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THE THERMAL DECOMPOSITION OF
HYDROGEN PEROXIDE VAPOR

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FOREWORD

This final report was prepared by K. R. Bilwakesh, W. A. Strauss, and R. Edse of the Department of Aeronautical and Astronautical Engineering of The Ohio State University on Contract AF 33(615)-3775, Project 3012, Air Force Aero Propulsion Laboratory. The research on this project was administered under the direction of the Air Force Aero Propulsion Laboratory with Lt. Wayne A. Zwart as project engineer. This report was submitted by the authors, February 1968.

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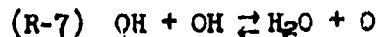
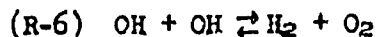
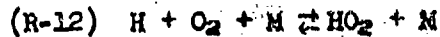
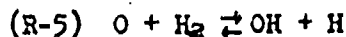
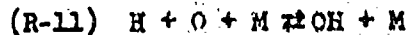
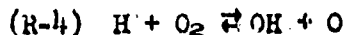
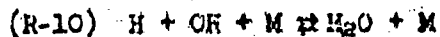
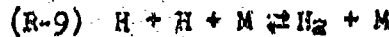
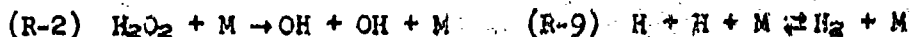
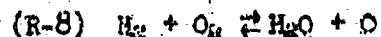
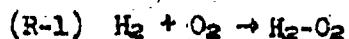
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SECTION I

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. The stagnation pressure losses and the difficulty in recovering the chemical energy from highly dissociated combustion gases make the ramjet utilizing subsonic combustion very inefficient. One possible solution to the problem is to limit the reduction of the air speed through the engine to moderately supersonic levels so that the static pressures of the gas are low enough to satisfy structural requirements. The fuel is then added to this supersonic flow of air. This scheme necessitates mixing and burning of gases which are flowing at supersonic speeds. Both of these processes are extremely important since they must be accomplished in a combustion chamber of reasonable length. The present study pertains to the combustion process which involves a series of elementary chemical reactions, each of which requires a finite time to occur. This investigation, as a part of a continuing program, deals with some elementary reactions involving the OH radical. The decomposition of hydrogen peroxide served as a source of the OH radical.

The important chemical reactions occurring in the combustion of hydrogen with oxygen (or air) are listed below:



Numerical values of the rate constants of many of these reactions are given in Table I. The initiation reaction of the oxidation of hydrogen is listed as the first reaction in the table. The activated complex formed in this reaction may be considered as an unstable form of hydrogen peroxide which represents only a loose association complex of hydrogen and oxygen. The decomposition of this activated complex in which OH radicals are produced is of great importance to the overall oxidation

TABLE I

Reaction	Rate Const. (cm ³ /g·mol)(°K)(sec)
R3 f	$6.3 \times 10^{13} \exp(-5900/RT)$
R3 r	$2.4 \times 10^{14} \exp(-20,700/RT)$
R4 f	$2.4 \times 10^{14} \exp(-16,750/RT)$
R4 r	$3.2 \times 10^{11} T^{0.47} \exp(-100/RT)$
R5 f	$3.3 \times 10^{12} \exp(-7140/RT)$
R5 r	$1.4 \times 10^{12} \exp(-5190/RT)$
R7 f	$7.5 \times 10^{12} \exp(-1000/RT)$
R7 r	$6.9 \times 10^{12} \exp(-17,750/RT)$
R9 f (M = H ₂)	$5 \times 10^{18} T^{-1}$
(M = H ₂ O)	$1.5 \times 10^{19} T^{-1}$
(M = H)	$2.0 \times 10^{19} T^{-1}$
R9 r (M = H ₂)	$3.6 \times 10^{18} T^{-0.82} \exp(-103,200/RT)$
(M = H ₂ O)	$1.1 \times 10^{19} T^{-0.82} \exp(-103,200/RT)$
(M = H)	$1.4 \times 10^{19} T^{-0.82} \exp(-103,200/RT)$
R10 f (M = H ₂ O)	$1.8 \times 10^{22} T^{-1.5}$
all others	$0.45 \times 10^{22} T^{-1.5}$
R10 r (M = H ₂ O)	$6.8 \times 10^{22} T^{-1.81} \exp(-118,000/RT)$
all others	$1.7 \times 10^{22} T^{-1.81} \exp(-118,000/RT)$
R11 f	6×10^{14}
R11 r	$1.4 \times 10^{14} T^{0.21} \exp(-101,300/RT)$
R12 f	3×10^{16}
R12 r	$1 \times 10^{16} T^{0.21} \exp(-45,920/RT)$

rate of hydrogen since the OH radical is one of the most important chain branching species. The rates of decomposition of hydrogen peroxide by the "static method" at low pressures (0.2 to 20 mm Hg) and in the temperature range of 573-873°K have been measured by Giguere and Liu.¹ Their experiments were conducted in clean pyrex or vycor glass reaction vessels and the reaction rates determined from the change in gas pressure with time. For this system both homogeneous and heterogeneous decomposition reactions occurred. After correcting for surface decomposition, they reported a homogeneous decomposition rate equation as

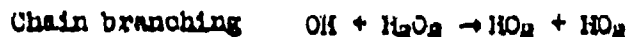
$$k = 10^{13} \exp(-48,000/RT) \text{sec}^{-1} \quad (1)$$

Giguere and Liu based this rate equation on the following mechanism:

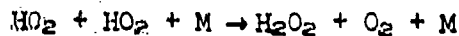


The authors further reported that the rate-determining step in this series of reactions is reaction number (R-0) because of its high activation energy. Although active radicals are involved in this mechanism, it is obvious that it does not represent a chain.

