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AND REFLECTED SHOCK WAVES.

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THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR AT ELEVATED TEMPERATURES BEHIND INCIDENT AND REFLECTED SHOCK WAVES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By
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The Ohio State University
1969

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ACKNOWLEDGMENTS</td>
<td>ii</td>
</tr>
<tr>
<td></td>
<td>Vita</td>
<td>iii</td>
</tr>
<tr>
<td></td>
<td>List of Tables</td>
<td>vii</td>
</tr>
<tr>
<td></td>
<td>List of Figures</td>
<td>viii</td>
</tr>
<tr>
<td>I</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>Earlier Investigations of Thermal Decomposition of Hydrogen Peroxide</td>
<td>6</td>
</tr>
<tr>
<td>III</td>
<td>Shock Tube in Chemical Kinetic Studies</td>
<td>11</td>
</tr>
<tr>
<td>IV</td>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. Introduction</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>B. Passivation of Apparatus</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>C. Optical Arrangement</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>D. Velocity Measurements</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>E. Gas Mixtures</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>F. Necessity for Diluents</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>G. Experimental Procedure</td>
<td>29</td>
</tr>
<tr>
<td>V</td>
<td>Methods of Analysis and Results</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. Analysis</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>B. Results</td>
<td>38</td>
</tr>
<tr>
<td>VI</td>
<td>Discussion</td>
<td>41</td>
</tr>
<tr>
<td>VII</td>
<td>Mechanism</td>
<td>55</td>
</tr>
<tr>
<td>VIII</td>
<td>Conclusions</td>
<td>61</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS (continued)

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>64</td>
</tr>
<tr>
<td>2.</td>
<td>69</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>95</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Important Reactions in the Combustion of Hydrogen with Oxygen</td>
</tr>
<tr>
<td>2</td>
<td>Determination of $s$ and $E^*$ for $\text{H}_2\text{O}_2 + \text{Argon}$ Mixtures</td>
</tr>
<tr>
<td>3</td>
<td>Determination of $s$ and $E^*$ for $\text{H}_2\text{O}_2 + \text{N}_2$ Mixtures</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gas Mixture Handling System</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>Overall Shock Tube Set-up</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>Absorption Spectrum of H₂O₂ Vapor</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>Spectral Response of RCA 1P28 Photomultiplier</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>Spectrum of Osram High Pressure Xenon Lamp</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>Photomultiplier Base Circuit</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>Power Supply for Applying &quot;Suppressed - Zero Voltage&quot; at Zero Lamp Intensity</td>
<td>83</td>
</tr>
<tr>
<td>8a</td>
<td>Typical Oscilloscope Trace; H₂O₂ + Argon</td>
<td>84</td>
</tr>
<tr>
<td>8b</td>
<td>Typical Oscilloscope Trace; H₂O₂ + Nitrogen</td>
<td>84</td>
</tr>
<tr>
<td>9</td>
<td>Sketch of Typical Experimental Trace Showing Intensity Designations</td>
<td>85</td>
</tr>
<tr>
<td>10</td>
<td>t versus ln.ln. (I/I₀) for H₂O₂ + N₂</td>
<td>86</td>
</tr>
<tr>
<td>11</td>
<td>Initial Slope Method of Determining Initial Reaction Rate Constant</td>
<td>87</td>
</tr>
<tr>
<td>12</td>
<td>Arrhenius Plot for H₂O₂ + Argon Mixtures</td>
<td>88</td>
</tr>
<tr>
<td>13</td>
<td>Arrhenius Plot for H₂O₂ + Nitrogen Mixtures</td>
<td>89</td>
</tr>
<tr>
<td>14</td>
<td>Comparison with Low Temperature Data</td>
<td>90</td>
</tr>
<tr>
<td>15</td>
<td>Shape of a Hydrogen Peroxide Molecule</td>
<td>91</td>
</tr>
<tr>
<td>16</td>
<td>Absorption at 3090 Å by a Mixture of 2% H₂O₂ + Argon behind Incident Shock Wave</td>
<td>92</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>17</td>
<td>Absorption at 3090 Å by a Mixture of 2% H₂O₂ + Argon behind Incident Shock</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>Wave T₂ = 1400°K</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Wave Diagram of Simple Shock Tube Flow</td>
<td>93</td>
</tr>
<tr>
<td>19</td>
<td>Coordinate Systems for Shock Wave Calculations</td>
<td>94</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

Ramjets are being considered as power plants for hypersonic aircraft. Because of structural considerations, the high stagnation enthalpies of the air with respect to the engine precludes the energy release from combustion in a subsonic stream. Decelerating the flow to subsonic velocities from hypersonic velocities involves large losses in stagnation pressure. Further, the very high temperatures attained due to such a deceleration before entering the combustion chamber causes the combustion and chemical energy recovery processes to be very inefficient.

One possible solution to the problem is to limit the reduction of the airspeed through the engine to moderately supersonic levels so that the static pressure of the gas is low enough to satisfy structural requirements. The fuel is then added to this supersonic flow of air. Hydrogen is being considered as a possible fuel for future hypersonic ramjets. This scheme necessitates mixing and burning of gases which are flowing at supersonic speeds. These processes of mixing and burning are extremely important since they must be accomplished in a combustion chamber of reasonable length. Although a coupling exists
between these processes, they may be analysed separately and the results used in situations where one process is faster than the other.

This work is concerned with the chemical kinetic aspect of the supersonic combustion process. An accurate knowledge of the reactions taking place and their rates is essential to the design of the scramjet engine. Though many reactions are involved in the combustion, the present work deals with one of the important intermediate products.

The important chemical reactions occurring in the combustion of hydrogen with oxygen or air are listed in Table 1. (1)

Hydrogen peroxide is one of the important intermediate products formed in the reaction of hydrogen with oxygen. Kistiakowsky (2) found that in the photochemical reaction of hydrogen with oxygen initiated by an aluminum spark at 1700 Å, hydrogen peroxide was the only end product that was formed. The yield of hydrogen peroxide increased at higher temperatures. Marshall (3) used the resonance radiation from a mercury lamp as the source to initiate the photochemical reaction and found that the absorption of the 2537 Å line by a mixture of hydrogen and oxygen led to the production of hydrogen peroxide. The yield was variable, the average being about 2.5 molecules for each quantum of absorbed light. Frankenburger and Klinkhardt (4) made further investigations between 50 °C and 200 °C at pressure of one to eleven atmospheres and found that one molecule of hydrogen peroxide
and two of water were formed for each quantum of light absorbed. Further evidence for hydrogen peroxide being the main product of the photochemical reaction between hydrogen and oxygen was found by Bates and Salley and by Bates and Lavin. The latter authors also found that the hydrogen peroxide subsequently decomposed into water and oxygen.

Hydrogen peroxide is also found as an important intermediate product in the thermal reaction between hydrogen and oxygen. Pease used flowing mixtures of hydrogen and oxygen at 1 atmosphere and 540°C in a pyrex vessel and by chemical analysis of the exit gases found that hydrogen peroxide was formed under these conditions. He concluded that a stationary concentration of hydrogen peroxide was reached and that the formation of hydrogen peroxide and water is greater with hydrogen in excess than with oxygen in excess. Holt and Oldenberg carried out experiments at 530 to 540°C with residence times of 3 to 7 seconds and showed spectroscopically that hydrogen peroxide was formed in the reaction. They also concluded that the formation of hydrogen peroxide was enhanced by a large hydrogen to oxygen ratio. The ratio of hydrogen peroxide found spectroscopically to that determined chemically in the exit gases was approximately constant.

It has been found by all investigators that the yield of hydrogen peroxide was strongly dependent upon the nature of the surface. Linnett and Tootal conducted experiments on the thermal reaction between hydrogen and oxygen in a flow tube at a fixed pressure of 230 mm of
They found that hydrogen peroxide was formed and that the partial pressure of hydrogen peroxide remained constant for residence times up to 5 or 6 seconds after which it fell off rapidly. Apparently the condition of the surface of the vessel was an important factor in the formation and stability of hydrogen peroxide. This work was done close to the second limit of the hydrogen-oxygen reaction. Greene and Linnett\(^{(10)}\) studied the formation of hydrogen peroxide during the hydrogen-oxygen reaction in a flow system at 538°C at 300 to 400 mm of mercury in a vessel coated with boric acid. They found that with increasing residence time, the partial pressure of hydrogen peroxide continued to rise after the rate of production had become steady and also the yield of hydrogen peroxide was strongly dependent upon the nature of the vessel.

Further evidence of the hydrogen peroxide formation in the thermal reaction between hydrogen and oxygen was obtained by several investigators\(^{(11, 12, 13, 14)}\). Venugopalan\(^{(15)}\) has discussed in detail the formation of hydrogen peroxide in spark and hot wire ignited explosions in hydrogen and oxygen systems, in flames, in explosions initiated by flash photolysis and in shock waves in hydrogen-oxygen mixtures.

These and several other studies indicate the importance of hydrogen peroxide in the overall hydrogen-oxygen reaction scheme. Hydrogen peroxide, with the exception of water is the most stable molecule containing hydrogen and oxygen atoms exclusively. Moreover, the
structure of the hydrogen peroxide molecule is comparatively simple. Experimental difficulties arising from the low vapor pressure at room temperature, thermal decomposition at moderate temperatures and reactivity with mercury have been deterrents to extensive studies of hydrogen peroxide.

In the present study, the homogeneous thermal decomposition of hydrogen peroxide is investigated at high temperatures behind incident and reflected shock waves. Hydrogen peroxide vapor is diluted with excess of argon or nitrogen in order to obtain a condition of constant temperature behind the shock wave and also to study the relative efficiency of argon and nitrogen as collision partners. The decomposition is followed by monitoring the absorption by hydrogen peroxide of the UV radiation from a high pressure mercury or xenon lamp. The rate constants for the initiating step in the decomposition are obtained and compared with those of other investigators obtained at lower temperatures. The relative efficiencies of argon and nitrogen as collision partners are obtained. The possible mechanism in the decomposition is discussed as also are the advantages of the shock tube method over the flow techniques used at lower temperatures.
II. EARLIER INVESTIGATIONS OF THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR.

The thermal decomposition of hydrogen peroxide has been investigated by several investigators at temperatures up to 900 K. All these studies were conducted either in static or flowing systems with residence times long enough that the heterogeneous decomposition had to be taken into account.

McLane (16) saturated a stream of oxygen and nitrogen with hydrogen peroxide by passing the carrier gas twice through 90% hydrogen peroxide (aqueous) kept at room temperature. The mixture was then allowed to flow through glass reaction vessels coated with boric acid. He showed that at partial pressures of 1 to 2 mm of mercury of hydrogen peroxide in which the total pressure was one atmosphere, at least part of the decomposition was homogeneous, in a temperature range of 740 K to 810 K. The apparent activation energies were 40 kcal/mole in vessels with a surface to volume ratio of 7 cm⁻¹ for both nitrogen and oxygen as diluents, and 50 kcal/mole in 3 cm⁻¹ vessels with nitrogen as diluent. These results indicated that heterogeneous effects had to be accounted for in the study of the homogeneous decomposition.
Harris\(^{(17)}\) passed a stream of nitrogen at 1 atmosphere through 65% hydrogen peroxide solution in water at a temperature of 325\(^\circ\)K and introduced the mixture into a quartz reaction tube whose temperature could be closely controlled. The fraction of peroxide decomposed was not reproducible, but it was found that it increased in tubes containing a few crystals of potassium chloride or mercury. Washing the tube with a salt solution also increased the amount of decomposition. Half lives at various temperatures in clean vessels indicated that a substantial part of the reaction was homogeneous, in agreement with McLane's findings.

