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TG 331-3

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ARPA Order No. 22-59
Task 5

THE JOHNS HOPKINS UNIVERSITY
APPLIED PHYSICS LABORATORY
8621 GEORGIA AVENUE SILVER SPRING, MARYLAND

Operating under Contract NOrd 7386 with the Bureau of Naval Weapons, Department of the Navy

# TASK R

## Quarterly Progress Report No. 3

for the period

1 October - 31 December, 1959

Task R is a program of research in basic phenomena associated with the behavior of materials in high temperature gas environments. It is supported by the Advanced Research Projects Agency through Contract NOrd 7386 with the Bureau of Naval Weapons, Department of the Navy.

TG 331-3
January 22, 1960

ARPA Order No. 22-59
Task 5

# TASK R

Quarterly Progress Report No. 3
for the Period
1 October - 31 December, 1959

## GENERAL OBJECTIVES OF TASK R

Many of the wide variety of problems associated with the use of materials at high temperatures occur in connection with advanced propulsion systems, and of these, some of the most critical and complex are encountered in high performance rocket motors. Present trends in rocket design and propellant formulation resulting in gas flows of increased temperature, pressure, and corrosiveness may be expected to aggravate the materials situation. It seems self-evident that future, long-range solutions to these problems must rely on more sophisticated approaches and broader knowledge of the behavior of materials in high temperature gas environments than is characteristic of the usual "quick-fix", or expensive cut-and-try test procedures. It also seems likely that improvement in structural materials themselves (i.e., higher strength at high temperature, higher melting point, etc.) has reached the point of diminishing returns, so that various other subterfuges must be tried.

Research performed under Task R at the Applied Physics Laboratory or its subcontracting agencies is intended to provide some of the fundamental knowledge necessary for a rational understanding of the behavior of materials at high temperatures. This is a very broad and very complex field involving many different scientific disciplines. While no attempt is made to rigidly limit the scope of Task R, the general emphasis is on appropriate research in the flow and physical chemistry of high temperature gases such as are characteristic of advanced solid propellant rocket motors, and the phenomena basic to heat transfer and cooling techniques in such environments, rather than in the properties of materials themselves.

A. A. Westenberg
Program Coordinator

# SUMMARY



The approach taken in this project is to obtain high temperature chemical kinetic information by means of the detailed analysis of laminar flame structure. Net rates of appearance or disappearance for all the stable species found in the 1/10 atmosphere $CH_4-O_2$ flame are presented as profiles through the flame zone. The expected relations between these rates are given and shown to be borne out by the data. The over-all rate constant for the oxidation of CO is evaluated in terms of an empirical mechanism and shown to be essentially temperature - independent in the range 1650-1950°K. Comparisons with other work are made.



Extension of a method previously developed at APL for the accurate measurement of high temperature molecular diffusion coefficients to the measurement of thermal conductivity is being attempted. Improvements in both the line heat source and the wake temperature measuring equipment are described. Previously noted difficulties with the perturbation caused by the velocity wake of the source wire appear to have been solved satisfactorily. These wake corrections are described and results on room temperature $N_2$ and He of considerable precision are given. These compare well with values measured by the conventional technique.



Methods of measuring diffusion coefficients and thermal conductivity in gases composed of labile atoms and their present molecules are being explored. A proposed diffusion experiment is described, as are some preliminary experiments being performed to gain experience in generating and detecting dissociated atoms.



The idea in this work is to derive chemical kinetic data by analyzing the concentration wake downstream of a point source trace gas injected into a laminar flow of a second gas with which it reacts. The theory of the technique is discussed, and the apparatus being tried out is described.

V. Rocket Nozzle Fluid Dynamics . . . . . . . . . . . . . . . . . . . Page 27

This project aims at careful experimental measurements of the flow properties in a rocket nozzle employing a typical solid propellant. Pitot pressure surveys in nozzles of $12.5^{\circ}$ and $26^{\circ}$ total divergence angle of stations corresponding to the same expansion ratio show appreciable differences which are attributed to chemical non-equilibrium effects. Some preliminary results with a fast-scanning infrared spectrometer to measure relative gas composition in the nozzles are given.

AAW/ccl

## I. HIGH TEMPERATURE CHEMICAL KINETICS IN LAMINAR FLAMES

(R. M. Fristrom, C. Grunfelder, S. Favin, A. A. Westenberg)

### Objective

The effect of chemical reactions is one of the important problems in the dynamics of high temperature, high speed gas flow. Chemistry and aerodynamics (and sometimes molecular transport processes) are strongly coupled in various nozzle flow and boundary layer phenomena. Advances in understanding in these areas cannot be made without a great deal more knowledge of high temperature chemical kinetics than is presently available. The important reactions are extremely rapid and lie in temperature regions where materials present problems. Therefore, conventional experimental techniques are not generally applicable, and the extrapolation of information from lower temperature reaction rate studies is not satisfactory. Several experimental techniques have been devised to surmount these difficulties. Shock tube studies are useful for very simple reaction systems. Molecular beam studies of chemical kinetics (inelastic scattering) are in their infancy, but offer interesting and exciting possibilities. The approach taken in this project is to study high temperature kinetics by a detailed quantitative analysis of laminar flame structure. From this analysis it is hoped that eventually the kinetics of elementary combustion reactions can be obtained. The present work allows the determination of the rates of appearance or disappearance of all of the stable species in a flame as a function of position (or time), temperature, and chemical composition. This is the same type of data obtained in conventional kinetic studies, and a much wider temperature range is accessible.

Experimental Techniques

The experimental techniques used to obtain the temperature, composition, and aerodynamic profiles through laminar flame zones are described in Quarterly Progress Report No. 1 (Ref. 1).

Kinetic Analysis of the 1/10 Atmosphere $CH_4$-$O_2$ Flame

The set of data obtained in a flat $CH_4$-$O_2$ flame (initial mole fractions: $X_{CH_4} = 0.0785$, $X_{O_2} = 0.914$) at 1/10 atmosphere pressure were presented in earlier Quarterly Progress Reports (Refs. 1, 2), as were the analyses of these data in terms of conservation of matter and energy. During the present report period, emphasis has been on interpreting the data in terms of chemical kinetics.