Satterfield and Stein² also studied the decomposition of hydrogen peroxide gas by passing a mixture of ($H_2O_2 + H_2O$) through a heated tube and analyzing the gases at the inlet and outlet. The analysis was carried out by rapid quenching of the sample as it was withdrawn from the tube and analyzing the condensate with standardized permanganate solution. These experiments were carried out for a range of temperatures of 500-775°K and at hydrogen peroxide partial pressures of 0.02 atmosphere. The authors reported an order of reaction of 3/2 and an activation energy of 55,000 cal/mole. They postulated the following chain reaction mechanism:



Chain breaking



The postulated three-body chain-breaking reactions result in an overall reaction of order 3/2, which agreed with their experimental data.

Moore et al.³ correlated the above data with data of their own (made by flowing the hydrogen peroxide and a carrier gas through pyrex and silica reaction vessels, cleaned with 40% hydrofluoric acid and analyzing the gases at the entrance and exit). The analysis in this case was carried out by freezing the sample with a liquid air cold trap and analyzing the products by titration with 0.01 N acid potassium permanganate solution. These authors studied the decomposition rates for a temperature range of 514-932°K and reported a second-order rate constant equation of

$$k = 10^{15.4} \exp\left(-\frac{48,000}{RT}\right) \frac{\text{lit}}{\text{mole-sec}} \quad (2)$$

for the reaction (R-1). The reaction rate equation given above applies to the case where M is also hydrogen peroxide and the overall order of the reaction is two.

So far the rate constant of the decomposition of hydrogen peroxide is known only at temperatures up to approximately 900°K. Air for the hypersonic ramjet will probably be shocked and diffused to temperatures of approximately 1500°K. It is therefore desirable to have decomposition data at higher temperatures so that a realistic evaluation of the overall combustion process can be made. The study of the mechanism and the reaction rates of the hydrogen peroxide decomposition for temperatures in the range of 1000-1400°K have been investigated and are reported herein.

SECTION II

EXPERIMENTAL PROCEDURES

The high gas temperatures required for the experiments were obtained by means of a shock tube apparatus which is shown schematically in Fig. 1. In addition to increasing the temperature, the shock increases the species concentration by compressing the mixture. The shock tube used was a pressure-driven type having a driver section of 13 feet and a driven section of 23 feet. Helium-air mixtures were used as the driver gas while hydrogen peroxide-argon and hydrogen peroxide-nitrogen mixtures were the two test gas mixtures used. The two sections were separated by a mylar diaphragm.

The leak rate of the driven section of the shock tube (test section) was less than 1.5 microns per minute. The shock tube was made of No. 316 stainless steel. The driven section was lined with commercial polyethylene well casing tubing (Yardly Plastics, Golden Jet NST) to prevent H_2O_2 decomposition while stored in the tube. The inside diameter of this tubing is 1.5 inches. Heterogeneous decomposition of hydrogen peroxide stored in this vessel is relatively small.

Passivation of the tube and the vapor mixing system presented considerable difficulty. The glassware used was pyrex and the tubing was teflon, pyrex, and polyethylene. The glassware was passivated by cleaning first thoroughly with double-distilled water and then immersing it in 35% sulphuric acid for about two hours at room temperature. It was then cleaned again and rinsed thoroughly with double-distilled water and air-dried.

The connecting tubings of teflon and polyethylene were cleaned and rinsed several times with double-distilled water. These and the glassware did not present any serious problems.

The shock tube, made of 316 stainless steel, was found to catalyze the heterogeneous decomposition of H_2O_2 . It had been used earlier in other experimental work and hence it was felt that the inner surface might have been corroded by other gases. Hence the inner surface was honed and cleaned later with alcohol and distilled water. This treatment did not reduce the catalytic effect. Hence the passivating procedure recommended by the manufacturers of H_2O_2 (Becon) was followed. In this method, the tube was completely filled with 70% nitric acid solution and left for seven hours at room temperature. It was then cleaned with distilled water and treated with a 30% solution of hydrogen peroxide which was left in the tube for about six hours. The tube was then rinsed and cleaned again with distilled water several times. After this, tests were conducted to check the activity of the surface of the tube. It was found to have improved but still the decomposition was high. Therefore, the entire passivating process was repeated. Another series of tests indicated at this stage that the decomposition was still rather high.