Satterfield and Stein\(^{(18)}\) passed a mixture of hydrogen peroxide and water at one atmosphere total pressure through a pyrex tube held in a constant temperature bath. Samples were taken and analysed before and after passage the reaction vessel. They observed a transition from homogeneous to heterogeneous reaction in the temperature range of 400\(^\circ\)C to 450\(^\circ\)C at a partial pressure of 0.02 atmosphere. The heterogeneous reaction showed an activation energy of 10 kcal/mole. The homogeneous reaction had an activation energy of 55 kcal/mole assuming a rate proportional to the 3/2 power of hydrogen peroxide concentration. They concluded that long unbranched chains were involved in the decomposition.

Giguere and Liu\(^{(19)}\) measured the rate of thermal decomposition of hydrogen peroxide vapor under static conditions at low pressures in the
range of 0.2 to 20 mm of mercury in the temperature range of 570 to 870 K. The course of the reaction was followed by recording the pressure increase by means of a pressure transducer. The reaction was found to be of first order with respect to time and the final products were water and oxygen only. Around 670 K, the character of the reaction changed gradually from heterogeneous to homogeneous. With initial pressures of 10 mm of mercury, the experimental reaction rates above 670 K gave an apparent activation energy of 43 kcal/mole, which after correction for the residual surface decomposition becomes 48 kcal/mole. The corrections were needed because the observed rate constants $k_e$ were the sum of two terms: $k_g$ for the gas phase reaction and $k_s$ for the residual surface reaction. To correct for the latter, the low temperature portion of the Arrhenius curve extending to about 570 K was extrapolated into the region of homogeneous decomposition, and the approximate values of $k_s$ thus obtained were subtracted from the measured values of $k_e$ above 670 K. Giguere and Liu concluded that the decomposition proceeded mainly, if not exclusively, by means of the initial splitting of the hydrogen peroxide molecule into two OH radicals followed by fast non-chain reactions.

Forst(20) investigated the thermal decomposition of hydrogen peroxide vapor by the static method using initial peroxide pressures upto 22 mm of mercury in the absence and presence of inert gases (Helium, oxygen or water vapor upto 100 mm of mercury). In each case, the apparent first order rate constant increased linearly with pressure.
Under the experimental conditions used, Forst found that the pyrolysis of hydrogen peroxide vapor showed behavior typical of an elementary unimolecular reaction in its low pressure second order region. The reaction was accompanied by a heterogeneous decomposition which in the presence of a foreign gas was inhibited. Helium was used as an inhibitor over the temperature range 700 to 740°K to permit calculation of the activation energy of peroxide alone and in the presence of helium. The results were accounted for by assuming a critical energy of 47-50 kcal/mole and five effective classical oscillators for activation with peroxide and three with helium provided deactivation occurs in every collision.

Hoare et al\(^{(21)}\) used a flow system to study the decomposition between 514°K and 932°K. They observed that the heterogeneous reaction was predominant up to 690°K after which the homogeneous reaction became the dominant one. The heterogeneous reaction was found to have an activation energy of 10 kcal/mole. The homogeneous second order reaction did not consist of a chain. The rates could be expressed as 

\[ k \left[ H_2O_2 \right] \left[ M \right] \]

upto pressures of at least one atmosphere of nitrogen. According to these authors, the first step in the decomposition at ordinary pressures must be the second order reaction

\[ H_2O_2 + M \rightarrow 2OH + M \]

the experimental order of efficiencies of collision partners being
When hydrogen peroxide was taken as M, the activation energy was found to be 48 kcal/mole.

Baldwin and Brattan (22) studied the vapor phase decomposition of hydrogen peroxide vapor with nitrogen carrier in a flow system. They used boric acid coated vessels of different surface to volume ratio to study both the heterogeneous and homogeneous effects. It was found that at a given temperature, the percentage hydrogen peroxide decomposed due to surface decomposition was constant in a given time over a tenfold range of hydrogen peroxide initial concentration. They concluded that the homogeneous reaction was first order with respect to hydrogen peroxide and that the decomposition involved a unimolecular non-chain reaction in the second order range.

Bilwakesh, Strauss, Edse and Fishburne (39) used incident shock wave techniques to investigate the decomposition between 1350 K and 1600 K in argon diluent and between 1220 K and 1370 K in nitrogen diluent. They found that the homogeneous decomposition of hydrogen peroxide vapor had an activation energy of 50 kcal/mole with argon as diluent and 53 kcal/mole with nitrogen as diluent. It was later found that the gas sampling techniques used could have led to some errors in concentration measurements, which may account for the somewhat high activation energies that they have reported.
III. SHOCK TUBE IN CHEMICAL KINETIC STUDIES

The survey of earlier investigations of hydrogen peroxide decomposition revealed that the most serious difficulty encountered in the studies was the heterogeneous reaction on the wall surface. A disadvantage of the experiments with statically heated gases consists in the non-uniform heating of the gas. Furthermore, the time interval during which the gas is heated is long and the analysis of the final products cannot give a true picture of the reaction products. Therefore, it is not possible to determine the instantaneous time rate of change of concentration of any species. Because of these conventional techniques, it had not been possible to extend the study of the decomposition rates of hydrogen peroxide to higher temperatures.

On the other hand, it is possible to heat the test gas by means of normal shock waves so rapidly that only a few collisions occur. (23) Of course, for many systems, inherent relaxation times are much longer than this heating time, so that the final equilibrium temperature may not be achieved until much longer periods. The rapid heating provides a tool for kinetic studies of very fast processes. Behind normal shocks, most of the work done by the driver gas is converted into thermal energy of the driven gas. For a given shock velocity,
the temperature rise depends upon the heat capacity of the system. Shock tubes permit the attainment of practically any temperature of interest to the kineticist.\(^{(23)}\) Shock waves can be made nearly one-dimensional so that the chemical changes occurring are the same whether in the interior or near the walls of the container. Because of the very short times, convection is unimportant and usually diffusion may be neglected. While the shock tube apparatus is easy to design and construct, the associated measuring and monitoring instrumentation is usually quite complicated. Yet, it is often possible to continuously monitor the concentration of certain species in the reaction with a time resolution of a few microseconds by means of optical and spectroscopic techniques.
IV. EXPERIMENTAL

A. Introduction

A shock tube was employed to heat the gases to the required temperature. The shock tube consisted of a driven section 24 feet long and a driver section 14 feet long. The I.D. of both sections originally was 2 inches but the I.D. of the driver section was later reduced to 1 1/2 inches by insertion of a polyethylene liner for reasons explained below.

One of the major problems involved in this study was the presence of heterogeneous reactions on the walls of the shock tube at room temperature. The same problems were encountered by the earlier investigators also who performed the work at lower temperatures in conventional flow systems. But at lower temperatures, the main effect of the surface decomposition was the net contribution that it made to the overall decomposition rate which is observed over a large time period as compared to the test times of a shock tube. In the shock tube studies like the present one, in view of the very short test times and much higher temperatures involved, it is not necessary to consider the surface decomposition during the test time. Hence the decomposition
observed spectroscopically in the shock tube is almost exclusively the result of the gas phase decomposition. Yet, it is necessary to reduce the surface decomposition in view of the fact that during the time of filling of the shock tube with the test gas, considerable amount of hydrogen peroxide could have decomposed in the shock tube resulting in a mixture consisting of $\text{H}_2\text{O}_2$, $\text{H}_2\text{O}$, $\text{O}_2$ and the intended diluent. The presence of these products poses the problem of uncertainty in the initial concentration of the mixture. Further, it becomes increasingly difficult to ascertain the efficiency of one species as collision partner with hydrogen peroxide when collisions are also taking place with other relatively inert species.

Considerable amount of work has been done by earlier investigators to passivate the reaction vessels with respect to surface decomposition of hydrogen peroxide by applying certain coatings to the surfaces. McLane coated his vessels by rinsing with a saturated solution of crystalline boric acid in 95% ethyl alcohol and then drying with air followed by heating in an oven. Then a stream of oxygen or nitrogen saturated with the vapor of 90% hydrogen peroxide at room temperature was passed slowly for a period of several hours until the concentration of hydrogen peroxide in the effluent gases reached a maximum and remained stationary. The vessels with such coatings were found to be better than an uncoated pyrex vessel in reducing the surface decomposition of hydrogen peroxide. Satterfield and Stein (18) used pyrex vessels
coated with phosphoric acid. Giguere and Liu\textsuperscript{(19)} used vessels of pyrex or vycor. They first cleaned their vessels with hot fuming sulfuric acid and after rinsing thoroughly, they fused the vessels in a blast lamp or treated for several hours with concentrated hydrogen peroxide. Even after such treatments, they found that whereas vycor flasks gave immediately consistent results, the pyrex flasks required several preliminary runs before giving consistent results. Hoare et al\textsuperscript{(21)} used pyrex and silica vessels which had been cleaned by rinsing with 40% hydrofluoric acid.

B. Passivation of Apparatus

The shock tube in this study had been originally constructed out of 316 stainless steel. But this material was found to decompose the hydrogen peroxide so strongly that when a mixture of hydrogen peroxide and argon was passed through the tube at a rate of 6cc/sec, more than 50% of the hydrogen peroxide had decomposed before reaching the exit. To eliminate this decomposition, the inner surface of the tube was honed and cleaned thoroughly with double distilled water and dried several times. This treatment did not reduce the catalytic effect of the wall. Hence, the passivating procedure recommended by Becco\textsuperscript{(24)} was followed next. In this method, recommended for stainless steel, the tube was completely filled with 70% aqueous solution of nitric acid which was then left in the tube for seven hours at room tempera-
After cleaning with distilled water thoroughly, the tube was then treated with a 30% aqueous solution of hydrogen peroxide which was left in the tube for several hours. The tube was again flushed and rinsed with distilled water. Tests conducted after this procedure revealed that the surface decomposition of the peroxide vapor had not decreased appreciably.

Tests were also conducted to determine if the hydrogen peroxide was being adsorbed on the walls of the tube. It was argued that if the hydrogen peroxide was adsorbed instead of being decomposed on the walls of the tube, then the effluent gases would show a decrease in the hydrogen peroxide concentration. On the other hand, decomposition of the peroxide in the tube would result in an increase in the water and oxygen concentration in the effluent mixture. Samples of the mixture were frozen out at liquid nitrogen temperatures before and after passage through the shock tube and analysis showed an increase in water concentration corresponding to the decrease in hydrogen peroxide concentration indicating that considerable amount of decomposition occurred in the tube.

At this stage, it was decided to line the inner surface of the tube with a material inert with respect to hydrogen peroxide. The driven section was lined with polyethylene well casing tubing (Yardley Plastics Golden Jet NST). The polyethylene liner was thoroughly
cleaned with double distilled water. Samples of hydrogen peroxide-argon mixture were taken after being held in this tube for ten minutes and they showed only about 5% decomposition at room temperature.

Extreme care was taken in designing other equipment which also came into contact with hydrogen peroxide. The bubbler and all the stopcocks (fig. 1) were made of pyrex glass and these were all treated in the manner recommended by Becco\(^{(24)}\) for glassware. They were first rinsed in distilled water and then immersed in 35% aqueous solution of sulfuric acid for two to three hours at room temperature. They were then rinsed thoroughly again in double distilled water and air-dried. The flow throttling valve which admits the mixture into the shock tube was teflon, window flanges were type 1100 aluminum and flow lines were polyethylene tubing. All these were passivated by passing hydrogen peroxide vapor through them for several hours periodically. The windows of the shock tube were sapphire which also shows good compatibility with hydrogen peroxide\(^{(24)}\). During the course of the experiments, the tube was cleaned after every two or three runs with double distilled water and dried by prolonged evacuation. Only dry pure air was used for flushing the tube.

C. Optical Arrangement

Fig. 2 shows the experimental setup used including the optical
arrangement. The decomposition of hydrogen peroxide was followed by monitoring the absorption of the ultraviolet radiation at 2537 Å, 2600 Å and 2900 Å by hydrogen peroxide behind the shock wave. Hydrogen peroxide is known to absorb continuously in the UV from 4000 Å to 1850 Å, the extinction coefficient increasing with decreasing wavelength. The extinction coefficients have been measured at room temperature and below, but no measurements had been made at higher temperatures. Fig. 3 shows the absorption spectrum of hydrogen peroxide vapor in the UV region. It is seen that higher values of extinction coefficient are obtainable at lower wavelengths but there are other limitations to how low it is possible to go in wavelength.