It has been convenient to use the quantity $G_i$ defined by the relation

$$G_i = \frac{f_i \ (v + V_i)}{v} \tag{1}$$

where $f_i$ is the mass fraction of species i at any point in the flame, $V_i$ the diffusion velocity, and v the macroscopic gas velocity (mass average velocity). $G_i$ thus represents the fraction of the total mass flux at any point due to species i, and includes the effect of diffusion. It may then be shown from elementary species continuity considerations that $K_i$, the volumetric net rate of appearance or disappearance of i due to chemical reaction is given by

$$K_i = \left(\frac{\rho v}{M_i}\right)\left(\frac{dG_i}{dz}\right) \tag{2}$$

where $\rho$ is gas density, $M_i$ is molecular weight, and z the distance coordinate normal to the flame front. When the usual cgs units are used, $K_i$ has the units of moles $cm^{-3}$ $sec^{-1}$.

The rate variable $K_i$ was calculated for all stable species at regular intervals throughout the flame by means of Eq. (2), using the previously derived $G_i$ profiles. The differentiation was done numerically. Since the evaluation of the $G_i$ required a numerical differentiation of the original composition profiles, the determination of the $K_i$ involves implicitly a second derivative of the experimental data. This is an obvious and unavoidable source of error. Since errors may be expected to roughly double upon each differentiation, this whole procedure probably multiplies original errors in composition by a factor of about four. It is estimated that the precision (reproducibility) of the composition data is about 2-3%, so that precision in the $K_i$ after the data analysis may be about 10%. This says nothing about other sources of error, which are discussed in detail elsewhere (Ref. 3). The $K_i$ profiles derived in this way are given in Fig. I-1. The profile for $O_2$ is not included since it is not an independently derived quantity, while that for HCHO is not shown because it is quantitatively negligible compared to the others. The rates are not plotted to zero value at the cold boundary side of the figure because reliable derivatives of the $G_i$ curves could not be obtained from the data all the way to their asymptotic values. The rates approach zero rapidly to the left of the first plotted points of the curves, however. It should be noted that the free radicals actually present in the flame are not analyzed for by present techniques, and show up in the stable species concentrations. Thus their influence on the rate profiles cannot be assessed quantitatively as yet.

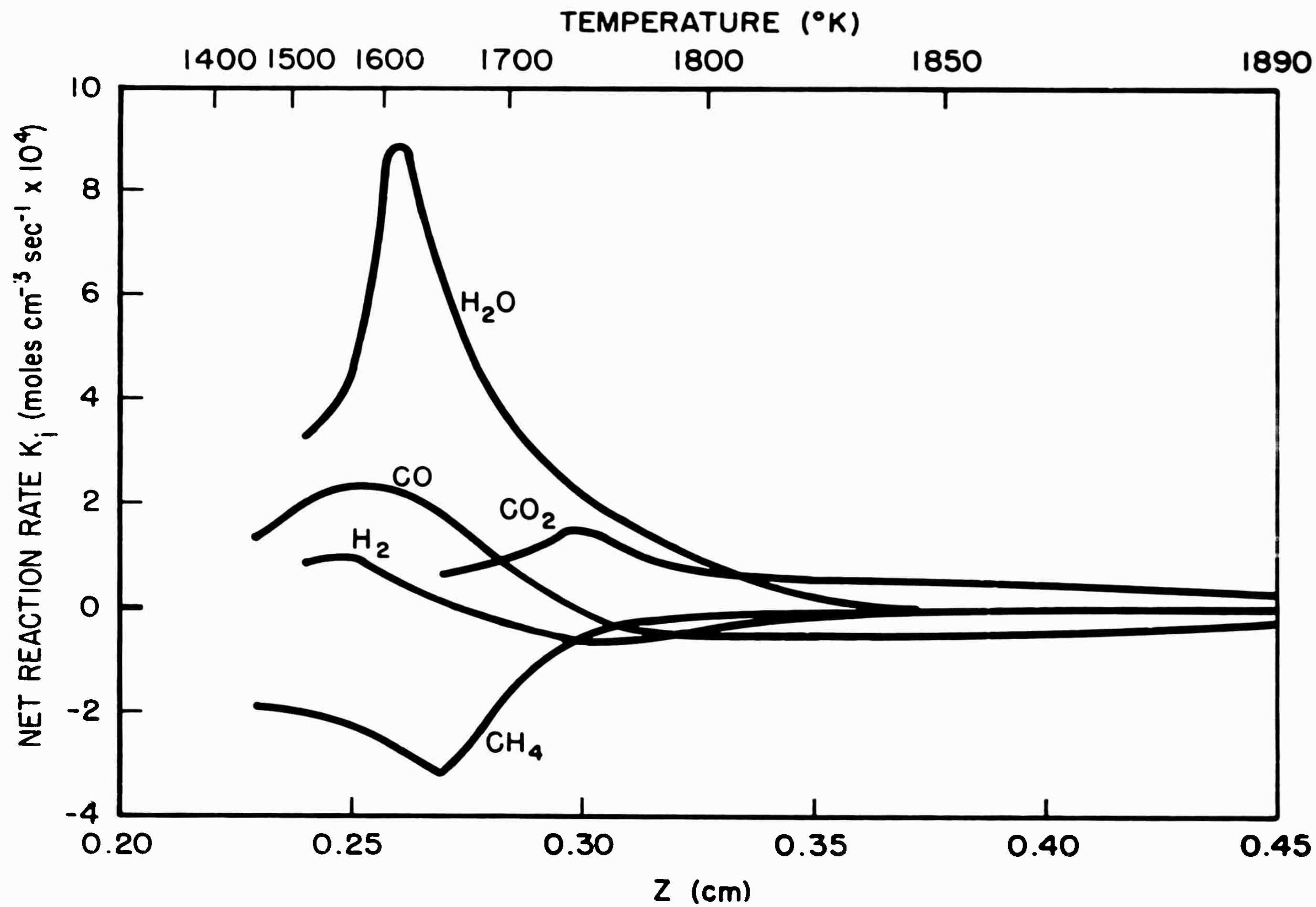


Fig. I-1 REACTION RATES IN $CH_4$ - $O_2$ FLAME. PRESSURE = 0.1 ATM.

Some interesting qualitative observations can be made from these rate profiles first of all. It will be noted that the flame can be conveniently divided into three zones. The first, extending from the screen ($z = 0$) to approximately $z = 0.2$ cm, corresponds to a region where all changes in composition and temperature are due simply to transport processes. There is essentially no chemical reaction until a temperature of about 1300° is reached. The second zone, covering the approximate range $z = 0.2 - 0.3$ cm, is where most of the fast reactions occur. Here the $CH_4$ largely disappears with formation of most of the $H_2O$, CO, and $H_2$. The third zone, from $z \approx 0.3$ cm on out to the hot boundary at $z \approx 0.9$ cm (far beyond the limit shown on Fig. I-1), is a slow reaction zone where CO is converted to $CO_2$. This is the CO "afterburning" region previously noted by others (Ref. 4).