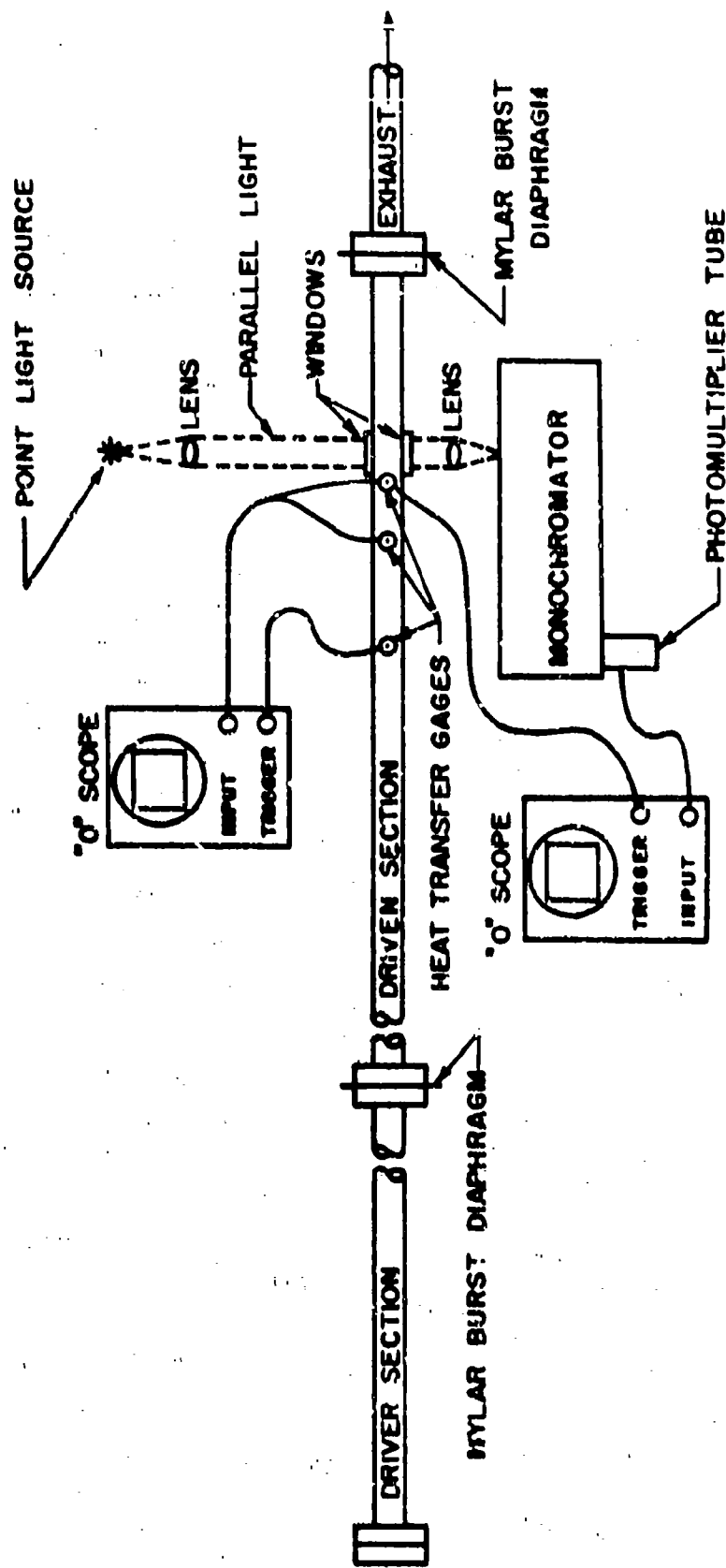


FIG. 1 APPARATUS FOR THE STUDY OF REACTION KINETICS BY ABSORPTION METHODS

Next a hydrogen peroxide vapor-argon mixture was passed continuously through the tube for about an hour and then the ends were closed and the mixture allowed to remain in the tube for 10 minutes. A sample test before and after the 10-minute fill showed that about 50% of the H_2O_2 admitted remained after 10 minutes. Tests were also conducted to see whether a large percentage of H_2O_2 was adsorbed on the walls of the tube. This test consisted of passing the hydrogen peroxide-argon mixture continuously through the tube, the tube being evacuated on the other end. Between the tube and the pump was a cold trap with dry ice in acetone to freeze out H_2O_2 and H_2O . An analysis of the condensate showed that there was no adsorption, while decomposition occurred as before. At this stage it was decided to use a polyethylene insert.

Care was also taken to avoid hydrogen peroxide decomposition on the surface of other components which contacted the test gas. For example, the flow-throttling valves were made of teflon, the flow-conducting lines were polyethylene tubing, the test-section window flanges were made of type 110 aluminum, and Kel F-90 grease was employed for the stopcocks. When all these materials were employed, the surface decomposition of the hydrogen peroxide for the total time to fill and test the mixture was always less than 15% of the initial concentration of hydrogen peroxide admitted into the test section.

In order to obtain the reaction rates and the rate constant, we should have knowledge of the temperature and pressure behind the shock wave. This is measured by measuring the velocity of the shock wave and theoretically calculating the temperature and pressure ratios across the shock. Tests were run to check the attenuation and it was found to be negligible.

Shock speed is determined by measuring the time of passage of the shock wave between two platinum strip thermal gages. The resistance of the platinum strip increases when subjected to a temperature increase and this initial change occurs in less than one microsecond. The platinum strip is placed in one branch of an electrical bridge. Thus a change in its resistance on arrival of the shock wave will cause a voltage drop which is amplified and used as a timing pulse. Referring to Fig. 1, the first gage starts a trace in an oscilloscope and the remaining two probes generate deflections of the trace measuring the time of passage of the shock wave between the two strips placed 0.5 meter apart.

Initial pressure was measured by a mercury manometer with fluorolube oil on top of mercury to prevent immediate contact between mercury and hydrogen peroxide. The manometer was cleaned frequently and refilled with fresh mercury. The pressure was cross-checked with a Heise gauge and it was found that there was no difference between the readings obtained in the two ways.

The absorption of U-V radiation ($\sim 2600 \text{ \AA}$) by the heated hydrogen peroxide was monitored. Light from a high-pressure mercury lamp was transmitted through a sapphire window (1 mm x 5 mm) and the test gas

and focused on the entrance slit of a monochromator. A Perkin-Elmer Model 98 monochromator was used to isolate the particular wavelength region of interest, and the transmitted light was focused on an IP 28 photomultiplier. The signal output from the photomultiplier was recorded on an oscilloscope. Because of the low absorption level compared to the total light transmitted at the monochromator setting, a suppressed zero was obtained by applying a 1.2 V DC potential from a battery to the photomultiplier signal thereby allowing more accuracy when evaluating the data. Details of the relationship between light intensity and hydrogen peroxide concentration are given in Section III of this report.

The test gas mixture constituted 2 to 3% hydrogen peroxide in a carrier gas of argon or nitrogen. Commercial helium-and water-pumped nitrogen gases were employed as carrier gases while 98% liquid hydrogen peroxide was used (supplied by the Becco Company). Hydrogen peroxide carrier gas mixtures were produced ($T = 25^{\circ}\text{C}$) by slowly bubbling the carrier gas at the rate of approximately 6 cc/sec (tube conditions) through a porous plug which was completely submerged in liquid hydrogen peroxide (approximately 30 cc). The mixture was then passed into the driven section of the shock tube to a test pressure of 40 mm mercury (Fig. 2). The initial concentrations of hydrogen peroxide vapor in the gas mixtures were sampled prior to being admitted into the shock tube and near the test windows and determined quantitatively by the Kingzett's titration procedure (Appendix II).