Fig. 4 shows the spectral response of the RCA 1P28 photomultiplier. Fig. 5 shows the spectrum of the xenon lamp that was used. It is noticed that the output of the xenon lamp decrease sharply at lower wavelengths and the radiation is further reduced by the several quartz lenses in the optics, the lithium fluoride prism in the monochromator and the sapphire windows. With the sharply declining response of the photomultiplier added to this, it became very difficult to obtain any appreciable signal at the lower wavelengths. The voltage applied to the photomultiplier could not be increased to raise the signal output since this increased the noise considerably and made data interpretation very difficult. Hence experiments were conducted at 2537 Å with a mercury lamp and at 2600 Å and 2900 Å with a xenon lamp.
In the initial stages of the work, a high pressure mercury lamp (Osram HBO 100 W/l) was used as a source. This lamp gives a fairly intense UV spectrum consisting of the mercury lines superposed on a continuum. The fluctuations of the arc and consequently of the intensity made it very difficult to make direct measurements of extinction coefficient at room temperature. It was found that with the lamp on, the trace in the oscilloscope would gradually drift and sometimes exhibit spontaneous intense fluctuations. The fluctuations and drift were negligible during the time of a shock tube run (test times of up to 500 microseconds). Hence it was still possible to use the mercury lamp for the data, although no direct room temperature extinction coefficients could be measured.

The xenon lamp (Osram XBO 150 W/l) is considerably more stable than the mercury lamp and operates at considerably higher pressures. This lamp gives a smooth continuum of gradually decreasing intensity in the UV region. The advantage of this lamp over the mercury lamp for this work is that there are no lines in the wavelength region of interest with the xenon lamp. This smooth continuum appears to give more stability to the output from the lamp. It was also found that operating the xenon lamp at 9 amperes instead of the 7.5 amperes recommended by the manufacturer gave more stability to the output. The measurement of concentration of a particular species is only possible when the absorption is due to a broad band or continuum.
In calculating the concentration of the species, it is necessary to assume the Beer-Lambert law which is valid when the value of the extinction coefficient is constant over the wavelength interval being studied. If the species does have a line spectrum in the region of interest, then a source producing a similar line spectrum may be used in absorption studies.

The beam from the lamp was collimated by means of quartz lenses and then was passed through the shock tube windows. The windows were mounted flush with the wall of the shock tube in type 1100 aluminum mountings. The window on the lamp side was 0.7 mm wide and 5 mm high. The window on the opposite side was 1.2 mm wide and 5 mm high. The additional width on the exit side was provided to reduce the Schlieren effect on the passage of the shock wave past the window. The Schlieren effect is caused by the refraction of the light beam due to the sharp density gradient across the shock front on arrival of the front at the window section. The light beam transmitted through the windows of the shock tube is then focussed by a quartz lens on to the slit of a Perkin Elmer Model 98 monochromator whose slit could be varied from 0 to 2 mm. The linear dispersion of the monochromator in the wavelength region observed was between 25 and 40 Å per mm of slit width. The calibration of monochromator dial setting versus the wavelength transmitted through the exit slit was done periodically with the help of a Pen-Ray neon mercury lamp. The photomultiplier RCA 1P28 mounted
behind the exit slit of the monochromator picked up the signal which was then fed into a Tektronix 555 dual beam oscilloscope. As the shock wave passed the shock tube window, the gas behind it gets heated and compressed rapidly thereby increasing the absorption by the particular species. Subsequently as the hydrogen peroxide decomposes, the absorption decreases according to Beer's law and this absorption could be monitored by the monochromator and the photomultiplier.

The photomultiplier setup caused considerable problems. The extinction coefficient of hydrogen peroxide in the UV is very small. In addition, the small path length and small concentration cause the maximum absorption to be very small. Hence it was necessary to operate the oscilloscope at 1 or 2 mv/cm to be able to pick up small variations. The signal to noise ratio of a photomultiplier is dependent on the ratio of the output current to the gain so that a combination of high intensity with lowest permissible gain is required for maximum sensitivity. This is quite important since the noise level is usually the limitation on the response which can be attained from the particular setup. It was found that it was optimum to operate the photomultiplier at 400 volts. Fig. 6 gives the circuit diagram for the base used. The time constant introduced through the use of this base was measured by the cathode ray tube method. In this method, an oscilloscope is used as a pulsed light source, the cathode ray tube face being masked off except for a small opening. The sweep
traverses this opening rapidly and provides a step pulse of radiation. By placing the photomultiplier close to this light source and by recording its output signal on a second oscilloscope, the time constant for the electronic circuitry associated with the tube can be obtained. With a type D preamplifier, the rise time was found to be about 0.5 microseconds. Linearity of the photomultiplier output changes with changes in incident light intensity was checked for the photomultiplier currents used. Care was taken to avoid saturating the photomultiplier.

D. Velocity Measurements

Shock wave velocity measurements were made at two section 1-2 and 4-5 in fig. 2. Both segments are 50 cm wide and the time taken by the shock wave to traverse this distance at the two sectors gave, in addition to velocity of the shock wave, information on the attenuation of the shock wave. Platinum strip heat transfer gages were used at each of these stations to sense the arrival of the shock wave. These gages were made from 7 mm pyrex rods which were thoroughly cleaned with alcohol and water after the edges were fire-polished smoothly. A thin strip of liquid platinum was then painted with a thin brush. The strips were then dried in an oven at 750°C for thirty minutes followed by another 45 minutes at 1250°C. After slow cooling, leads were soldered on to the platinum. The resistance was measured to be between 50 and 150 ohms. The gages have been found to withstand temperatures up to 2000°K for several
hundred runs of the shock tube. The probe was then mounted flush
with the inner wall of the shock tube with the long dimension in a
plane at right angles to the axis of the shock tube.

Due to the rapid heating behind the shock wave, the resistance
of the platinum strip rises sending a pulse of a few millivolts
through the circuit. This pulse is then amplified by an amplifier
circuit and is displayed on an oscilloscope and a counter. It was
established from velocity measurements at the two different locations
that the velocity attenuation of the shock wave was negligible.

In a typical experiment, probe 3 would trigger the upper trace
which is the velocity trace and probes 4 and 5 put the two deflections
as seen in fig. 8. Probe 5 also triggers the lower beam which is
connected to the photomultiplier output. The rise time of the circuit
was less than one microsecond and the uncertainty in the velocity
measurements was less than 0.3%. The oscilloscope time bases were
calibrated every fifteen runs against the output from a Tektronix
Model 180A time marker unit and the vertical scales also were calib-
rated at the same time.

E. Gas Mixtures

Mixtures of hydrogen peroxide vapor and the appropriate carrier
gas (nitrogen or argon) were obtained by passing the gas through a 98% hydrogen peroxide solution in water stored in a bubbler. A flow meter measured the rate at which the inert gas was passed through. The hydrogen peroxide-water mixture was obtained from Becco and was not further purified.

Pressure was measured by means of Wallace and Tiernan gauges which were periodically checked for proper calibration. After the shock tube was filled to the desired pressure, a sample was drawn into the sampling flask (fig.1) from the shock tube and analysed by titration against sodium thiosulfate in the presence of potassium iodide and sulfuric acid. By controlling the flow rate of the carrier gas, it was possible to obtain mixtures containing from 2 to 3% hydrogen peroxide. Several dry runs of the mixing systems was made to make sure that the mixture composition was repeatable. Samples were taken after allowing the mixture to remain in the shock tube for six minutes and it was found that the surface decomposition in the shock tube at room temperature was negligible. All runs were made within a minute after filling the shock tube driven section to minimise this decomposition.

F. Need For Diluents

According to the Beer-Lambert's law, the amount of intensity of
radiation transmitted by an absorbing medium is given by

\[ I = I_0 \exp\left( -\mu c L \right) \]  

(1)

where

- \( I \) = transmitted intensity with the absorber present in the path
- \( I_0 \) = transmitted intensity when there is no absorber in the path; i.e. an evacuated shock tube in our case
- \( \mu \) = extinction coefficient of the medium at the wavelength of interest
- \( L \) = path length through the absorbing medium
- \( c \) = concentration of the absorbing species.

Equation (1) assumes that the radiation from the gas is negligible in the wavelength region of interest. This condition was checked frequently in the present work. For this check, the lamp was shut off and the photomultiplier was set a very high voltage (1000 volts) since its amplification increases with applied voltage to the circuit. The oscilloscope gain was also made as high as possible. The shock wave was then generated and the trace obtained was recorded in the manner explained in section IV G. The monochromator slit opening was also set at the full width of 2 mm. The
source of radiation can be hydrogen peroxide, the carrier gases, decomposition products or any impurities in the shock tube. One of the frequent sources of impurities in a shock tube consists of fragments of the mylar diaphragm which are blown down the tube by the driver gas.

The tube was cleaned frequently with double distilled water and evacuated to make sure that no impurities remained in the tube. It was found that no radiation in the wavelength region of interest could be observed even at the highest sensitivity settings. The sensitivity at which these tests were conducted was several orders of magnitude higher than the sensitivity for the absorption data runs.

Equation (1) can be rewritten as

\[ \ln \frac{I_0}{I} = \mathcal{D} = \mu C \ell \]  \hspace{1cm} (2)

Equation (2) can be used to determine the extinction coefficients at various temperatures. With known initial concentrations, shocks of known strength can be generated and values of temperature and density ratios can be calculated (see appendix 1). The intensity ratio in equation (2) can be measured from the absorption trace and \( \mu \) can be evaluated as a function of wavelength and temperature.

We must next consider the effect of temperature and pressure on the transmitted intensity. Both temperature and pressure change
behind the shock wave because of the chemical changes that occur. Thus both the concentration and the extinction coefficient $\mu$ change. We can write for the change in species concentration the following expression:

$$ C = C_0 \frac{S}{S_0} (1 - \alpha) \quad (3) $$

where

$S_0$ = initial density immediately behind the shock wave

$C_0$ = initial concentration of species immediately behind the shock wave

$\alpha$ = degree of dissociation which is the fractional amount of species $C$ which has disappeared.

From equation (3) we have

$$ \frac{dC}{C} = \frac{dS}{S} - \frac{d\alpha}{(1-\alpha)} \quad (4) $$

From equation (2) we have

$$ \frac{dD}{D} = \frac{d\mu}{\mu} + \frac{dc}{c} \quad (5) $$

Substituting from equation (4) into equation (5), we get
This analysis shows that the transmitted intensity depends on $\mu$, $g$, and $\alpha$ which in turn are affected by temperature and pressure. At a given wavelength $\mu$ is a function of temperature $\mu(\mathbb{T})$ and does not depend upon the amount of gas present. As mentioned earlier, $\mu$ can be determined from absorption measurements behind the shock wave. Although a tedious process, the changes in temperature and density can be expressed in terms of $\alpha$ for a given shock strength from the one dimensional analysis of flow with heat exchange.

According to equation (6), the transmitted intensity will initially decrease immediately on arrival of the shock wave due to the sharp rise in density and thus the concentration when the rate of disappearance of the absorbing species dominates the expression. Then as the absorbing species disappears gradually, the transmitted intensity will increase, as can be seen in fig. 8. If the changes in $\mu$, $g$ and $T$ are high as the decomposition proceeds, they will have a significant effect on the transmitted intensity. Taking account of their variation as the decomposition proceeds is a complicated process. Therefore, the gas is diluted with a large quantity of an inert gas like argon, helium, xenon or nitrogen.
(at low temperatures). This ensures that the changes in temperature and density due to the heat released or absorbed in chemical reactions are small so that the assumption of constant temperature and density during the reaction is justified. One drawback of this procedure is that inert gases may have different efficiencies as collision partners in the reactions and hence the results obtained may differ slightly from those obtained with pure species alone. But the increased ease of data interpretation makes it necessary to use diluents.

