1900
42			0.795	4.16	0.709	18.10	2.91	18.74	.845	.1874
43			0.832	4.44	0.690	17.63	2.91	19.13	.814	.1826
44			0.735	4.11	0.687	17.53	2.94	19.36	.765	.1805
40.56	10.44		0.320	4.78	0.263	18.64	1.62	10.02	0.631	0.1329
57			0.352	4.88	0.268	18.23	1.64	10.40	0.634	.1332
58			0.310	4.62	0.271	18.28	1.56	9.98	.620	.1405
59			0.310	4.69	0.264	17.96	1.55	10.05	.606	.1382
60			0.347	4.76	0.273	18.42	1.54	9.83	.681	.1430
61			0.316	4.78	0.279	19.64	1.83	10.07	.570	.1259
62			0.334	4.79	0.274	19.23	1.61	9.76	.658	.1384
63			0.318	4.74	0.274	19.23	1.48	9.07	.683	.1490
64			0.308	4.69	0.266	18.59	1.62	10.11	.597	.1338
100			0.279	4.00	0.262	17.06	1.51	10.03	.624	.1409
41.42	35.25		4.56	9.45	0.926	12.87	4.44	35.15	0.912	0.1644
43			4.64	9.40	0.918	12.38	4.44	36.2	.895	.1630
44			3.80	10.21	0.856	12.25	4.69	37.8	.678	.1469
45			4.79	9.51	0.878	12.73	4.44	35.3	.937	.1571
46			4.53	9.18	0.818	12.06	4.60	37.5	.859	.1435
47			4.65	9.37	0.812	11.97	4.48	37.1	.875	.1455
48			4.65	9.37	0.812	11.98	4.44	36.7	.886	.1471
49			4.63	9.53	0.800	12.31	4.63	37.0	.861	.1400
50			4.61	9.45	0.782	12.46	4.44	35.5	.907	.1424
51			4.66	9.46	0.775	12.25	4.69	37.4	.860	.1346

II. MOLE FRACTION HYDROGEN PEROXIDE

Y₁ - Entering catalyst tube.Y₂ - Leaving catalyst tube.

RUN	Y ₁	Y ₂	RUN	Y ₁	Y ₂
19.49	0.0698	0.0277	24.59	0.107	0.0298
50	.0661	.0257	60	.111	.0298
51	.0640	.0266	61	.108	.0297
52	.0684	.0272	62	.115	.0302
53	.0665	.0261	63	.110	.0304
54	.0704	.0244	64	.106	.0300
55	.0846	.0281	65	.108	.0293
			66	.110	.0283
20.24	0.0856	0.0306	67	.104	.0298
25	.0810	.0308	68	.111	.0296
26	.0850	.0310			
27	.0910	.0298	25.23	0.0509	0.0203
28	.0877	.0299	A 24	.0576	.0193
29	.0836	.0287	25	.0528	.0204
30	.0965	.0297	26	.0514	.0203
31	.0846	.0289	27	.0514	.0185
32	.0776	.0292	28	.0286	.0189
33	.0880	.0298			
			25.38	0.0486	0.0205
21.35	0.0935	0.0362	B 39	.0495	.0208
36	.0885	.0355	40	.0491	.0229
37	.0917	.0343	41	.0509	.0195
38	.0885	.0341	42	.0644	.0298 (?)
39	.0896	.0345	43	.0500	.0218
40	.0868	.0337			
41	.0885	.0334	26.21	0.0247	0.0117
			22	.0252	.0114
22.46	0.0636	0.0229	23	.0241	.0113
47	.0639	.0304	24	.0263	.0120
48	.0634	.0305	25	.0253	.0121
49	.0576	.0298	26	.0271	.0120
50	.0608	.0300	27	.0244	.0114
51	.0613	.0292	28	.0253	.0114
52	.0610	.0282	29	.0239	.0118
			30	.0239	.0111
23.07	0.103	0.0327			
8	.0966	.0335	27.41	0.0524	0.0247
9	.0965	.0316	42	.0512	.0244
10	.0941	.0314	43	.0463	.0236
11	.102	.0321	44	.0511	.0233
12	.0946	.0320	45	.0519	.0252
13	.0920	.0317	46	.0504	.0244
14	.0880	.0324	47	.0490	.0235
15	.1005	.0316	48	.0508	.0234
			49	.0490	.0236
24.57	0.106	0.0295	50	.0510	.0232
58	0.107	0.0299			

<u>RUN</u>	<u>Y₁</u>	<u>Y₂</u>	<u>RUN</u>	<u>Y₁</u>	<u>Y₂</u>
28.25	0.0743	0.0368	40.56	0.0348	0.00723
26	.0790	.0366	57	.0362	.00754
27	.0775	.0366	58	.0340	.00765
28	.0743	.0368	59	.0335	.00759
29	.0743	.0374	60	.0368	.00806
30	.0754	.0371	61	.0334	.00731
31	.0796	.0363	62	.0353	.00735
32	.0755	.0377	63	.0341	.00736
29.10	0.0959	0.0430	64	.0332	.00739
11	.1025	.0465	100	.0352	.00790
12	.1112	.0456	41.42	0.202	0.0336
13	.0989	.0462	43	.205	.0344
14	.1072	.0470	44	.159	.0323
15	.1077	.0451	45	.208	.0322
39.39	0.0916	0.0198	46	.204	.0314
40	.0910	.0198	47	.205	.0314
41	.0880	.0200	48	.206	.0314
42	.0861	.0196	49	.201	.0302
43	.0895	.0196	50	.203	.0294
44	.0853	.0197	51	.203	.0293

III. TEMPERATURE DATA

T_0 - Temperature indicated by upstream thermometer, 17.5 inches from beginning of catalyst tube; T_0^* , superheated.