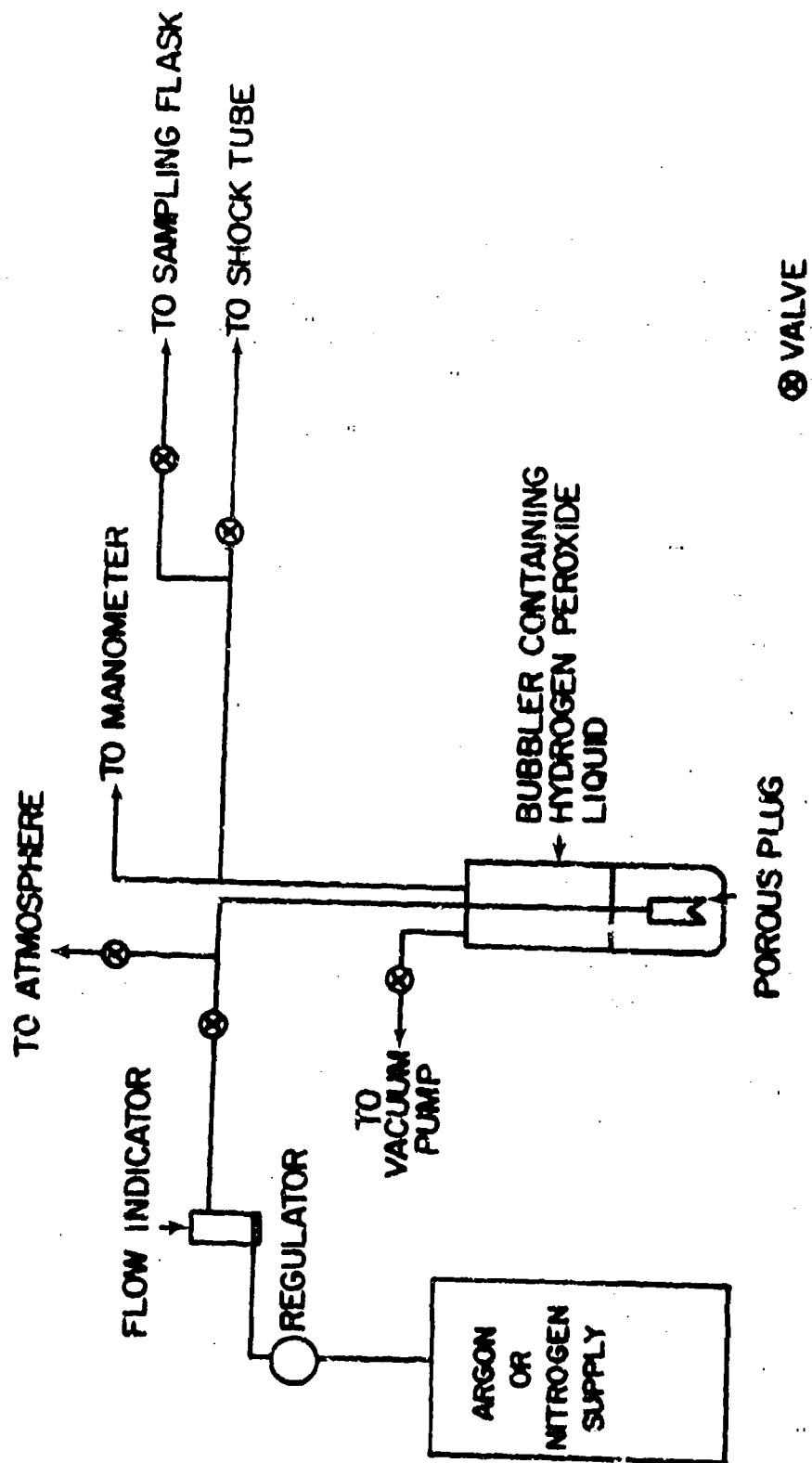


FIG 2 SCHEMATIC FOR PREPARATION OF TEST GAS MIXTURES

SECTION III

METHOD OF ANALYSIS AND RESULTS OF THE EXPERIMENTS

ANALYSIS

Based on available hydrogen peroxide decomposition data below 900°K, Hoare et al.⁵ reported that hydrogen peroxide vapors decompose according to the following second-order chemical reaction:



The rate equation for this reaction can be given as

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2][\text{M}] \quad (3)$$

where

[M] = concentration of inert species M,
k = rate constant, and
t = time.

Upon integration (the concentration of M can be considered as constant) we obtain

$$\ln \frac{[\text{H}_2\text{O}_2]_1}{[\text{H}_2\text{O}_2]} = k[\text{M}](t - t_1) = -K_{\text{exp}}(t - t_1) \quad (4)$$

where

(t - t₁) = length of time interval gas has been heated in shock wave;
(subscript 1 denotes the condition immediately after passage of the shock wave (beginning of decomposition)).

Hydrogen peroxide absorbs continuously in the ultraviolet in the region from 4000 to 2000 Å.⁵ This absorption has been experimentally observed by different authors⁵ but the potential curves at the excited electronic levels are not clearly known. The concentration of the decomposing species (H₂O₂) is related to the intensity of the absorbing wavelength (~2600 Å for H₂O₂) and according to Beer's law is given as

$$I = I_0 \exp(-\mu[C]L) \quad , \quad (5)$$

where

I = instantaneous intensity of transmitted light,
 I_0 = intensity of transmitted light without hydrogen peroxide
 (zero absorption),
 μ = extinction coefficient,
 L = absorption path length, and
 $[C]$ = concentration of absorbing species C.

The value of μ has not been determined because it is of no practical interest. The absorption coefficient μ can be eliminated if we compare absorption intensities at two different concentrations as the decomposition proceeds. When the concentration of the hydrogen peroxide decreased to the value at which the difference between the initial intensity of the transmitted light (I_1) and the instantaneous intensity (I) is 10% of the difference between the zero absorption intensity (I_0) and the initial intensity (I_1), the expression of the rate constant as given in Eq. (4) becomes

$$k[M] = -K_{\text{exp}} = \frac{\ln \left[\frac{\ln \frac{I_0}{I_1} - \ln \left(0.9 + 0.1 \frac{I_0}{I_1} \right)}{\ln \frac{I_0}{I_1}} \right]}{\frac{\rho_2}{\rho_1} (t - t_1)} \quad , \quad (6)$$

where ρ_2/ρ_1 is the density ratio across the shock wave. The density ratio in the denominator of Eq. (6) is the multiplication factor which converts the time from the laboratory reference to the gas reference. This correction was necessary to account for the fact that the gases are in motion behind the shock wave.