G. Experimental Procedure

A typical experiment was carried out as follows. A mylar diaphragm (2 mil to 10 mil depending upon the velocity and temperature desired) was installed between the driver and the driven sections. In the case of the incident shock experiments, another mylar diaphragm was installed (2 mil) between the driven section and the vent. The driver and the driven sections were evacuated independently. At the same time, the vacuum pump to the bubbler also was turned on to bring the pressure in the bubbler to the vapor pressure of hydrogen peroxide at room temperature. The lamp was turned on several minutes before the start of the run to give it time to stabilise.

After the driven section is evacuated to a pressure of a few microns of mercury and the evacuation continued for at least fifteen
more minutes, the pump was shut off and the carrier gas was passed through hydrogen peroxide in the bubbler and the mixture admitted into the tube. When the pressure in the driven section attained the desired initial value (40 mm of mercury), the pump was turned on and the evacuating rate adjusted so that a continuous flushing operation took place at 40 mm of mercury with the test gas mixture admitted from one side and the pump evacuating it from the other side. In this manner, the gas mixture in the shock tube was changed once every four minutes. This was done so that the adsorption on the wall, though small could be stabilised. After several fills had been drawn through the tube, the filling and evacuation was stopped by shutting off valves V1, V6, and V9 (fig.1). Valve V7 was then opened and a sample drawn into the sampling flask.

The shock wave was then generated by rupturing the diaphragm with high pressure helium admitted into the driver through a solenoid-operated valve. Upon passage of the shock wave past the probes, the velocity was obtained from probes 1, 2, 3, 4, and 5 as explained earlier. Probe 5 also triggered the lower beam of the oscilloscope which was connected to the photomultiplier output and monitored the UV absorption of the radiation from the source. The sharp pip on the gas trace upon passage of the shock wave past the window was caused by the Schlieren effect. The test was essentially complete when the contact surface arrived at the window, but so long a test time was never used.
For the reflected shock studies, a reflecting end was introduced into the shock tube and the distance between the reflecting end and the windows could be varied between 1 cm and 5 cm by means of spacers. Due to slight imperfections, there was a small gap of less than 1/2 mm between the plug and the tube wall. Toennies and Greene have shown that gaps up to 1 mm do not have any effect on the reflected shock and the minor leak behind the reflected shock did not have any effect on the chemical kinetic studies.

In order to obtain the line corresponding to zero transmission, the source was shut off and an accurately measured D.C. voltage was then applied to the gas trace to bring it back within the scope face. The voltage was measured very accurately by means of a voltmeter. Fig.7 shows the power supply used. For velocity measurements, in addition to frequently checking the time base calibration, time mark signals were put on the scope from a Tektronix time mark generator type 180 A.
V. METHODS OF ANALYSIS AND RESULTS

A. Analysis

Fig. 8b shows a typical trace obtained from an experiment with the pertinent data provided. Time is measured from right to left in both upper and lower traces. The speed of the shock wave can be obtained from the upper trace and from this we can obtain the temperatures and density ratios behind the incident and reflected shock waves. The lower trace records the UV light of the specified wavelength passing through the test section. Absorption is indicated as an upward deflection in the trace. The lower beam was triggered by the last probe (probe 5) which also put the second velocity pip. The first sharp upward deflection in the lower beam is due to the passage of the incident shock past the observation window. There is a finite absorption level between the times of passage of the incident shock wave past the window and the arrival of the reflected shock which is seen as the second sharp upward deflection. This finite absorption increase is due to the rise in temperature and density of the gas behind the incident shock. But the temperature behind the incident shock is too low for an appreciable reaction to set in during the short time between the passage of the incident and reflected shock waves past
the window. Hence the level remains constant until the arrival of the reflected shock.

Fig. 9 shows a sketch of a typical experimental trace. This has been drawn to facilitate marking the various intensity designations. AB represents zero intensity falling on the photomultiplier which, in other words, means that the particular wavelength is completely absorbed in the tube or that there is no light falling on the test section at all. As explained earlier, it was necessary to operate the optical and photoelectric system in such a manner as to obtain a high intensity and yet at a high sensitivity. Hence, if the oscilloscope trace remained on the face of the scope with the chosen sensitivity with the light on, then, when the light was turned off, the trace vanished from the screen due to excessive deflection. To obtain the line corresponding to no light, an accurately measured D.C. voltage was applied in order to bring the trace back on the face of the scope. This voltage is now added to the values directly measured from the trace for $I_0, I_1, I_2, I_5$ and I.

F represents 100% transmission of light through the test section which means that the test section contains no absorbing molecules. Due to slight changes in the intensity of radiation from the lamp, this level had to be obtained only in an indirect manner. If there were no fluctuations in the intensity of the lamp, this line can
be located after the shock tube is evacuated and before filling the driven section with the test gas. But since there were fluctuations in the output, it was noticed that between the time a level was recorded photographically and the time of generating the shock after the tube was filled, the trace would have moved up or down, in a manner unrelated to the amount of absorber in the test gas. In order to obtain the true zero absorber level, very high temperature runs were made where total decomposition of hydrogen peroxide took place and the relation between $I_o$ and $I_1$ obtained from these shots. This relation could then be used in slower runs also at lower temperatures to locate the zero absorber level even when 100% decomposition of hydrogen peroxide had not occurred. This way, since each experiment could be individually calibrated, experiments could be made at different times under different lamp operating conditions.

CD represents the level at the start of an experiment after the driven section was filled with the test gas mixture. Hence $I_o - I_1$ corresponds to the intensity absorbed by the hydrogen peroxide at room temperature. $E_I$ and $E_R$ correspond to the intensity levels immediately behind the incident and reflected shock waves respectively.

The data are evaluated by noting that hydrogen peroxide vapor follows Beer's law of absorption. Hence, we can write

$$I = I_o \exp(-\mu c l) \quad (1)$$
Taking logarithms and then differentiating with respect to time \( t \), we obtain

\[
\frac{d}{dt} \frac{\ln c}{c} = \frac{d}{dt} \left( \frac{\ln \ln \frac{I}{I_0}}{I_0} \right) \quad (7)
\]

Now, we can write the basic expression for the disappearance of hydrogen peroxide as

\[
\text{H}_2 \text{O}_2 + M \rightarrow \text{Products} \quad (8)
\]

Using \( K_{\exp} \) to denote an apparent first order rate constant,

\[
-\frac{d}{dt} \left[ \text{H}_2 \text{O}_2 \right] = K_{\exp} \left[ \text{H}_2 \text{O}_2 \right] \quad (9)
\]

\[
- K_{\exp} = \frac{d}{dt} \left( \ln \left[ \text{H}_2 \text{O}_2 \right] \right) = \frac{d}{dt} \left( \ln \ln \frac{I}{I_0} \right) \quad (10)
\]

From equation (10), we note that a plot of \( \ln \ln \frac{I}{I_0} \) against time \( t \) for each experiment will give \( K_{\exp} \) for that temperature and initial concentration. The schlieren effect causes some uncertainties in some of the traces in the first few microseconds. But the curve can be extrapolated back to time \( t=0 \) and the slope measured.
to obtain the initial rate. To read \( t \) and \( I \) accurately a magnifier with cross-hairs was used. A typical plot of \( \ln \frac{I}{I_0} \) against \( t \) is given in fig. 10.

In order to make a quick rough check on the data as the experiments were being made, another simple method of analysis was devised. This method was primarily intended to give a first estimate on the initial reaction rate, but the agreement between the rates found by this method and those determined more rigorously by use of equation (10) was very good. In this method, a tangent is drawn through the first 10% of the decomposition as accurately as possible with a fine scriber. Fig. 11 illustrates the method.

Again, from equation (1) we can write

\[
C_x = C_i \left( \frac{\ln \frac{I_x}{I_0}}{\ln \frac{I_5}{I_0}} \right) \tag{11}
\]

where

\[ C_i = \text{initial concentration of hydrogen peroxide behind the reflected shock} \]

and

\[ C_x = \text{concentration of hydrogen peroxide after a time } t_x. \]

Now, integrating equation (10) and combining with equation (11)
we can get

\[-(K_{\text{exp}})_{\text{initial}} = \frac{\ln \left( \frac{I_x}{I_o} \right)}{\ln \left( \frac{I_{x5}}{I_{o5}} \right)} / \Delta t \quad (12)\]

Here $\Delta t = t_x$ if we measure time from the arrival of the reflected shock at the window.

We can obtain $t_x$ in the following manner to make the measurement easier and more reliable. $t$ can be measured accurately from the figure. Then noting that at 10% decomposition condition

\[
\frac{I_x}{I_o} = \left( \frac{I_{5}}{I_{o5}} \right)^{0.9}
\]

we can get, from the triangles shown

\[-(K_{\text{exp}})_{\text{initial}} = \frac{\ln \left( 0.9 \right)}{t \left\{ \left( \frac{I_{5}}{I_{o5}} \right)^{0.9} - \left( \frac{I_{5}}{I_{o5}} \right) \right\} / \left( 1 - \frac{I_{5}}{I_{o5}} \right)} \quad (13)\]

Since we need only intensity ratios, we can measure the intensities in an arbitrary convenient scale. But it should be noted that $-(K_{\text{exp}})_{\text{initial}}$ obtained in this manner is valid only for the initial rate and as will be seen later, the overall rate constant is different from the initial rate constant.
B. Results

Rate constants obtained in the above manner can now be presented in Arrhenius form. Noting that we can write a second order rate constant \( k = k_{e\text{xp}}/[M] \) where \([M]\) represents the concentration of the diluent, we write

\[
k = A \exp\left(-\frac{E_{\text{act}}}{RT}\right)
\]

(14)

where

\(A = \text{frequency factor and}

E_{\text{act}} = \text{activation energy for the reaction.}

It is shown in section VIII that the initiating step in the thermal decomposition of hydrogen peroxide is

\[
\text{H}_2\text{O}_2 + M \overset{k_{15}}{\rightarrow} \text{OH} + \text{OH} + M
\]

(15)

Now, from equation (14) we have

\[
\log_{10} k = \log_{10} A - \frac{E_{\text{act}}}{2.303 \cdot RT}
\]

Thus, a plot of \(\log_{10} k_{15}\) against \(1/T\) will result in a straight line yielding the experimental values of activation energy \(E_{\text{act}}\) and the frequency factor. Fig. 12 shows the Arrhenius plot for mixtures of argon and hydrogen peroxide for total concentrations behind
the shock wave in the range \((1.0 \pm 0.3) \times 10^{-5}\) moles per c.c. and temperatures behind the incident and reflected shock waves in the range of 1200 K to 1500 K. The hydrogen peroxide content in the mixtures varied between 2 and 3%. A least squares straight line through the data yields an activation energy of 43.25 kcal/mole and the following rate constant:

\[
\frac{\varphi}{K_{16}} = 1.87 \times 10^{16} \exp \left(-\frac{43250}{RT}\right) \frac{\text{cm}^3}{\text{mole.sec}}
\]  

Fig. 13 shows similar plots for mixtures of 2 to 3% hydrogen peroxide in nitrogen in the temperature range of 1100 K to 1380 K with total concentrations behind the shock wave being \((2.38 \pm 0.26) \times 10^{-5}\) moles per c.c. A least squares straight line through the data yields the result

\[
\frac{\varphi}{K_{16}} = 2.86 \times 10^{16} \exp \left(-\frac{43150}{RT}\right) \frac{\text{cm}^3}{\text{mole.sec}}
\]  

It is noted that the experimental activation energy is the same in both cases. We can now compare the relative efficiencies of argon and nitrogen as collision partners in the activation step. Taking the efficiency of nitrogen to be 1, we find that the efficiency of argon relative to nitrogen is 0.65. This value agrees very well with the values found by other investigators at lower temperatures.
Fig. 14 shows the results from this work compared with the consolidated results of (16,18,19,20,21 and 22) summarised by Baldwin and Brattan(22). These results representing the temperature range of 720 K to 950 K were obtained from static and flowing systems. It is seen that the agreement is very good.
VI. DISCUSSION

Several earlier investigators of the thermal decomposition of hydrogen peroxide at lower temperatures in flowing and static systems have postulated that the reaction proceeded as a unimolecular reaction. Giguere and Liu (19) observed that experimental difficulties hindered them from performing their experiments at the limiting values of concentrations and pressures, but the data obtained at lower pressures, when extrapolated suggested the existence of such a limiting value. They found a pressure dependence of the apparent first order rate constant which indicated that under their experimental conditions, the reaction behaved like a unimolecular decomposition in its low pressure, second order region. Forst (20) investigated the decomposition by the static method at pressures up to 22 mm of mercury and in the presence of inert gas (helium, oxygen or water) up to 100 mm of mercury. In each case the apparent first order rate constant increased linearly with pressure. He also noted that under his experimental conditions, the reaction exhibited behavior typical of a unimolecular reaction in its low pressure, second order region. Hoare et al (21) also came to the conclusion that the decomposition behaved like a unimolecular reaction.
A unimolecular reaction is one in which the activated complex is formed from a single reactant molecule. Unimolecular reactions are of the first order under certain circumstances, but they become of the second order at low pressures. We will make a brief review of the theory of unimolecular reactions and show how the present work fits into the scheme. Since the present work was conducted with a large amount of diluent, the expressions are shown only for such a special case.