From a quantitative viewpoint, the data may be used to derive considerable information. These are noted as follows:

i) Without specifying any details of the actual mechanism which may prevail in the flame the various rates should be related to one another in a predictable way. Since atoms of a particular element are neither created nor destroyed in the combustion process, it is possible to write in general that

$$\sum_i n_i K_i = 0 \tag{3}$$

where $n_i$ is the number of atoms of an element in a molecule of species i. Eq. (3) should be obeyed for each element throughout the flame. Thus for carbon

$$K_{CO} = - K_{CH_4} - K_{CO_2} - K_{CH_2O} \tag{4}$$

Figure I-2 shows a comparison of these experimental quantities, i.e., $K_{CO}$ and $(-K_{CH_4} - K_{CO_2})$. The contribution of $K_{CH_2O}$ was neglected. The agreement is generally very good. The two curves have similar shapes, have their maxima and minima at about the same spatial positions, and the absolute magnitudes agree quite well - especially in the long CO afterburning region where $K_{CH_4}$ has vanished. Similarly, for hydrogen, Eq. (3) yields

$$K_{H_2O} = -2K_{CH_4} - K_{H_2} - K_{CH_2O} \qquad (5)$$

and the comparison of the two sides of Eq. (5) is given in Fig. I-3 (neglecting $K_{CH_2O}$). Again the agreement is generally good. The worst deviations occur, as usual, in the region of most rapid reaction, which might be expected. The fact that the requirements of element conservation are met reasonably well by the data shows that they are internally consistent and the analytical treatment used to derive the rates is sound.

ii) For use in practical calculations (such as in the case of nonequilibrium nozzle flow), it is often necessary to have data on the over-all kinetics of a given reactant. Even in the rare case where a reasonable kinetic mechanism is available, it is usually so complex as to be impractical to use in calculations which are already very involved. From the over-all (also sometimes denoted by the execrable term "global") viewpoint, nothing whatever is implied about the actual elementary reaction steps in the process. A rate expression is set up which involves the concentrations of the reactants and an adjustable proportionality constant

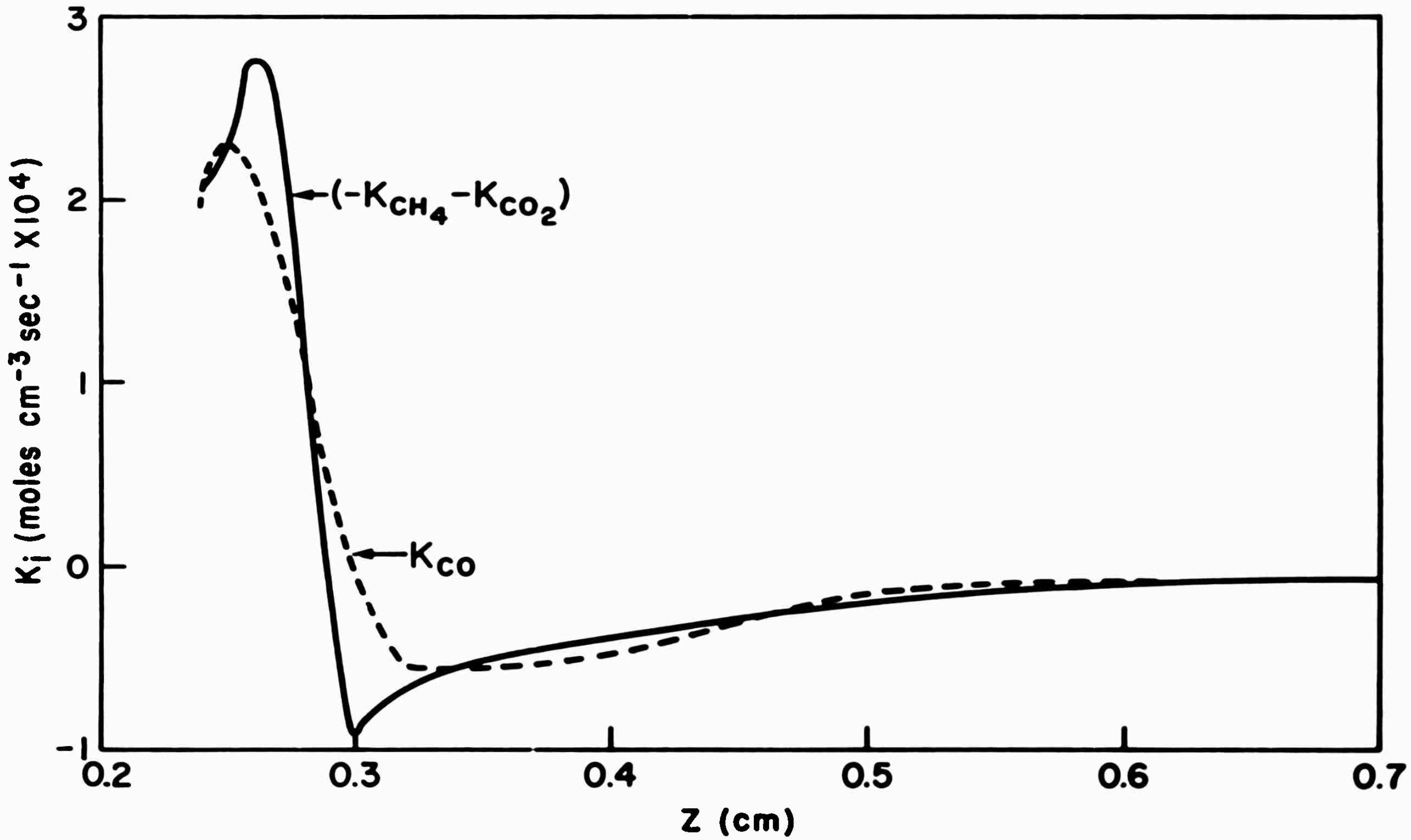


Fig. I-2 COMPARISON OF $K_{CO}$ WITH THE COMBINED RATE ( $-K_{CH_4} - K_{CO_2}$).
PRESSURE = 0.1 ATM.