This may be understood by considering the passage of a particle through the shock front when the front is a distance d from the observing point. If the flow velocity is denoted by u_2 and the shock velocity by U , then the particle is observed at a time d/u_2 after it passed through the front. However, the front itself arrived at a time d/U so that the difference in arrival time between the shock front and the particle (i.e., the laboratory time) is $d/u_2 - d/U$. The particle time, t_p , is then related to the laboratory time t_l by

$$\frac{t_p}{t_L} = \frac{a/u_2}{\frac{d}{u_2} - \frac{d}{U}} = \frac{U}{U - u_2} = \frac{v_1}{v_2} = \frac{\rho_2}{\rho_1}$$

The evaluation of Eq. (6) was based only on the first 10% of the decomposition to justify the assumption of a constant temperature during the decomposition and also to examine the initiating step in the decomposition mechanism.

The experimental data were evaluated by first calculating the conditions behind the normal shock on the basis of a thermally perfect, nonreacting gas. The ratio of intensities and the time to decompose the first 10% of hydrogen peroxide (lab scale) were obtained from the oscilloscope trace which showed the intensity-versus-time relationship. Substitution of these data into Eq. (5) gave the value of k_{exp} . The actual decomposition rate constant (k) is then obtained from the experimental rate constant by dividing the latter by the concentration of the inert species (N).

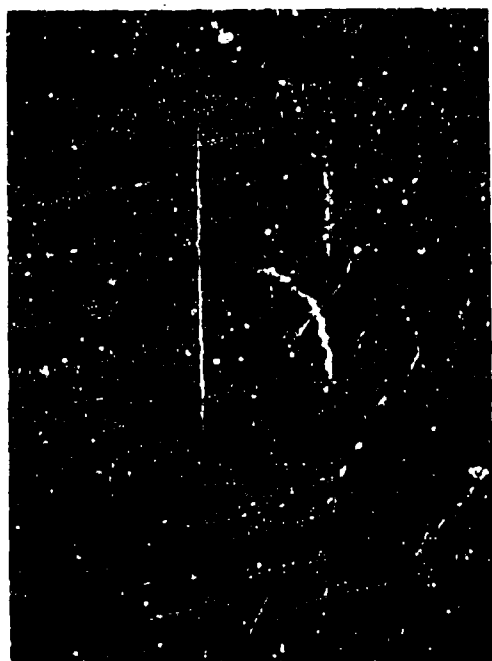
RESULTS

Typical experimental data showing the relative decomposition rate of hydrogen peroxide at high temperatures and in collision with argon and nitrogen are given in Fig. 3. The shock speed, the temperature behind the shock, and other data pertinent to these experiments are listed in this figure. A total of 11 experimental rate constant values over a temperature range from 1220 to 1370°K were determined for the decomposition of hydrogen peroxide in collision with nitrogen molecules. In collision with argon, 13 experimental rates were determined over a temperature range from 1350 to 1600°K. Results of these second-order reaction rate data are plotted in Fig. 4. Also plotted in this figure are the consolidated data reported by Hoare *et al.*⁶ for the rate constants of the hydrogen peroxide for a lower range of temperatures. If we assume that the rate constant given by an expression of the form

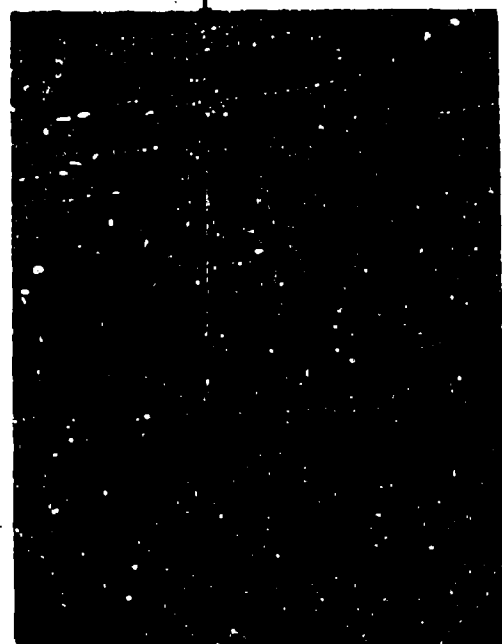
$$k = A \exp\left(-\frac{E_{act}}{RT}\right) \frac{\text{cm}^3}{\text{mole-sec}}$$

then

$$\ln k = \ln A - \frac{E_{act}}{RT}$$



ARGON DILUENT
 SCALE TIME - 20 μ s/div
 INTENSITY - 20 mv/div
 SHOCK SPEED - 1220 m/sec
 TEMP - 1569 °K



NITROGEN DILUENT
 SCALE TIME - 20 μ s/div
 INTENSITY - 20 mv/div
 SHOCK SPEED - 1510 m/sec
 TEMP - 1265 °K

FIG.3 EXPERIMENTAL HYDROGEN PEROXIDE DECOMPOSITION DATA
 (BEHIND NORMAL SHOCK)