The process of activation by collision is given by

\[ A + M \xrightarrow{k_a} A^* + M \] (18)

In this expression, \( A \) represents the normal molecule and \( A^* \) the activated molecule. The activated molecules can now be either deactivated by collision as

\[ A^* + M \xrightarrow{k_a} A + M \] (19)

or decompose and form products as

\[ A^* \xrightarrow{k_b} \text{Products} \] (20)

We can apply the steady state treatment to \( A^* \), which implies that the rate of production of \( A^* \) is equal to the sum of the rates of
decomposition and deactivation.

\[
-k_a [A][M] = k_a [A^*][M] + k_b [A^*]
\]

From this, it follows that

\[
[A^*] = \frac{k_a [A][M]}{k_b + k_a [M]}
\]

Since we monitor only the concentration of A in the present work, we can write, for the rate of the reaction, the expression

\[
- \frac{d[A]}{dt} = \frac{k_a [A][M] - k_a [A^*][M]}{k_b + k_a [M]}
\]

Two distinct cases exist. At sufficiently high pressures, the rate at which the activated molecules are deactivated by collisions will be high compared to the rate at which the activated molecules are converted into products. Since the activated molecules are in equilibrium with normal molecules, their concentration will be proportional to that of the normal molecules. The rate of the reaction being proportional to the concentration of activated molecules will thus be proportional to the concentration of normal molecules and the reaction will thus be of first order. This can be seen from equation (21).

When \(k_a [M] \gg k_b\), we get

\[
- \frac{d[A]}{dt} = \frac{k_a \cdot k_b \cdot [A] / k_a}{k_b + k_a [M]}
\]
which is of first order.

However, at sufficiently low pressures, if the collisions cannot maintain a supply of activated molecules, the rate of reaction will depend upon the rate of activation and the reaction will therefore be of second order. This case occurs when \( \frac{K_b}{K_a} \gg [M] \) in equation (21) to give

\[
- \frac{d[A]}{dt} = K_a [A] [M]
\]

(23)

Such a change from first order kinetics to second order kinetics as lower pressures are reached has been observed experimentally in a number of instances. Hinshelwood (31) observed that \( K_a \) should not be calculated from the simple collision theory which gives

\[
K_a = \frac{z}{\zeta} \exp \left( -\frac{E^*}{R_T} \right)
\]

(24)

where \( E^* \) is the critical energy. The simple expression is actually only applicable to a molecule having one degree of vibrational freedom. A molecule having greater number of degrees of freedom has a greater possibility of concentrating the energy \( E^* \) on one bond since this energy may now be taken from all the degrees of freedom in the molecule. The rate of activation of a complex molecule may be much
higher than that of a simple molecule, since the probability that it
has an energy greater than \( E^* \) is given by

\[
\left( \frac{E^*}{RT} \right)^{s-1} \cdot \frac{\exp \left( - \frac{E^*}{RT} \right)}{(s-1)!}
\]

where \( s \) represents the number of degrees of vibrational freedom that
may contribute to the energy of activation. The expression to be
used for \( k_a \) therefore becomes

\[
k_a = \frac{Z}{(s-1)!} \cdot \left( \frac{E^*}{RT} \right)^{s-1} \cdot \exp \left( - \frac{E^*}{RT} \right)
\]

This correction accounts for the frequently observed experimental
fact that the kinetics remained of the first order down to a pressure,
at which, according to the simple collision theory, the rate of activa-
tion would not be sufficient to maintain the concentration of active
molecules. In practice, \( s \) is found usually by a method of trial and
error and it is usually possible to explain the results by using a
value of \( s \) that is not greater than the total number of normal vibra-
tional modes in the molecule.

It has been assumed that the critical energy \( E^* \) is such that
one of the oscillators is a weak bond which will break when energy
\( E^* \) is present in it. The experimental activation energy \( E_{act}^* \) differs from \( E^* \) owing to the temperature dependence of the pre-exponential factor in equation (26). It can be shown that the experimental activation energy is related to the critical energy \( E^* \) by the relation

\[ \frac{E_{exp,act}}{E_{act}} = E^* - (s - \frac{3}{2}) kT \]  

(27)

The significance of this result is not that molecules with energy less than \( E^* \) may react but rather that the experimental activation energy will be the difference in the average energy between the reacting molecules and the normal molecules. At the low pressures, where equation (27) is valid, the specific rate of reaction of molecules with energies in excess of \( E^* \) is so great compared to the rate of their production that the steady state concentration of such molecules is negligible compared to that of molecules with energies very close to \( E^* \). Since the average molecule in the system has energy \( skT \), we see that at these low pressures, the average reacting molecule has energy \( E^* + kT \). The difference is \( E^* - (s-1) kT \) and this differs from \( E^* - (s-3/2) kT \) by the quantity \( 1/2 kT \) contributed by the temperature dependence of collision frequency.

An attempt was made to conduct experiments at different total pressures of the mixture. The limitation of the monitoring equipment
precluded such a study. The shock tube being of only 1.5 inches I.D. presented a very small path length for absorption. Further, due to the very low extinction coefficient of hydrogen peroxide and the necessarily low partial pressure of the peroxide in the mixture, the percentage absorption was very low. Hence, decreasing the partial pressure of hydrogen peroxide further decreased the absorption so much that no reliable measurements could be made. The problem was a combination of effects from the source of illumination, the low path length, the low extinction coefficient, the photomultiplier and the corresponding circuitry. Considerable effort was put in designing a suitable circuitry for the photomultiplier base to filter the noise from the lamps, but it was found to be impossible to design one without an accompanying tremendous loss in response time characteristics. Since the absorption was small, the oscilloscope had to be set at a very high sensitivity at which the noise from the lamp drowned out the absorption trace almost completely. This precluded studies with peroxide concentrations below $2.0 \times 10^{-7}$ moles/c.c. in the shock tube. Hence pressure could not be varied much in the lower region.

Higher pressures also could not be used for a different reason. The saturated vapor pressure at room temperature for hydrogen peroxide is only 1.9 mm of mercury and this low value creates condensation problems at high pressures. Another method that can be resorted to is keeping the mixture at higher initial temperature to raise its
vapor pressure. This would then permit the use of higher total pressures in the driven section prior to generating the shock. But this involves enormous problems of keeping a constant temperature surrounding from the mixing system through the inlet ports and then the entire length of the driven section of the shock tube. The shock tube had a polyethylene liner and this meant that any heating arrangement would have to take account of the double walls of the shock tube. It was felt that it would be extremely difficult to maintain a constant temperature throughout the system. Possibilities of forming isolated hot and cold spots were strong and this might create local pockets of condensation and surface reaction. Also temperature measurements of the driven gas prior to being shock-heated would be subject to errors. Errors in $T_1$ would cause considerable errors in $T_2$ and $T_5$, the temperatures behind the incident and reflected shocks respectively. This error would tend to make the data unreliable.

Another method of varying concentration or pressure is to vary the shock strength considerably in order to get higher pressure ratios and temperature ratios. There is a limitation to this approach also. At the low temperature end, below the lowest temperatures measured in argon and nitrogen runs, the rate of disappearance of hydrogen peroxide was too slow to be observed with accuracy within the test times. At the high temperature end, experiments were made up to the highest temperatures at which reasonably accurate evaluation of
the oscilloscope trace was possible. With the rates getting very high above 1500 K in argon and 1380 K in nitrogen mixtures, the slope of the absorption curves on the oscilloscope trace was too steep even at a sweep rate of 5 μsec/cm. It was found to be undesirable to sweep faster than this in view of the Schlieren effect which would then severely interfere with the decomposition trace.

By comparison with the pressure ranges of the low temperature work quoted earlier, it is apparent that the pressure range of the present work falls within the low pressure limit of unimolecular decomposition. The indication that a unimolecular reaction may be expected comes from the high pre-exponential factor and also the experimental activation energy which appears to be several kcal less than the energy required to break the O-O bond in hydrogen peroxide molecule.

Now, writing the initial step as a unimolecular decomposition step, we have

\[ \text{H}_2\text{O}_2 + \text{M} \xrightarrow{R_{28}} \text{H}_2\text{O}_2^* + \text{M} \tag{28} \]

\[ \text{H}_2\text{O}_2^* + \text{M} \xrightarrow{R_{29}} \text{H}_2\text{O}_2 + \text{M} \tag{29} \]

\[ \text{H}_2\text{O}_2^* \xrightarrow{R_{30}} \text{OH} + \text{OH} \tag{30} \]
We may write the subsequent steps as (see section VII)

\[
\text{OH} + \text{H}_2\text{O}_2 \xrightarrow{K_{31}} \text{HO}_2 + \text{H}_2\text{O} \tag{31}
\]

\[
\text{OH} + \text{HO}_2 \xrightarrow{K_{32}} \text{H}_2\text{O} + \text{O}_2 \tag{32}
\]

Assuming steady state concentrations for \(\text{OH}, \text{HO}_2\) and \(\text{H}_2\text{O}_2\) we have

the following expressions:

\[
\left[\text{H}_2\text{O}_2^*\right] = \frac{K_{28} \left[\text{H}_2\text{O}_2\right] \left[M\right]}{K_{29} \left[M\right] + K_{30}} \tag{33}
\]

\[
[\text{OH}] = \frac{2 K_{30} \left[\text{H}_2\text{O}_2^*\right]}{K_{31} \left[\text{H}_2\text{O}_2\right] + K_{32} \left[\text{HO}_2\right]} \tag{34}
\]

\[
[\text{HO}_2] = \frac{K_{31} \left[\text{OH}\right] \left[\text{H}_2\text{O}_2\right]}{-K_{32} \left[\text{OH}\right]} \tag{35}
\]

The rate of disappearance of \(\text{H}_2\text{O}_2\) is then given by

\[
\frac{d \left[\text{H}_2\text{O}_2\right]}{dt} = -K_{28} \left[\text{H}_2\text{O}_2\right] \left[M\right] + K_{29} \left[\text{H}_2\text{O}_2^*\right] \left[M\right] \]

\[-K_{31} \left[\text{OH}\right] \left[\text{H}_2\text{O}_2\right]
\]

Substituting from equations (33) and (34), we get
The expression for the observed apparent first order rate constant thus becomes

\[
\begin{align*}
\frac{d[H_2O_2]}{dt} &= -k_{28} [H_2O_2] [M] + \frac{k_{28} \cdot k_{29} [H_2O_2][M]^2}{k_{29} [M] + k_{30}} \\
&\quad - \frac{k_{28} \cdot k_{30} [H_2O_2][M]}{-k_{29} [M] + k_{30}}
\end{align*}
\]

(35)

Equation (37) shows that the rate constant for the overall reaction is twice the rate constant \( k_{28} \) for the activation of
hydrogen peroxide to $H_2O_2^*$. Earlier, we showed that $k_{28}$ is equal
to the rate constant $k_{15}$ for the overall initiating step under the
conditions of low pressure second order unimolecular decomposition.
It is thus seen that subsequent reactions double the rate constant
for the overall disappearance of hydrogen peroxide.