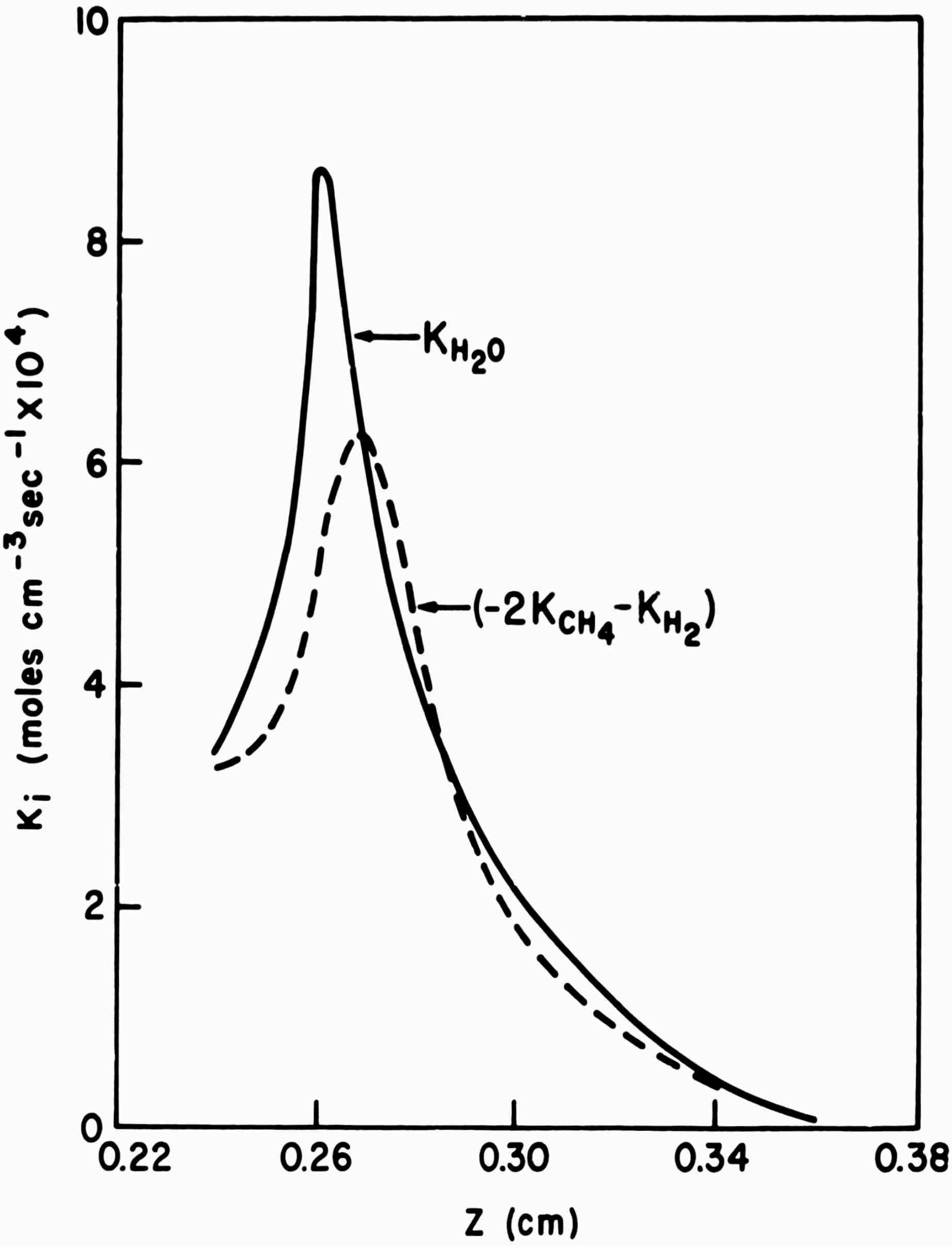


Fig. I-3 COMPARISON OF $K_{H_2O}$ WITH THE COMBINED RATE $(-2K_{CH_4} - K_{H_2})$. PRESSURE = 0.1 ATM.

(i.e., a rate constant - function of temperature in general), and the experimental data are fitted to this expression. It is strictly an empirical procedure, justified only if it is useful.

The methane-oxygen flame data can be treated in this way. The CO oxidation provides a good example. Let us write the expression

$$\frac{d(CO_2)}{dt} = K_{CO_2} = k\,(CO)(O_2) = k\,N^2\,X_{CO}\,X_{O_2} \qquad (6)$$

where the parentheses indicate concentration in moles $cm^{-3}$, $N$ is the total molar concentration, and the $X$'s are mole fractions. $k$ is an empirical second order rate constant having units of $cm^3\ mole^{-1}\ sec^{-1}$. We presume that such an expression holds when there is considerable $H_2O$ present, since the rate of oxidation of CO with very little $H_2O$ is strongly dependent on the $H_2O$ concentration. It is better to write Eq. (5) in terms of the appearance rate of $CO_2$ rather than the disappearance rate of CO, since the latter is not directly determined experimentally except in the afterburning region (see Eq. (3)). Using the experimental values of $K_{CO_2}$, $N$, and the mole fractions, the rate constant $k$ was determined throughout the region where there were valid $K_{CO_2}$ data, i.e., $z = 0.27 - 0.60$ cm corresponding to temperatures 1650-1940°K. The values of $k$ so obtained were essentially independent of temperature and centered around the value

$$k \approx 8 \times 10^9\ cm^3\ mole^{-1}\ sec^{-1}$$

The temperature-independence presumably is an indication that the CO oxidation actually is a free radical reaction of low or zero activation energy.

It is of interest to compare this value with those obtained by other workers. Fenimore and Jones (Ref. 5), using flames of several different hydrocarbons at atmospheric pressure, concluded that the rate constant defined in Eq. (5) had a value of about $1\text{-}2 \times 10^9$ in a similar temperature range. They attributed an Arrhenius-type temperature dependence to k, however, and assigned an activation energy. Friedman and Cyphers (Ref. 6), using a propane-air flame at 46 mm pressure, obtained data which can be corrected to conform to our definition of k. The result at $1600^\circ K$ was about $4 \times 10^9$. For a flame of CO and $O_2$ with several percent of $H_2O$ present burning at 30 mm pressure, Friedman and Nugent (Ref. 7) obtained data which yields a value of about $1 \times 10^9$ at $1800^\circ K$, while with $H_2$ in the original mixture burning to give the same amount of $H_2O$ the values of k computed are 2-3 times higher than this. These various experimental rate constants are summarized in Table I-1.