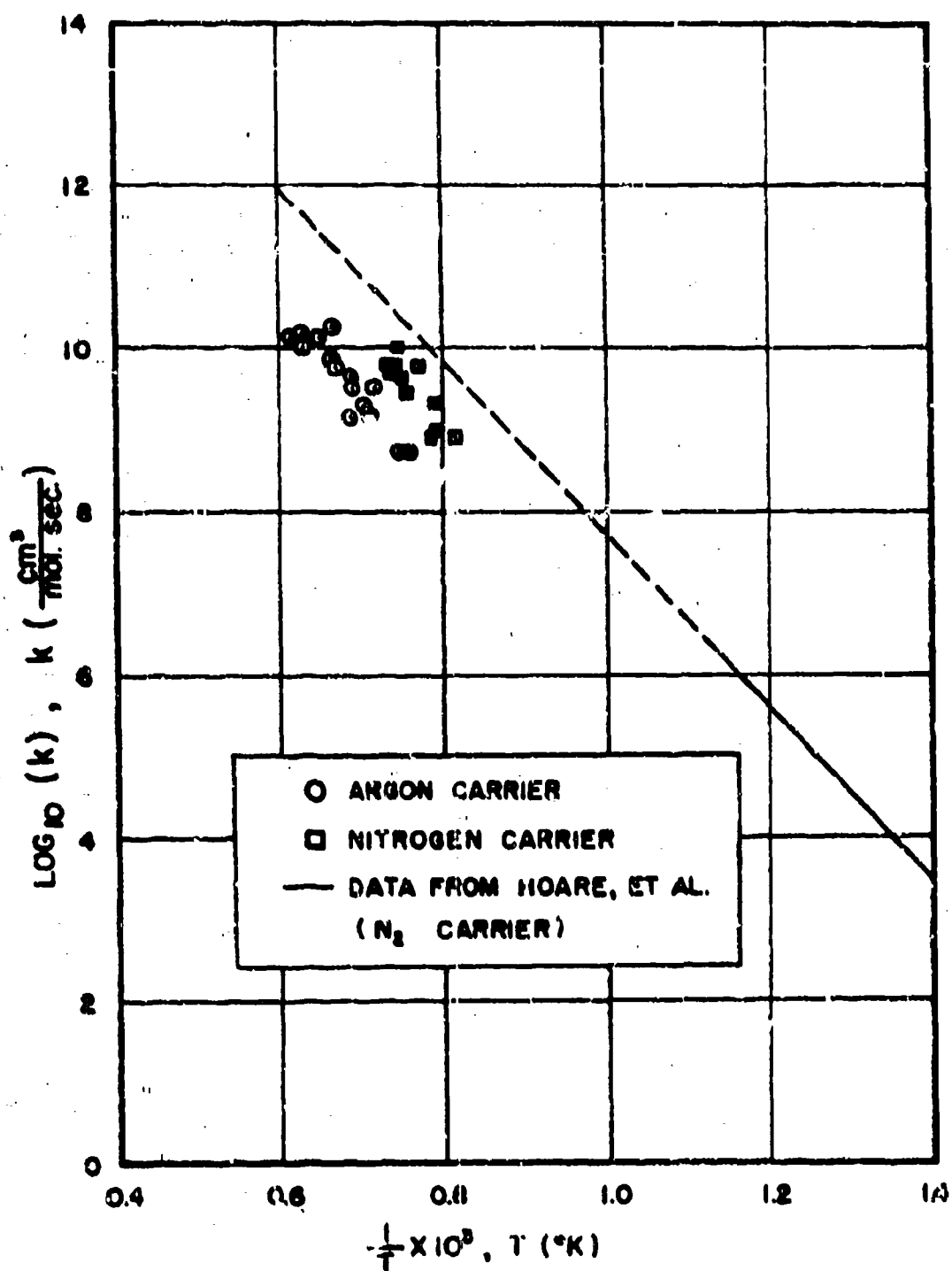


FIG. 4 THE EFFECT OF TEMPERATURE ON THE SECOND-ORDER RATE CONSTANT OF HYDROGEN PEROXIDE DECOMPOSITION

Thus a plot of $1/T$ vs $\ln k$ should produce a straight line, the slope of which is $-E_{act}/R$. Using a "least-mean-square" (Appendix III) technique for determining the equation of the line passing through the data points, the following equations were obtained:

Argon: $k_{Ar} = 1.08 \times 10^{17} \exp\left(-\frac{49,800}{RT}\right) \text{ cm}^3/\text{mole-sec}$ (7)

Nitrogen: $k_{N_2} = 2.525 \times 10^{16} \exp\left(-\frac{53,300}{RT}\right) \text{ cm}^3/\text{mole-sec}$ (8)

As noted in the above equations, the activation energies for argon and nitrogen as the carrier gases were calculated to be 49,800 and 53,300 cal/mol respectively. The activation energy reported by Hoare et al.⁶ at lower temperatures for nitrogen inert gas case was 48,000 cal/mol.

Experiments were conducted to establish the rate of formation of hydroxyl (OH) during the initial phase of the decomposition of hydrogen peroxide. By correlating this information with the initial decomposition rate of hydrogen peroxide it is possible to establish the exact initiation reaction of the hydrogen peroxide decomposition. The experimental procedure for these experiments was essentially the same as outlined above except that the OH radical concentration was to be established from the 3064 Å band emission spectra. The contract period came to an end before sufficient data could be obtained to arrive at any conclusion.

SECTION IV

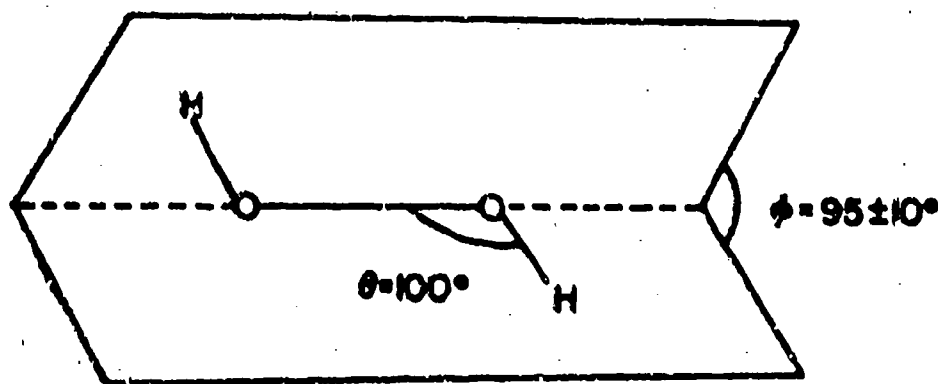
DISCUSSION OF RESULTS

The first step in the thermal decomposition of hydrogen peroxide is considered to be the following endothermic second-order chemical reaction:⁵



Since, for the present studies, the concentration of the inert species (argon or nitrogen) in the test gas usually exceeded 97% of the total, it was assumed that the hydrogen peroxide collision partner (M) was the inert species. Since the fraction of the reacting species used in the experiments was very small, the change in the reaction temperature was negligibly small.