With the use of the experimentally determined rate constants in
the expressions (26) and (27), the critical energy and the number
of effective classical oscillators involved in activating the mole­
cule to its critical energy can be determined by a trial and error
method as follows .

Rewriting the expressions for convenience, we have

$$\frac{R}{R_{\text{theor}}} = \frac{Z}{(8-1)!} \left( \frac{E^*}{R^*T} \right)^{(8-1)} \cdot \exp \left( -\frac{E^*}{RT} \right)$$  \hspace{1cm} (26)

$$E^* = E_{\exp, \text{act}} + (8 - \frac{3}{2}) RT \quad \hspace{1cm} (27)$$

Here $Z$ is the collision number defined as the number of colli-
sions per second when there is only one molecule of each species per

c.c. 

$$Z = \sigma_{AB}^2 \cdot N_A \left[ \frac{1}{2} \pi \cdot m \cdot (m_A + m_B) \cdot m_A m_B \right]^{1/2} \quad \hspace{1cm} (38)$$
where
\[ \overline{\sigma_{AB}} = \text{mean collision diameter} = \frac{\sigma_A + \sigma_B}{2} \]
and \( k = \text{Boltzmann constant} \)

\( m_A \) and \( m_B \) are the mass per particle of species A and B respectively.

Using appropriate values, we can get

\[ Z_{\text{Ar}, \text{H}_2\text{O}_2} = 6.3 \times 10^{12} \times T^{1/2} \text{ c.c./mole.sec} \]
\[ Z_{\text{N}_2, \text{H}_2\text{O}_2} = 7.15 \times 10^{12} \times T^{1/2} \text{ c.c./mole.sec} \]

Values of \( s \) from 1 to 6 are used in equation (27) to obtain the corresponding values for \( E^* \). Substituting these known values in equation (26), a value of \( \frac{E_{\text{theor}}}{E_{\text{exp}}} \) is found for each \( s \) and compared with the \( \frac{E_{\text{theor}}}{E_{\text{exp}}} \) at the two extremes of the temperature range in each case. The value of \( s \) which gives the value of \( \frac{E_{\text{theor}}}{E_{\text{exp}}} \) closest to the \( \frac{E_{\text{theor}}}{E_{\text{exp}}} \) at the two extremes of temperature is chosen as the best value. Another point that should be checked is a comparison of the value of \( E^* \) with the known bond energy for the 0-0 bond of hydrogen peroxide. Tables (2) and (3) give the calculations for the case of hydrogen peroxide-argon mixtures and hydrogen peroxide-nitrogen mixtures respectively. From the tables, it is seen that \( s = 4 \) fits best for both cases. Also, in both cases, the average critical energy for activation is about 49.5 kcal/mole.
This value agrees closely with the energy of 48.5 kcal/mole for the O-O bond of hydrogen peroxide.
VII. MECHANISM

There are several possibilities for the first step in the thermal decomposition of hydrogen peroxide. The structure of the molecule is shown in fig. 15. Obviously, the only two direct possibilities for the first step are the breaking of the O-O bond to form two OH radicals or rupture of an OH bond to form an HO\textsubscript{2} radical and a hydrogen atom. The first of these possibilities requires about 99 kcal/mole as compared to about 90 kcal/mole for the splitting of an O-H bond\textsuperscript{(1)} and would therefore appear more probable. Evidence for this initiating step has been obtained by several authors in photochemical decomposition. Volman\textsuperscript{(26,33)} did not find any evidence of atomic hydrogen due to the initiating step in the photodecomposition of hydrogen peroxide. Urey, Dawsey and Rice\textsuperscript{(34)} also found that atomic hydrogen was absent in the products of an electrical discharge through hydrogen peroxide vapor. They also observed OH emission indicating its presence. G. von Elbe\textsuperscript{(35)} also found evidence of OH radicals in the decomposition of hydrogen peroxide. More recently Greiner\textsuperscript{(36)} found that the only products from flash photolysis of pure hydrogen peroxide vapor and hydrogen peroxide mixtures containing deuterium, argon and water were OH ($^{2}\text{I}_{\frac{1}{2}}$) and OH ($^{2}\text{I}_{\frac{3}{2}}$). No evidence
of atomic hydrogen was found. Giguere and Liu (19) analysed the products from complete thermal decomposition of hydrogen peroxide vapor at 470°C by mass spectrometry and found negligible quantities of molecular hydrogen. If free hydrogen atoms were formed at any stage of the reaction, then measurable amounts of molecular hydrogen would have appeared as a result of secondary reactions such as

\[ H + H_2O \rightarrow H_2 + OH \]

and

\[ H + H + M \rightarrow H_2 + M \]

It has also been found that no free oxygen atoms were formed indicating that the step \( H_2O_2 + M \rightarrow H_2O + O + M \) is also not possible. Further this step is too complex for a single act in the gas phase. By similar reasoning

\[ H_2O_2 + M \rightarrow H_2 + O_2 + M \]

\[ H_2O_2 + M \rightarrow H + H + O + O + M \text{ etc} \]

can also be abandoned either from energy considerations or obvious probability considerations. Hence, it appears from energy considerations that the most probable initiating step in the thermal decomposition of hydrogen peroxide is the splitting of the peroxide molecule into two OH radicals. Yet, no direct experimental evidence is available to confirm this step in the thermal decomposition mechanism since OH concentration could not be monitored in the thermal decompo-
sition experiments at lower temperatures. Since the shock tube provides a unique facility to observe such species, it was decided to verify experimentally that OH was formed in the thermal decomposi-
tion of hydrogen peroxide.

The apparatus was the same as described in section IV. The wave length region of observation was changed since the head of the 0-0 band of the \( ^2\Sigma - ^2\Pi \) transition of OH radical occurs at 3064 Å. Hydrogen peroxide also absorbs in this region continuously without showing a discrete spectrum. Absorption by peroxide created compli-
cations since at any time the absorption is the combined effect of absorption due to the disappearing hydrogen peroxide and the OH that is expected to be formed from the disappearing hydrogen peroxide. It was difficult to determine the rate of the OH formation quanti-
tatively due to this competing effect. Hence this study was limited to showing qualitatively that OH was formed.

Figure 16 shows a trace obtained at 3090 Å with a slit width of monochromator of 20μ giving a resolution of 2 Å. The tempera-
ture behind the incident shock wave was 2200°K in a 2% hydrogen peroxide + Argon mixture. It is seen that there is a very sharp rise in the absorption level followed by a period of constant absorption. This sharp rise in absorption can be attributed to the formation of OH behind the shock due to the almost instantaneous decompostion of hydrogen peroxide. From the rate constant \( k_{Ar} \), it is seen that for 90% of the initial concentration of hydrogen
peroxide to disappear at a temperature of 2200°K, it takes only 0.25 \mu\text{sec}. This fact was verified by running experiments at these temperatures at 2700 Å which showed that the hydrogen peroxide disappearance was so rapid that only the Schlieren effect was seen after which the trace returned to the zero-absorber level. OH does not absorb at 2700 Å. The other species that may exist in the shock tube besides hydrogen peroxide and OH are \( \text{H}_2\text{O}, \text{O}_2, \text{H}_2, \text{HO}_2 \), etc. and none of these has absorption spectra at 3090 Å. This indicates strongly that OH is the absorber in the tube and it should have come from the decomposition of hydrogen peroxide only.

For further confirmation, experiments were made at different wavelengths around the 3064 Å band of OH. Experiments made at 3020 Å and 3150 Å at these temperatures showed no absorption at all and from (40) it is seen that there are practically no OH lines at these wavelengths. Experiments were also made at closely spaced wavelength intervals from 3000 Å and it was possible to observe the distinct onset of absorption in the region of 3064 Å confirming the presence of OH.

Figure 17 shows a trace obtained at 1400°K behind the incident shock at 3090 Å with a slit width of 1.1 mm corresponding to about 40 Å. It is noticed that a product is formed gradually, stays stationary for a short time and then starts disappearing. Comparing Figure 17 with Figure 16 it is obvious that at the lower temperature in Figure 17, peroxide disappearance is slower and hence a gradual
formation of OH causes the gradual rise in the absorption level. After a certain interval of time, a steady state is attained in the OH concentration following which OH is consumed in further reactions. This fits in well with the mechanism described in section VII. Experiments made at this temperature at a wavelength of 2700 Å which is outside of the OH region show a finite rate of decomposition of hydrogen peroxide which confirms the observation in this figure. It is not possible to measure a rate of formation of OH from Figure 17 since no calibration of the absorption intensity with respect to OH concentration could be made.

It is seen from the above discussion that it was possible to obtain qualitative information that the products of the initial step in the hydrogen peroxide decomposition are two OH radicals. Hence it appears safe to assume the reaction

\[ \text{H}_2\text{O}_2 + M \rightarrow \text{OH} + \text{OH} + M \]

as the first step.

The most probable following step is the reaction of these OH radicals with hydrogen peroxide as follows:

\[ \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2 \]

The recombination reaction

\[ \text{OH} + \text{OH} + M \rightarrow \text{H}_2\text{O}_2 + M \]

is very unlikely since the probability of such three body collisions in the gas phase is negligible considering the low steady state
concentration of OH radicals. Next, all possible branching chain mechanisms involving the above species have been shown to be endothermic \(^{(1)}\) from energy values available. These are thus unlikely.

Giguere and Liu \(^{(19)}\) have summarized reasons from tests and observation from other investigators to show that a chain mechanism is very unlikely. Following Giguere and Liu \(^{(19)}\) and Forst \(^{(20)}\), we can write the final step as

\[
\text{OH} + \text{HO}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2
\]  

(41)

The overall reaction thus becomes

\[
\text{H}_2\text{O}_2 + \text{M} \longrightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + \text{M}
\]  

(42)
VIII. CONCLUSIONS

From the investigation conducted and results presented, it has been shown that the homogeneous thermal decomposition of hydrogen peroxide occurs via the initial splitting of the peroxide molecule into two OH radicals. The direct experimental observation of the presence of OH behind the shock wave proves conclusively the above statement for the first time. This initiating step has been shown to occur as a unimolecular reaction in its low pressure second order region requiring an activation energy of about 49 kcal/mole which compares very well with the value of 48.5 kcal/mole for the breaking of the O-O bond of the peroxide molecule. At the temperature range investigated, argon has been found to be 0.65 times as efficient as nitrogen as a collision partner in the decomposition reaction. This shows that nitrogen may contribute rotational and vibrational energies in the collision whereas argon transfers only translational energy and this leads to the difference in their efficiencies.

This investigation illustrates the advantage of using the shock tube technique in investigating the thermal decomposition of hydrogen peroxide at higher temperatures over the conventional flow techniques. It has been possible to monitor the concentration of the peroxide
itself spectroscopically providing time resolution heretofore not possible in this reaction using flow techniques. Earlier attempts at investigating this reaction at temperatures above 900°K by several authors have been unsuccessful apparently due to the high rate of the reaction and the competing heterogeneous reactions. The shock tube technique has allowed study of the homogeneous reaction at temperatures up to 1500°K.

The use of a polyethylene liner on the inside of the shock tube has been shown to reduce the surface decomposition considerably at room temperature. Though high temperatures are obtained in the shock tube, the time that the gas is at these high temperatures is so small that the temperature of the inner wall of the tube is far below that of the gas. Hence damage to the liner is not a problem unless excessively high temperatures are attained. In conventional flow systems the reaction vessel generally acts as a furnace the walls of which are nearly at the temperature of the gas. Use of a polyethylene liner in such systems is not possible due to possible damage to the material on account of the high temperature.