T_w - The surface temperature of the tube indicated by thermocouples located as follows,

<u>Number</u>	<u>Inches Downstream</u>
1	1
2	3
3	10
4	16
5	22

T_2 - Temperature of bulk stream 1 inch below end of catalyst tube.

T_a - Adiabatic decomposition temperature for the fractional decomposition obtained, based on T_0 ; T_a^+ based on estimated temperature at beginning of catalyst tube.

-----Temperature, °F.-----										
RUN	FEED CONC	Cat. Surface Temperature:								
		T_0	1	2	3	4	5	T_2	T_a	T_a^+
19	18.6	236	498	498	468	459	435	358	444	
20	20.2	240	580	586	545	550	519	435	515	
21	20.3	240	583	591	540	536	510	424	509	
22	14.9	235	383	395	400	405	392	287	396	
23	20.8	242	565	592	578	582	557	455	525	
24	20.8	247	697	685	680	633	637	526	630	
25A	10.1	234	424	417	415	392	395	341	395	
25B	10.1	234	380	367	347	327	323	287	390	
26	5.1	225	287	283	290	282	293	259	290	
27	9.7	231	305	305	295	336	390	319	374	
28	14.7	236	326	332	416	452	491	392	422	
29	19.7	247	358	352	533	568	607	479	507	
37	0	361*	315	301	304	298	286	307	361	361
39	20.3	306*	614	630	616	605	577	532	640	574
40A	10.4	310*	413	423	410	403	381	381	451	380
40B	10.4	422*	461	476	457	450	427	440	557	481
41	35.3	310*	915	1000	926	895	866	840	1110	1020

LOCATION OF ORIGINAL DATA

The original data book and computations based on the data have been deposited with the Hydrogen Peroxide Laboratory, Massachusetts Institute of Technology (D.I.C. 6552).

NOMENCLATURE

- A Catalyst surface area, cm.^2 ; A_D , area available for mass transfer, A_H , available for heat transfer.
- a Temperature coefficient, defined by Eqn. (A-22).
- a Peroxide equivalent to oxygen measured by wet test meter, gms.
- b Defined by Eqn. (A-22).
- C_p Molar heat capacity at constant pressure, $\text{cal.}/(\text{g.mol})(^\circ\text{K.})$
- C_v Molar heat capacity at constant volume, $\text{cal.}/(\text{g.mol.})(^\circ\text{K.})$
- C Concentration of peroxide in liquid feed, weight percent; C^* , concentration of pseudo-feed.
- d Tube diameter, cm.
- D Diffusivity, $\text{cm.}^2/\text{sec.}$; D_{AB} , the diffusivity of A in diffusion through B; D_m , the mean diffusivity of A in a complex system; D_T , thermal diffusivity.
- f Fraction decomposed of peroxide entering as liquid feed; f_1 , entering catalyst tube; f_2 , leaving catalyst tube.
- F Fraction not decomposed, $F = 1 - f$.
- G Mass rate of flow, $\text{g.-mol.}/(\text{cm.}^2)(\text{sec.})$
- H_p Heat of decomposition of peroxide.
- h Enthalpy, $\text{cal}/\text{g.-mol.}$
- h Local coefficient of heat transfer, $\text{Btu.}/(\text{ft.}^2)(\text{hr.})(^\circ\text{F.})$
- K Diffusional constant, defined by Eqn. (A-6).
- k_G Local coefficient of mass transfer, $\text{lb.-mol.}/(\text{ft.}^2)(\text{hr.})(\text{atm.})$
- L Axial length of catalyst tube, experimental quantity, inches.
- ln Natural logarithm.
- M Molecular weight.
- m Rate of flow of peroxide, $\text{g.-mol.}/\text{sec.}$; m_1 entering tube.

- N Rate of diffusion of peroxide, g.-mol./ $(\text{cm}^2)(\text{sec.})$
- n Rate of diffusion of peroxide, g.-mol./sec.
- P Peroxide in liquid samples, experimental quantity, gms./min.
- P Partial pressure, atm.
- Q Heat loss, cal. or Btu./min.
- R Gas Constant, $82.06 (\text{cm}^3)(\text{atm.})/(\text{g.-mol.})(^\circ\text{K.})$
- T Temperature, $^\circ\text{K.}$; T_b , boiling temperature; T_o , temperature of stream at entrance to catalyst tube; T_w and T_B , $^\circ\text{F.}$, temperature of catalyst surface and bulk stream respectively.
- V Atomic volume.
- v Convection velocity, Eqn. (1).
- W Molar ratio of water to peroxide in pseudo-feed.
- X Water equivalent to oxygen measured by wet test meter, gms./min.
- x Effective film thickness, cm.
- Z Water collected as liquid sample, experimental quantity, gms./min.
- Z Predicted axial length of reaction tube, cm.
-
- δ Change in total moles per mole of peroxide reacted.
- Δ Difference
- μ Viscosity
- π Total pressure, atm.; 314159-
- ρ Density
- Σ Summation

Subscripts

- A Component A, hydrogen peroxide.
- B Component B, water.
- C Component C, oxygen.

- m Mean value.
- o Condition in feed; condition at zero decomposition of peroxide.
- 1 Condition in bulk stream; condition at entrance to silver tube.
- 2 Condition at catalyst surface; condition leaving silver tube.

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