Table I-1. Comparison of over-all rate constants for the $CO\text{-}O_2$ reaction from work of various authors. Excess $H_2O$ present.

| Author | Flame Type | k ($cm^3 mole^{-1} sec^{-1}$) |
|---|---|---|
| This work | $CH_4\text{-}O_2$ at 76 mm | $8 \times 10^9$ ($1650\text{-}1940^\circ K$) |
| Fenimore & Jones (Ref. 5) | Hydrocarbon-air at one atm. | $1\text{-}2 \times 10^9$ ($1700\text{-}1900^\circ K$) |
| Friedman & Cyphers (Ref. 6) | $C_3H_8$-air at 46 mm | $4 \times 10^9$ ($1600^\circ K$) (corrected) |
| Friedman & Nugent (Ref. 7) | $CO\text{-}O_2\text{-}H_2O$ at 30 mm | $1\text{-}3 \times 10^9$ ($1800^\circ K$) (corrected) |

All of these data were obtained by flame structural studies. No other data by other techniques are known to us, although such a comparison would be very valuable. In any case, the data given in Table I-1 appear in reasonable agreement - quite remarkable agreement considering the wide variety of experimental pressures, reactants, and technical details of sampling, analysis, correction for diffusion, etc. Accordingly, it seems likely that the over-all rate constant for the reaction defined as in Eq. (5) is quite reliably established in the indicated temperature range, and could be used in practical computations for which it is appropriate.

Heat Release Rates in the 1/10 Atmosphere $CH_4$-$O_2$ Flame

It is of some interest to compute the volumetric heat release rate profile from the experimental data. There are two ways of doing this, which can then be checked against each other. If we define Q as the rate of heat evolution (a positive quantity), then the simplest way to compute it is by way of the relation

$$Q = -\sum_i H_i K_i \tag{7}$$

where $H_i$ is the absolute molar enthalpy of species i. The negative sign is necessary to conform to the above sign convention, which is contrary to the usual thermodynamic convention. The alternative approach is to use the energy conservation and species continuity equations which may be combined to give

$$Q = \rho v \frac{dT}{dz} \sum_i \frac{G_i C_i}{M_i} - \frac{1}{A} \frac{d}{dz} \left(A \lambda \frac{dT}{dz}\right) \tag{8}$$

where $C_i$ is the molar heat capacity at constant pressure, A is the streamtube area ratio relative to some reference value, and $\lambda$ is the gas thermal conductivity.

The method of computing Q from Eq. (6) involves only the chemical rates and the corresponding enthalpies, so it is a direct measure of the rate of enthalpy change per unit volume due to reaction. The method of Eq. (7) regards Q as a source term in the enthalpy flux conservation equation and involves the temperature and $G_i$ profiles. The results of both approaches are shown plotted in Fig. I-4. Typically, the worst deviations occur in the fast reaction zone. This may be due to neglect of free radical effects, since presumably if these could be sampled and their rates $K_i$ (positive quantities in this region) determined, they would contribute positive enthalpy $H_i$ to the sum in Eq. (6) and thus lower the value of Q obtained, bringing it more nearly in agreement with the curve determined from Eq. (7). The two curves agree very well in the CO afterburning region.

## The 1/20 Atmosphere $CH_4$-$O_2$ Flame

The experimental data on this flame have now been obtained and are being analyzed. Results of this work will be described in the next Quarterly Progress Report.

## References

1) Task R Quarterly Progress Report No. 1 for the period 1 April - 30 June, 1959. The Johns Hopkins University, Applied Physics Laboratory Report No. TG-331-1 (July 1959).

2) Task R Quarterly Progress Report No. 2 for the period 1 July - 30 Sept. 1959. The Johns Hopkins University, Applied Physics Laboratory Report No. TG-331-2 (October 1959).

3) R. M. Fristrom, C. Grunfelder, and S. Favin. To be published in J. Phys. Chem.