Efforts made in this study to measure concentrations of OH behind the shock and to correlate the rate of formation of OH with the rate of disappearance of hydrogen peroxide proved unsuccessful due to the very difficult nature of the calibration and also due to the unsuitable light source. A flash discharge producing an intense OH line spectrum of the 3064 Å band would be a desirable source
but the synchronisation problem may be enormous. With proper synchronisation, it may be possible to calibrate a photomultiplier setup to give measured output currents for known amounts of OH in the discharge tube. This flash discharge may then be used as a source and absorption by the gas in the shock tube may be related to quantities of OH. Yet, the problem of simultaneous absorption of the radiation by hydrogen peroxide may still exist. This problem will have to be solved before obtaining quantitative results on the rate of formation of OH in the thermal decomposition of hydrogen peroxide.
APPENDIX 1

Calculation of Thermodynamic Properties behind Incident and Reflected Normal Shock Waves
Calculation of thermodynamic properties behind incident and reflected normal shock waves is very straight-forward for gases with constant specific heats. But under conditions where the specific heats vary with temperature, calculations must be based on the actual enthalpies of the gases. Calculations based on constant specific heats are valid only for cases where the internal degrees of freedom of the molecule are frozen, whereas calculations involving the actual enthalpies represent the case where complete thermodynamic equilibrium prevails.

It is convenient to use a coordinate system moving with the shock wave in order to derive the equations for determining the thermodynamic properties. The incident shock wave travels with a velocity \( w_1 \) into the stationary gas containing the mixture of hydrogen peroxide and the diluent in region 1. (Figure 18). We can then write the conservation equations as follows:

Continuity: \( Q_1 w_1 = Q_2 (w_1 - u_2) \) \hspace{1cm} (A1)

Momentum: \( p_1 + Q_1 w_1^2 = p_2 + Q_2 (w_1 - u_2)^2 \) \hspace{1cm} (A2)

Energy: \( h_1 + \frac{1}{2} w_1^2 = h_2 + \frac{1}{2} (w_1 - u_2)^2 \) \hspace{1cm} (A3)

Here \( u_2 \) is the particle velocity in region 2 with respect to the laboratory-fixed coordinate and \( h \) is the specific enthalpy. From equation (A1) and (A2), the shock velocity is obtained as
Substituting equations \(A4\) and \(A1\) into \(A3\), we get

\[
W_1 = \sqrt{\frac{p_1}{s_1} \frac{(\frac{p_2}{p_1} - 1)}{(1 - \frac{s_1}{s_2})}} \tag{A4}
\]

Since we are interested in conditions immediately behind the shock wave before the chemical reactions set in, we can write \(n_1 = n_2\) and obtain from \(A5\)

\[
h_2 - h_1 = \frac{1}{2} \frac{p_1}{s_1} \left( \frac{p_2}{p_1} - 1 \right) \left( 1 + \frac{s_1}{s_2} \right) \tag{A5}
\]

Here \(\gamma_i\) represents the mole fraction of species \(i\). The procedure to use these equations is to assume a value of \(\frac{T_2}{T_1}\) and calculate \(\frac{p_2}{p_1}\) from \(A5\) and thence obtain \(W_1\) from equation \(A4\) using the known conditions of \(p_1, T_1\) and \(\gamma_i\). Note that conditions in region \(I\) are assumed to be known.

To obtain the properties behind the reflected shock wave, we use a coordinate system attached to the reflected shock wave and the following nomenclature (also see Figure 19):
\( w_{R,R} \) = Velocity of reflected shock wave relative to the twice shocked gas.

\( w_{R,2} \) = Velocity of reflected shock wave relative to the once shocked gas.

We can then write the conservation equations as follows:

**Continuity:**

\[ S_2 W_{R,2} = S_R W_{R,R} \]  \( A7 \)

**Momentum:**

\[ P_2 + S_2 W_{R,2}^2 = P_R + W_{R,R}^2 \]  \( A8 \)

**Energy:**

\[ h_2 + \frac{1}{2} W_{R,2}^2 = h_R + \frac{1}{2} W_{R,R}^2 \]  \( A9 \)

We obtain as before

\[ W_{R,2}^2 = \frac{P_2}{S_2} \left( \frac{P_R}{P_2} - 1 \right) \left/ \left( 1 - \frac{S_R}{S_2} \right) \right. \]  \( A10 \)

Substituting from equation (A10) into (A9) we can get

\[ \left( \frac{P_R}{P_2} \right)_a = \frac{T_R}{T_2} \left[ \sum \gamma_i \left( \frac{H-E_o}{\partial T} \right)_{i,T_R} - \frac{1}{2} \right] - \left[ \sum \gamma_i \left( \frac{H-E_o}{\partial T} \right)_{i,T_2} - \frac{1}{2} \right] \]

\[ + \left/ \left[ \frac{T_R}{T_2} \left[ \sum \gamma_i \left( \frac{H-E_o}{\partial T} \right)_{i,T_R} - \frac{1}{2} \right] - \left[ \sum \gamma_i \left( \frac{H-E_o}{\partial T} \right)_{i,T_2} - \frac{1}{2} \right] \right] \right)^2 + \frac{T_R}{T_2} \]  \( A11 \)
But now \( \frac{T_R}{T_2} \) cannot be chosen arbitrarily. It is determined by a second relationship between \( \frac{P_R}{P_2} \) and \( \frac{T_R}{T_2} \) obtained from the continuity and momentum equations:

\[
\left( \frac{P_R}{P_2} \right)_b = \frac{1}{2} \left[ \frac{T_R}{T_2} + 1 + \left( 1 - \frac{P_1}{P_2} \right) \left( \frac{\gamma}{\gamma-1} - 1 \right) \right] + \sqrt{\left( \frac{1}{2} \left[ \frac{T_R}{T_2} + 1 + \left( 1 - \frac{P_1}{P_2} \right) \left( \frac{\gamma}{\gamma-1} - 1 \right) \right] \right)^2 - \frac{T_R}{T_2}}
\]

(A12)

This shows that for the conditions behind the reflected shock, we have to use an iterative procedure. The procedure is to assume a value of \( \frac{T_R}{T_2} \) and from the known values of \( \frac{P_R}{P_1} \), \( \frac{T_R}{T_1} \) etc. solve for \( \left( \frac{P_R}{P_2} \right)_a \) and \( \left( \frac{P_R}{P_2} \right)_b \) from equations (A11) and (A12) respectively until a value of \( \frac{T_R}{T_2} \) is chosen for which \( \left( \frac{P_R}{P_2} \right)_a = \left( \frac{P_R}{P_2} \right)_b \). This, then is the required value of \( \frac{T_R}{T_2} \).

A FORTRAN IV program was developed for use in the OSU computer (IBM 360) to solve for the conditions behind the incident and reflected shock waves. The program is reproduced in Appendix 2. The secant method was used for iteration for \( \frac{T_R}{T_2} \) and it was found that convergence was rapid. Values of \( \frac{H-E_0}{\gamma-1} \) were obtained from references (37) and (38).
APPENDIX 2

Computer Program for Calculation of Thermodynamic Properties behind Incident and Reflected Shock Waves in Hydrogen Peroxide - Inert Diluent Mixtures
REAL MWTRSMWTIS
COMMON H (245, 61), HT1 (4), HT2 (4), CP (113, 28), CP1 (4), T1, T2, ETAIS, ET
2ARS, MWTIS, MWTRSMWTIS, P1, P2, HT (4), P12, P21, RH012, RH021
DO 10 J = 1, 2
READ (5, 11) (H(J, I), I = 1, 61)
10 READ (5, 11) (CP(J, I), I = 1, 28)
WRITE (6, 12)
FORM A T (7F10.1)
READ (5, 11) (CH(J, I), I = 1, 61)
11 FORMAT (7F10.1)
WRITE (6, 12)
FORMAT (1H1, 10X, 82HTHERMODYNAMIC DATA USED FOR THE EVALUATION OF NO 2N-REACTING SHOCK WAVE CALCULATIONS/1H0.28HHEAT OF FORMATION OF SPE CIES/10X, 85HSPECIFIC HEATS (CONSTANT PRESSURE) OF SPECIES/1H0.4HTE MP/12H H202(G) , 12H CARRIER/12H H202(G) , 12H CARRIER/5)
DO 13 J = 1, 21
JK = (J - 1) * 100
13 WRITE (6, 13) JK, (H(I, J), I = 1, 2), (CP(I, J), I = 1, 2)
FORMAT (1H1, 114, 2F12.1, 2F12.4)
DO 14 J = 22, 61
JK = (J - 1) * 100
14 WRITE (6, 14) JK, (H(I, J), I = 1, 2)
FORMAT (1H1, 114, 2F12.1)
15 READ (5, 15) T2, T1, ETAPS, ETAIS, MWTRSMWTIS
14 FORMAT (1F10.3) T2 = T2 * EQ = 0.1 Go To 399
15 FORMAT (6F10.3) J = (T1 / 100.) + 1.0
DO 16 I = 1, 2
DH1 = (H(I, J + 1) - H(I, J)) / 100.
\[ DH_2 = \frac{H(I \cdot J+2) - H(I \cdot J+1)}{100}. \]
\[ DDH = \frac{DH_2 - DH_1}{200}. \]

16. \[ HT_1(I) = H(I \cdot J) \cdot \left( T_1 - \text{FLOAT}(J \cdot 10^2) \right) \cdot \left( DH_1 + \left( T_1 - \text{FLOAT}(J+1) \cdot 10^2 \right) \cdot DDH \right) \]
\[ J = \frac{T_2}{100} \cdot 1.0 \]

18. \[ DH_1 = \frac{H(I \cdot J+1) - H(I \cdot J)}{100}. \]
\[ DH_2 = \frac{H(I \cdot J+2) - H(I \cdot J+1)}{100}. \]
\[ DDH = \frac{DH_2 - DH_1}{200}. \]

19. \[ HT_2(I) = H(I \cdot J) \cdot \left( T_2 - \text{FLOAT}(J \cdot 10^2) \right) \cdot \left( DH_1 + \left( T_2 - \text{FLOAT}(J+1) \cdot 10^2 \right) \cdot DDH \right) \]
\[ T_21 = \frac{T_2}{T_1} \]
\[ A = \left( ETAIS \cdot (HT_2(2) - HT_1(?) \right) + ETAIS \cdot (HT_2(1) - HT_1(1)) \right) / \left( 1.9872 \cdot T_1 \right) + 0.5 - 0.25 \cdot T_21 \]
\[ P_21 = A \cdot \text{SQR} \left( A \cdot A + T_21 \right) \]
\[ R_021 = P_21 / T_21 \]
\[ R_012 = 1.0 / R_021 \]
\[ W_1 = \text{SQR} \left( 8314.3 \cdot T_1 / \text{AMOLWT} \right) \cdot \left( P_21 - 1.0 \right) / \left( 1.0 - R_012 \right) \]
\[ \text{WRITE} (6 \cdot 20) \]

20. \[ \text{FORMAT} (1H1, 1H0, 1S, 189, \text{H} \text{P} \text{R} \text{O} \text{P} \text{E} \text{R} \text{O} \text{D} \text{I} \text{E} \text{G} \text{A} \text{S} \text{ M} \text{I} \text{T} \text{U} \text{R} \text{E} \text{S} / 1 \text{HO}) \]
\[ \text{WRITE} (6, 21) \]

21. \[ \text{FORMAT} (1H0, 1S, 3H, 3H, 3H, 3H, 3H, 3H, 3H, 3H) \]
\[ \text{WRITE} (6, 21) \]

22. \[ \text{FORMAT} (1H0, 1S, 3H, 3H, 3H, 3H, 3H, 3H, 3H, 3H) \]
\[ \text{WRITE} (6, 21) \]