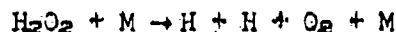
The assumption of the hydrogen peroxide decomposition reaction (Eq. R-2) as postulated by Hottel et al.⁵ was based on the accepted structure of the hydrogen peroxide molecule.⁵ The structure can be represented diagrammatically as shown in the sketch below.



The decomposition of the hydrogen peroxide can occur in one of two ways.

- (a) Breakage of the bond between the two oxygen atoms. This reaction requires an energy of 52,000 cal/mole and results in two hydroxyl (OH) radicals.
- (b) Breakage of the bond between a hydrogen and an oxygen atom. This reaction requires an energy of 30,000 cal/mole⁵ and yields an H atom and an HO₂ radical.

Because of the great difference between these two activation energies the more probable dissociation is the breakage of the bond between the two oxygen atoms. Other theoretical decomposition reactions such as



can also be ruled out because of energy considerations. Some experimental evidence was obtained (Appendix I) to support the theory that hydrogen peroxide decomposes indeed into two OH radicals.

From the experimental hydrogen peroxide decomposition rate constants, as shown in Fig. 4, it is seen that the activation energy ranges from 49,800 to 53,000 cal/mole. This value agrees reasonably well with that reported by Hoare *et al.*⁹ who calculated the activation energy as 48,000 cal/mole from data over a lower (500-900°K) temperature range. This value also agrees quite well with the energy required to break the bond between the two oxygen atoms in the hydrogen peroxide molecule.

As seen in Fig. 4, the hydrogen peroxide decomposition rate constants with nitrogen as the collision partner are about 6-7 times larger than those with argon as the collision partner. Hoare *et al.*⁹ have reported that nitrogen was about twice as effective as helium at temperatures from 500-900°K. Since for the present temperature range of 1100-1300°K for the nitrogen studies, rotational and vibrational modes may also contribute towards energy transfer, it is reasonable to assume that the reaction rate constants will be somewhat higher. Argon is expected to be more efficient than helium as a collision partner and this makes the efficiency of nitrogen relative to helium even higher than the factor of 6 or 7 obtained with argon. At the present time it is felt that more investigations may have to be undertaken before any definite conclusions may be drawn relative to this point.

APPENDIX I

A chemical reaction which may be of importance in the chain reaction of the hydrogen-oxygen combustion process is the dissociation and recombination of the OH radical. This reaction may be written as



Because of difficulty in obtaining free hydrogen and oxygen atoms, data on the rate constants of the recombination reaction ($\text{O} + \text{H} + \text{M} \rightarrow \text{OH} + \text{M}$) are not available.⁶ Therefore, the rate of disappearance of the OH radical in the shocked gas was measured at temperatures of from 2700 to 4200°K. The decomposition of the hydrogen peroxide at these temperatures occurred in times less than 1 μsec . The disappearance of the OH radical was determined by monitoring its ultraviolet emission in the spectral range from 3064 to 3090 Å. This emission corresponds to the (0,0) band of the $A^2\Sigma - X^2\Pi$ electronic transition of the OH molecule.

In the analysis, the following six reactions involving the OH species were considered:



The rates for all but the last of these chemical reactions were obtained from Kaskan and Brown⁶ (also see Table I). Estimates of the rates for reaction R-VII were made by the following method:

The dissociation energy of OH, HCl, and H₂ are 101.36, 102.2 and 103.26 cal/mole, respectively. The mass, vibrational frequency, and dipole moment of OH fall between the values of H₂ and HCl. Hence, it is reasonable to assume that the rate constant for the reaction $\text{OH} + \text{M} \rightarrow \text{O} + \text{H} + \text{M}$ would have a value between those involving H₂ and HCl.

By means of an extrapolation (Fig. 5) the latter reaction rate can be approximated as

$$k_{VII} = 9 \times 10^{13} \exp(-87,000/RT) \frac{\text{cm}^3}{\text{mole-sec}}.$$

Using the reported and estimated values of reaction rates for the system of reactions given above, the variation of the OH concentration with time was calculated for various initial concentrations of H_2O_2 , H_2O , and argon. It was assumed that at the start (immediately behind the shock wave) the hydrogen peroxide decomposed into two OH radicals. The concentrations of O, O_2 , H, H_2 , H_2O , and OH were calculated for the system of reactions in time increments of 0.1 μsec . The variation of the OH concentration with time was plotted and compared with the experimental OH decay rate data; the agreement was satisfactory. Also, the rate constant R-VII was varied over a wide range of values and the OH decay rate was calculated for each of these. These rates were found to be independent of the value of R-VII. This study clearly shows that the reaction $\text{O} + \text{H} + \text{M} \rightarrow \text{OH} + \text{M}$ does not contribute noticeably to the above system of reactions under the conditions investigated.

From the results available so far, there is strong reason to believe that the decomposition of hydrogen peroxide can be used as a source of OH radicals for any further study. Further studies should be undertaken to confirm this by observing the formation of OH radicals from the decomposition of hydrogen peroxide.

A literature survey was made to explore the possibility of detecting radiation emitted by the HO_2 radical in the infrared region in the shock tube during the decomposition of hydrogen peroxide. The difficulties encountered in this study were beyond the scope of time and financial resources of the contract.