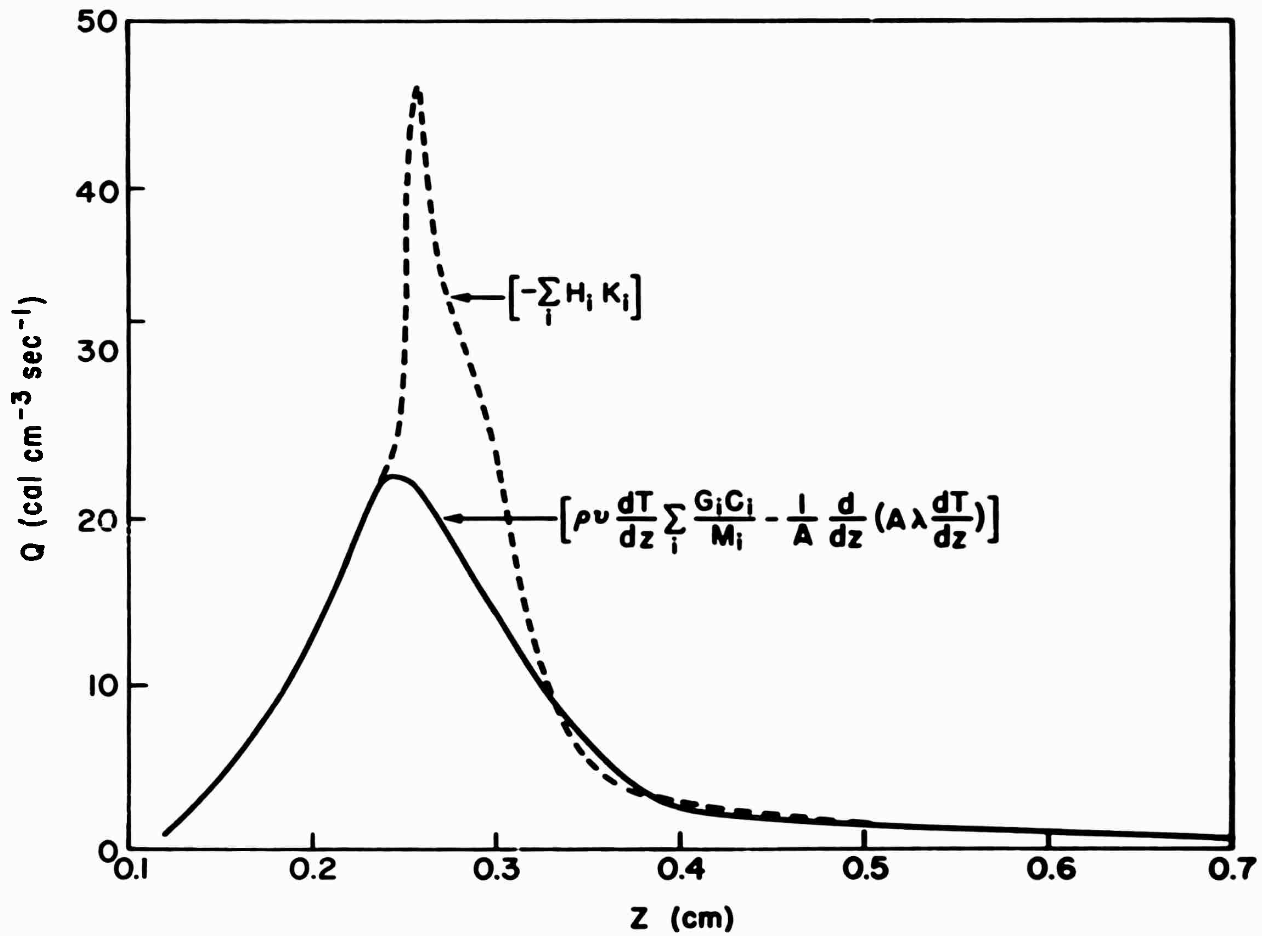


Fig. I-4 COMPARISON OF THE TWO METHODS OF COMPUTING VOLUMETRIC HEAT RELEASE RATE.

4) R. Friedman and E. Burke, J. Chem. Phys. 22, 824 (1954).

5) C. P. Fenimore and G. W. Jones, J. Phys. Chem. 61, 651 (1957).

6) R. Friedman and J. A. Cyphers, J. Chem. Phys. 23, 1875 (1955).

7) R. Friedman and R. G. Nugent, Seventh Symposium on Combustion (Butterworth's, Lond, 1959) p. 311.

## II. THERMAL CONDUCTIVITY OF GASES BY A NEW TECHNIQUE

(R. E. Walker, N. deHaas, A. A. Westenberg)

### Objective

The analysis of the problem of convective heat transfer both in the laminar and turbulent flow regimes requires that the properties of the gases involved be quantitatively understood. The coefficient of thermal conductivity is one such property. Measurement of thermal conductivity of gases has not been a forsaken field of research, and several common gases have been investigated up to temperatures approaching reaction motor temperatures. The primary shortcomings of past and present research in the study of thermal conductivity of gases for application to such heat transfer problems are: a) inability to apply present experimental methods to temperatures above about 1000°K (most measurements are made at substantially lower temperatures than this), b) the complexity and difficulty in using the usual apparatus for this measurement (thermal-conductivity cells), and c) the lack of measurements on species (and mixtures) prevalent in reaction motors. Other shortcomings could be listed.

Recent measurements of molecular diffusion coefficients - a closely related transport property (Ref. 1) - of common flame gases at temperatures in excess of 1000°K applied a simple concept (Ref. 2) that could, in principle, be used for measuring other gas transport properties (conductivity and viscosity). In this method, a point source of a trace gas is located in the center of a uniform, heated laminar jet of a second gas. A series of gas samples removed immediately downstream of the source and quantitatively analyzed is used to determine the molecular diffusion coefficient. The technique has good precision (±1-2%) and is quite adaptable to high temperatures and various gas types.

Application of this method to the measurement of thermal conductivity of gases is an obvious extension. The source of trace gas is replaced with a point (or line) source of heat and the temperature rise downstream of the heat source is measured with an appropriate technique. The method is simple, should have good precision (±2%), and can be used with a variety of gases at high ambient temperature (approaching flame temperatures). Thus, the objective of this research is to employ the point-source or the line-source technique in the measurement of gas thermal conductivity and, if successful, to use the method for obtaining data over a wide range of temperature on pure gases and mixtures of propulsive interest.

Theory of the Method

This has been described in detail in Ref. 3.

Experimental Technique

During the period of this report a number of changes in the experimental apparatus have been made from that originally described in Quarterly Progress Report No. 1 (Ref. 4). A description of these changes follows.

1. Line heat source. In the case of the line source, heat conduction along the wire to the flow tube walls where it is attached may give rise to a significant error in the determination of q, the heat dissipation per unit length, to be used in the working equation (Ref. 3) for the determination of the thermal conductivity of the gas. The proper q to be used in the working equation is the q which corresponds to the central portion of the source wire. The temperature decrease at the wire ends due to heat conduction to the walls decreases the resistance of the wire in this region,

so that the average q for the entire wire differs from the q in the central portion. This error may be reduced by using a wire of low thermal conductivity and low temperature coefficient of resistivity, and also by attaching the voltage measuring leads to the same wire at some distance from the walls. In view of these facts, a line source of 0.0005-in.-diameter platinum - 10% rhodium wire was mounted in a 3 cm flow tube and is now in use. This source wire has potential leads of the same wire welded to it at points approximately 4 mm from the walls.

2. Measurement of the temperature rise. The method of measurement of the temperature rise downstream of the source has been improved by the use of a high sensitivity DC breaker amplifier.* The output of the differential thermocouple (Ref. 4) is applied to the input of the amplifier and the output is displayed on a chart recorder. The input circuit to the amplifier was constructed so as not to introduce harmful thermoelectric potentials and was shielded to reduce the effect of stray fields. A known resistance was included in the input circuit for the purpose of applying an accurately known calibrating voltage to the amplifier. Also, a variable negative feedback system was installed in the amplifier. Adjustment of the feedback ratio changes the effective input resistance, which then provides a check on Peltier heating of the thermocouples.

The advantages of the above system over that of using a potentiometer** to measure the differential thermocouple EMF directly are briefly:

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* Beckman Instruments, Inc., Model 14.

** A Rubicon High Precision Type B Potentiometer.

(a) The precision of EMF measurement is increased from $\pm 1$ μv to approximately $\pm 1/20$ μv. This makes possible the accurate measurement of smaller temperature differences and the use of a thermocouple system of lower (and more precisely known) thermoelectric power, such as Pt-Pt, Rh. It also allows lower source heating rates to be used.