23. \[ \text{FORMAT} (1H0, 1S, 3H, 3H, 3H, 3H, 3H, 3H, 3H, 3H) \]
\[ \text{WRITE} (6, 21) \]

24. \[ \text{FORMAT} (1H0, 1S, 3H, 3H, 3H, 3H, 3H, 3H, 3H, 3H) \]
\[ \text{WRITE} (6, 21) \]

25. \[ \text{FORMAT} (1H0, 1S, 3H, 3H, 3H, 3H, 3H, 3H, 3H, 3H) \]
\[ \text{WRITE} (6, 21) \]

26. \[ \text{FORMAT} (1H0, 1S, 3H, 3H, 3H, 3H, 3H, 3H, 3H, 3H) \]
\[ \text{WRITE} (6, 21) \]

27. \[ \text{FORMAT} (1H0, 1S, 3H, 3H, 3H, 3H, 3H, 3H, 3H, 3H) \]
\[ \text{WRITE} (6, 21) \]
$DENSITY\ RATIO(RH02/RH01) = F16.4/1H0*46X*45H\ INVERSE\ OF\ INCIDENT\ DENSITY\ RATIO(RH01/RH02) = F16.4/1H0*46X*29H\ INCIDENT\ SHOCK\ VELOCITY(W1)\ G = 1F15.4*6H\ M/SEC/1H0*46X*20H\ REACTING\ SPECIES = F16.4/1H0*46X*14\ 7H\ INERT\ SPEC = F16.4/1H0*46X*1\ 87H\ MOLWT\ INERT\ SPEC = F16.4)$
$TRG = 1000.0$
$TRG1 = 1.05 * TRG$
$Y = F(TRG1)$
$Y1 = F(TRG1)$
$WRITE(6,22) TRG, TRG1, Y, Y1$
$DO 23 I = 2, 50$
$TRG2 = (TRG * F(TRG1) - TRG1 * F(TRG)) / (F(TRG1) - F(TRG))$
$TEMPCH = (TRG2 - TRG1) / TRG1$
$Y = F(TRG1)$
$Y1 = F(TRG2)$
$PRESCH = (Y1 - Y) / Y1$
$WRITE(6,24) I, TRG2, Y1, TEMPCH, PRESCH$
$FORMAT(1H4*4*4H, TRG2 = F10.4, 4X, 3HY1 = F10.4, 4X, 3HY2 = F10.4, 4X, 7H, TEMPCH = F10.4)$
$IF(ABS(TEMPCH) LE.01.AND. ABS(PRESCH) LE.01) GOTO 26$
$TRG = TRG1$
$23 TRG1 = TRG2$
$WRITE(6,25)$
$FORMAT(1H4*4*58H, NO\ CONVERGENCE\ IN\ FIFTY\ STEPS, PROCEEDING\ TO\ NEXT\ DATA\ CARD)$
$GOTO 142$
TR = TRG2
T = TR
J = (T/100.)*1.0
DO 27 I = 1, 2
   DH1 = (H(I*J+1) - H(I*J))/100.
   DH2 = (H(I*J+2) - H(I*J+1))/100.
   DDH = (DH2 - DH1)/200.
27   HT(I) = H(I*J) + (T-FLOAT(J)*100.)* (DH1+(T-FLOAT(J+1)*100.)*DDH)
   TR2 = T/T2
   B = ETAIS*(HT(2)-HT2(2)) + ETARS*(HT(1)-HT2(1))/(1.9872*T2)+0.5-0.5*
      2TR2
   PR2A = B + SQRT(B+B+TR2)
   P12 = 1.0/P21
   C = 0.5*(TR2+1.0+(1.0-P12)* (RHO21-1.0))
   PR2B = C + SQRT(C+C-TR2)
   PR2 = (PR2A+PR2B)/2.0
   PR1 = PR2*P21
   RHO2 = PR2/PR2
   RHO1 = RHO2*RHO21
   TR2 = TR/T2
   TR1 = TR2*T21
   WRITE (6*28) TR, TR2, TR1, RHO2, RHO1, PR2A, PR2B, PR2, PR1
   WRITE (6*32) TR, TR2, TR1, RHO2, RHO1, PR2A, PR2B, PR2, PR1
28   FORMAT (1H0, 2X, 3HTR=, F9.2, 4X, 4HTR2=, F9.2, 4X, 6HHR0R2=)
2*F10.4*4X*6HRH01= taper F10.4/2X*5HP R2A=*F10.4*4X*5HP R2B=*F10.4*4X*4HP R
32=*F10.4*4X*4HP R1=+1F10.4)
GOTO 142
999 CALL EXIT
END
FUNCTION F(T)
COMMON H(245*61),HT1(4),HT2(4),CP(113*28),CP1(4),T1,T2,ETAIS,ETARS,MWTIS,MWRS,P1,P2,HT(4),P12,P21,RHO12,RHO21
J=(T/100.)+1.0
DO 29 I=1+2
DH1=(H(I,J)+H(I-1,J))/100.
DH2=(H(I,J+2)-H(I,J+1))/100.
DDH=(DH2-DH1)/200.
HT(I)=H(I,J)+(T-FLOAT(J)*100.)*(DH1+(T-FLOAT(J+1)*100.))*DDH
TR2=T/T2
B=ETAIS*(HT(2)-HT2(2)) + ETAI*(HT(1)-HT2(1))/(1.9872*T2)+0.5-0.5*TR2
PR2A=B+SQRT(B*B+TR2)
P12=1.0/P21
C=0.5*(TR2+1.0+(1.0-P12)*(RHO21-1.0))
PR2B=C+SQRT(C*C-TR2)
F=PR2A-PR2B
RETURN
END
TABLE 1

IMPORTANT REACTIONS IN THE COMBUSTION OF HYDROGEN WITH OXYGEN

Possible initiating reactions:

\[ \text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2 \]  
(A)

\[ \text{H}_2\text{O}_2 + M = 2\text{OH} + M \]  
(B)

\[ \text{H}_2 + M = 2\text{H} + M \]  
(C)

\[ \text{H}_2 + \text{O}_2 = \text{HO}_2 + \text{H} \]  
(D)

Two-body gas phase reaction:

\[ \text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H} \]  
(E)

\[ \text{H} + \text{O}_2 = \text{OH} + \text{O} \]  
(F)

\[ \text{O} + \text{H}_2 = \text{OH} + \text{H} \]  
(G)

\[ \text{HO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}_2 + \text{OH} \]  
(H)

\[ \text{HO}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{OH} \]  
(I)

\[ \text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H} \]  
(J)

Three-body gas phase reactions:

\[ \text{HO}_2 + \text{H}_2 + M = \text{H}_2\text{O} + \text{OH} + M \]  
(K)

\[ \text{H} + \text{H}_2\text{O}_2 + M = \text{H}_2\text{O} + \text{OH} + M \]  
(L)

\[ \text{H} + \text{O}_2 + M = \text{HO}_2 + M \]  
(M)

Surface reactions:

\[ 2 \text{HO}_2 \overset{\text{surface}}{=} \text{H}_2\text{O}_2 + \text{O}_2 \]  
(N)

\[ 2 \text{H}_2\text{O}_2 \overset{\text{surface}}{=} 2 \text{H}_2\text{O} + \text{O}_2 \]  
(O)
<table>
<thead>
<tr>
<th>T° K</th>
<th>s</th>
<th>E* kcal/mole</th>
<th>k&lt;sub&gt;theor&lt;/sub&gt;</th>
<th>k&lt;sub&gt;exp&lt;/sub&gt;</th>
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<td>3</td>
<td>46.826</td>
<td>1.249 x 10&lt;sup&gt;8&lt;/sup&gt;</td>
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<tr>
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<td>2.465 x 10&lt;sup&gt;8&lt;/sup&gt;</td>
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</tr>
<tr>
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<td>47.274</td>
<td>7.978 x 10&lt;sup&gt;8&lt;/sup&gt;</td>
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<tr>
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<td>1.860 x 10&lt;sup&gt;9&lt;/sup&gt;</td>
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<tr>
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<td>56.664</td>
<td>2.801 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
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TABLE 3
DETERMINATION OF $s$ AND $E^*$ FOR $\text{H}_2\text{O}_2 + \text{N}_2$ MIXTURES

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$s$ (kcal/mole)</th>
<th>$E^*$ (kcal/mole)</th>
<th>$k_{\text{theor.}}$</th>
<th>$k_{\text{exp.}}$</th>
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<td>3</td>
<td>46.528</td>
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<tr>
<td>4</td>
<td>48.715</td>
<td>9.175 x 10^7</td>
<td>2.850 x 10^9</td>
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<tr>
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<td>50.901</td>
<td>2.242 x 10^8</td>
<td>7.305 x 10^7</td>
<td>2.850 x 10^9</td>
</tr>
<tr>
<td>6</td>
<td>53.087</td>
<td>4.739 x 10^8</td>
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</tr>
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<td>9.069 x 10^8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.313 x 10^9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.882 x 10^9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>9.037 x 10^9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Gas Mixture Handling System
Figure 2. Overall Shock Tube Set-Up

Light Source

Lengths
AB 168 in.
BC . 288 in.
B1 156 in.
1-2 19.65 in.
2-3 37 in.
3-4 1.965 in.
4-5 19.65 in.
5-6 2.625 in.
I.D. of liner 1.5 in.

Photomultiplier 1P28
to Lower In of Oscilloscope

Perkin - Elmer 98 Monochromator

Mylar Diaphragm

Used in Incident Shock Studies

I.D. of liner 1.5 in.

Amplifiers

Counter

Upper Beam Trigger

Upper Lower

Pin

Start Stop
Figure 3. Absorption Spectrum of $\text{H}_2\text{O}_2$ Vapor (from Ref. (26))

\[ \alpha = \frac{1}{cl} \ln \frac{I_0}{I} \]
Figure 4. Spectral Response of RCA 1P28 Photomultiplier

Figure 5. Spectrum of OSRAM High Pressure Xenon Lamp
Figure 6. Photomultiplier Base Circuit
Figure 7. Power Supply for Applying "Suppressed - Zero" Voltage at Zero Lamp Intensity
Fig. 8a. Typical Oscilloscope Trace; $\text{H}_2\text{O}_2 + \text{Argon}$;  
Incident Shock;  
Shock Speed $: 1115 \text{ m/sec}$  
Temperature $: 1340 ^\circ \text{K}$

Fig. 8b. Typical Oscilloscope Trace; $\text{H}_2\text{O}_2 + \text{Nitrogen}$;  
Reflected Shock; Temperature $: 1130 ^\circ \text{K}$  
Speed of Incident Shock $: 938 \text{ m/sec}$
Figure 9. Sketch of a Typical Experimental Trace Showing Intensity Designations
Figure 10. \( t \) versus \( \ln \ln \left( \frac{I}{I_0} \right) \) for \( \text{H}_2\text{O}_2 + \text{N}_2, \ T_R = 1255^\circ \text{K}, \)

\[
k = 1.06 \times 10^9 \ \frac{\text{cc}}{\text{mole \cdot sec}}.
\]
Figure 11. Initial Slope Method of Determining Initial Reaction Rate Constant
Figure 12, Arrhenius Plot for $H_2O +$ Argon Mixtures
Figure 13. Arrhenius Plot for $\text{H}_2\text{O}_2 + \text{N}_2$ Mixtures
Figure 14. Comparison with Low Temperature Data from (22)
Figure 15. Shape of a Hydrogen Peroxide Molecule
Fig. 16 Absorption at 3090 Å by a mixture of 2% H₂O₂ + Argon behind incident shock wave.

Temperature $T_2 = 2200^\circ$ K

Fig. 17 Absorption at 3090 Å by a mixture of 2% H₂O₂ + Argon behind incident shock wave.

Temperature $T_2 = 1400^\circ$ K
Figure 18. Wave Diagram of Simple Shock Tube Flow
Figure 19. Coordinate Systems for Shock Wave Calculations
BIBLIOGRAPHY


38. JANAF Thermochemical Tables.