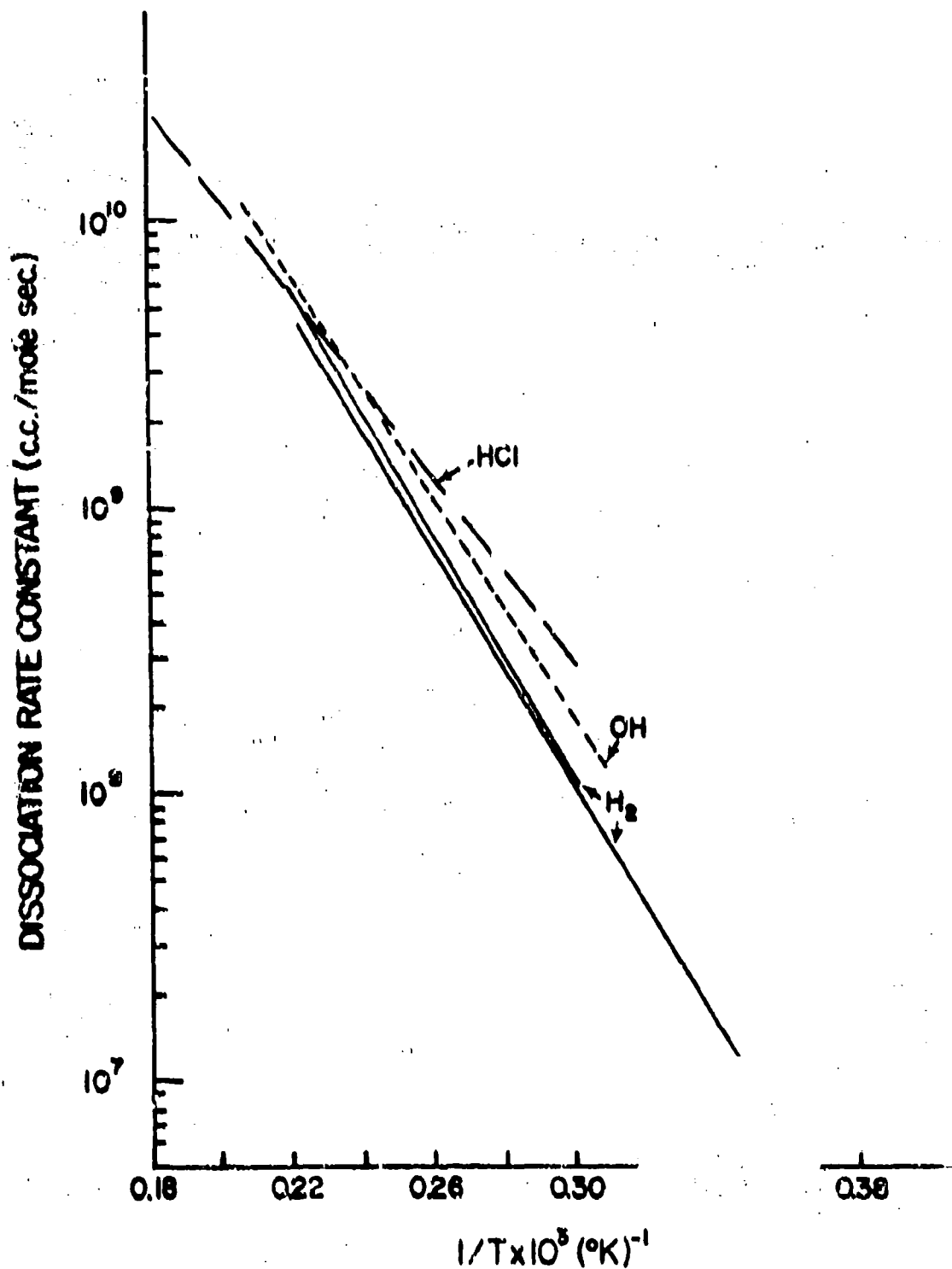


FIG 5 EXPERIMENTAL RATES OF DISSOCIATION OF H₂ AND HCl AND INTERPOLATED RATE OF DISSOCIATION OF OH

APPENDIX II

TITRATION PROCEDURE⁴

Required: 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution
18 N H_2SO_4
KI solution made up by dissolving 2 mg of KI in 200 ml distilled water.

Procedure: The sampling flask with a capacity of 1 liter is connected to the shock tube and evacuated along with the tube and later filled with the hydrogen peroxide vapor - argon mixture as is the tube.

The flask is now removed and 10 cc distilled water added to it to dissolve all the gases in it.

To 200 cc of the prepared KI solution is added 30 cc of the 18N H_2SO_4 and to this is added the contents of the sampling flask. This mixture is stirred well and let stand for five minutes and then titrated against the $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as needed.

Calculations:

$$1 \text{ liter of } 0.1 \text{ N } \text{Na}_2\text{S}_2\text{O}_3 = \frac{\text{H}_2\text{O}_2}{20}$$

$$= 1.7008 \text{ gm of } \text{H}_2\text{O}_2.$$

Let x cc of $\text{Na}_2\text{S}_2\text{O}_3$ be used for titration. Then

$$\text{moles of } \text{H}_2\text{O}_2 \text{ present} = \frac{1.7008 \times x}{1000 \times 34}$$

Total number of moles of H_2O_2 and argon

$$= \frac{P_1}{\text{atmospheric pressure}} \times \frac{1000}{82.05 \times 300}$$

From this, percentage of H_2O_2 by weight is calculated.

APPENDIX III

STRAIGHT LINE FIT FOR DATA

Plotting $1/T$ on the abscissa and $\ln k$ as the ordinate, from the equation

$$\ln k = \ln A - \frac{E}{RT}$$

we can write a straight line passing through the points as

$$Y_1 = A_0 + A_1 X_1$$

for each point i .

For a total of N points we can get

$$A_1 = \frac{\sum X_1 \sum Y_1 - N \sum X_1 Y_1}{(\sum X_1)^2 - N \sum X_1^2}$$

and

$$A_0 = \frac{\sum Y_1 - A_1 \sum X_1}{N}$$

for the least-mean-square straight line passing through these points.

REFERENCES

1. Giguere, P. A., and Liu, I. D., Can. J. of Chem., 35 (April, 1957), 283.
2. Scatterfield, C. N., and Stein, T. W., J. Phys. Chem., 61 (May 1, 1957), 537.
3. Hoare, D. E.; Protheroe, J. B.; and Walsh, A. D., Trans. of Faraday Soc., 55 (1959), 548.
4. Treadwell, F. P., and Hall W. T., Analytical Chemistry, Vol. II, John Wiley & Sons, Inc., London (1942).
5. Schumb, W. C.; Satterfield, C. N.; and Wentworth, R. L., Hydrogen Peroxide, Reinhold Publishing Corporation (1955).
6. Kaskan, W. E., and Drowns, W. G., "Kinetics of the $H_2/CO/O_2$ System," Report R 64SD37, General Electric Space Sciences Laboratory, (July, 1964).