(b) The total time required to make the number of measurements necessary for a thermal conductivity determination at a given temperature is reduced by a factor of 3. This is particularly desirable in regard to those changes in the entire system which effect the individual thermocouple EMF's and are not canceled out in the two opposing thermocouples.

(c) Looking forward to measurements at higher temperatures, it may be expected that the above-mentioned uncompensated drift may be greatly enlarged through time and position variations in the gas temperature. If this occurs, it may become necessary to chop the current to the wire, thus providing a square wave heat source. With the thermocouples fixed in position, adjustment for zero would be made during the time of zero current and a single potential measurement would be made while the current is flowing. With the currently alternately off and on for a period of 15 seconds each, it is then required that the uncompensated drift be small for approximately this length of time. The present amplifier-recorder system is particularly adapted for this method of measurement.

The reproducibility in the thermal wake temperature measurements using the line source and instrumentation described above is better than $\pm 1/2\%$.

Results of Measurements Using the Line Source

In Quarterly Progress Report No. 2 it was reported that the measured thermal conductivity of nitrogen at 300°K using the line source varied markedly with the downstream position (x) of the transverse profile measurements (see Fig. II-5 of Ref. 3). During the period of this report it has been shown that this variation of measured $\lambda$ with the profile x is due to non-uniformity in the velocity field downstream of the wire heat source. A theoretical study of this has pointed the way to a correction to the data which has given measured $\lambda$'s that are independent of the profile x. This will be shown in the presentation of results for nitrogen and helium at room temperature, obtained by using the apparatus described in the previous section.

Table II-1 lists three sets of measured quantities and computed thermal conductivities; two are for nitrogen at differing rates of heat release and the third is for helium. Each set consists of maximum profile potentials, $E_m (= a\Delta T_m)$, measured at a number of relative downstream distances, x, and half widths of the temperature profiles, z, corresponding to a given $E_m/E$ value at each relative x. In the section labeled "uncorrected" there appear computed $\lambda$'s which were obtained using the working equation

$$\lambda^2 = \frac{q^2 a^2}{8\pi \; xE_m^2} \cdot \frac{(r-x)}{\log\left\{\frac{E_m}{E}\sqrt{\frac{x}{r}}\right\}}$$

where a (= $E/\Delta T$) is the thermoelectric power of the downstream thermocouple. In this analysis of the data the relative x were displaced to make $xE_m^2$ independent of x. Fig. II-1 includes a curve of the uncorrected $\lambda$ plotted against the

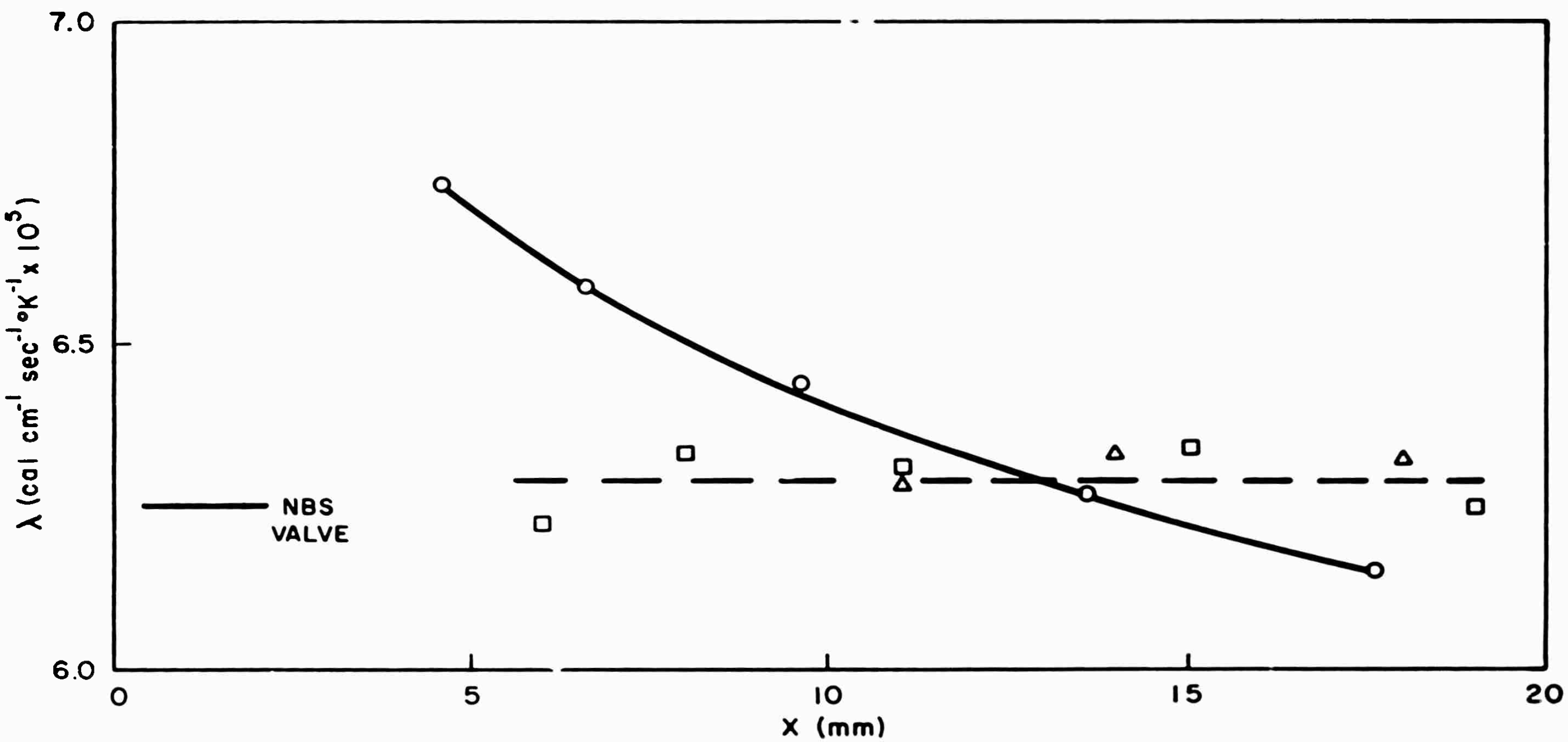


Fig. II-1 THERMAL CONDUCTIVITY MEASUREMENTS ON NITROGEN. T = 300°K.

0: UNCORRECTED DATA,

□ : CORRECTED DATA ($Q = 9.12 \times 10^{-3}$ CAL SEC$^{-1}$ CM$^{-1}$)

△ : CORRECTED DATA ($Q = 6.96 \times 10^{-3}$ CAL SEC$^{-1}$ CM$^{-1}$)

TABLE II-1

| Data Set | Uncorrected | | | | Corrected | | | Literature Values |
|---|---|---|---|---|---|---|---|---|
| | x (mm) | $E_n$ (μv) | z (mm) | $\lambda \times 10^5$ (cal/cm sec °K) | $x_c$ (mm) | $E_m^{(o)}$ (μv) | $\lambda \times 10^5$ (cal/cm sec °K) | $\lambda \times 10^5$ |
| A | 4.60 | 28.60 | .955 | 6.75 | 5.00 | 23.85 | 6.23 | |
| | 6.60 | 23.91 | 1.123 | 6.59 | 8.00 | 20.59 | 6.34 | |
| | 9.60 | 19.91 | 1.331 | 6.44 | 11.00 | 17.61 | 6.31 | 6.24 (Ref. 5) |
| | 13.60 | 16.65 | 1.543 | 6.27 | 15.00 | 15.04 | 6.34 | |
| | 17.60 | 14.65 | 1.717 | 6.15 | 19.00 | 13.40 | 6.25 | |
| | | | | | | | mean = 6.29 | |
| B. | 8.35 | 16.00 | 1.263 | 6.73 | 10.95 | 13.07 | 6.28 | |
| | 11.35 | 13.74 | 1.438 | 6.57 | 13.95 | 11.59 | 6.33 | |
| | 15.35 | 11.81 | 1.632 | 6.41 | 17.95 | 10.23 | 6.32 | 6.25 (Ref.5) |
| | 20.35 | 10.22 | 1.838 | 6.26 | 22.95 | 9.03 | 6.30 | |
| | 23.35 | 9.54 | 1.947 | 6.20 | 25.95 | 8.49 | 6.28 | |
| | | | | | | | mean = 6.30 | |
| C. | 3.35 | 9.88 | 1.169 | 45.2 | 5.85 | 6.80 | 36.9 | |
| | 4.35 | 8.78 | 1.290 | 43.4 | 6.85 | 6.34 | 37.1 | |
| | 6.35 | 7.33 | 1.490 | 40.9 | 8.85 | 5.63 | 36.9 | |
| | 8.35 | 6.32 | 1.647 | 39.8 | 10.85 | 5.06 | 37.6 | 35.9 (Ref.6) |
| | 10.35 | 5.69 | 1.806 | 38.4 | 12.85 | 4.67 | 37.1 | |
| | 12.35 | 5.17 | 1.924 | 37.7 | 14.85 | 4.33 | 37.1 | |
| | 14.35 | 4.76 | 2.060 | 37.3 | 16.85 | 4.05 | 37.3 | |
| | | | | | | | mean = 37.1 | |

A. $N_2$: U = 40 cm/sec, q = $9.12 \times 10^{-3}$ cal $sec^{-1}$ $cm^{-1}$, T = 300°K, $\frac{E_m}{E} = 2.00$.

B. $N_2$: U = 40 cm/sec, q = $6.96 \times 10^{-3}$ cal $sec^{-1}$ $cm^{-1}$, T = 301°K, $\frac{E_m}{E} = 2.00$.

C. He: U = 100 cm/sec, q = $8.75 \times 10^{-3}$ cal $sec^{-1} cm^{-1}$, T = 298°K, $\frac{E_m}{E} = 1.43$.

profile x for set A. The "corrected" section of Table II-1 presents $\lambda$ results which were obtained by applying a correction which was necessitated by the velocity wake from the heating wire. The treatment of the data including the wake correction proceeds as follows:

(1) The measured relative x are displaced to make $(r-x)/\log\left\{\frac{E_m}{E}\sqrt{\frac{x}{r}}\right\}$ * independent of x. The new downstream distances are designated $x_c$.

(2) The measured $E_m$ are adjusted according to $E_m^{(o)} = E_m(1-AE_m)$. The constant A is obtained by requiring $x_c E_m^{(o)2}$ to be equal to two separated $x_c$ values.

(3) $\lambda$ is determined using

$$\lambda^2 = \frac{q^2 a^2}{8\pi\left[x_c E_m^{(o)2}\right]} \cdot \frac{(r-x_c)}{\log\left\{\frac{E_m}{E}\sqrt{\frac{x_c}{r}}\right\}} .$$

Table II-1 lists the $\lambda$ values obtained by this method along with the corresponding $x_c$ and $E_m^{(o)}$ values. It is seen that the $\lambda$ values for the three sets of data are no longer dependent on the profile x value and that the average compares favorably with the measurements of others. Fig. II-1 shows the constancy of the corrected $\lambda$ with profile x for data sets A and B.

It is also to be noted that the origin of the heat source is nearly the same for the three sets of data, which is as expected. This is in contrast to the uncorrected data where the origins differ by more than a millimeter among the sets. (Compare the x's corresponding to $x_c$ = 11.00, 10.95, and 10.85 of the three sets.)

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* In almost all cases it is sufficient to replace this quantity by (r-x) and in a number of cases z is small enough that the quantity may be replaced by $z^2/2x$.

The correction on $E_m$, which is equivalent to

$$\Delta T_m^{(o)} = \Delta T_m(1-A'\Delta T_m)$$

was derived from a theoretical consideration of the velocity profile downstream of a wire. This was made along the lines presented by S. I. Pai (Ref. 7) for two-dimensional jet mixing, replacing the jet in a uniform stream by an obstacle (wire) in a uniform stream. The constant A' in the above equation is a function of the thermal conductivity and temperature of the gas, the heat release rate of the wire and the drag on the wire. Since the drag on the wire is not known, A' (thus A) is determined by requiring $\lambda$ to be the same at two separated x values.

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# III. TRANSPORT PROPERTY STUDIES IN DISSOCIATED GASES

(R. E. Walker and A. A. Westenberg)

## Objective

Convective heat transfer from dissociated gases to a catalytic wall is significantly affected by the chemical kinetics, the nature of the catalytic surface, and the transport properties of the mixture. Although gas phase kinetics for dissociated gases have been studied separately in shock tube experiments, attempts to measure the catalytic nature of a surface have revealed that it is difficult to separate the catalytic effects from those due to diffusion. Until very recently (Ref. 1) no separate measurements of diffusion coefficients had been made, so that gross estimates of this transport property are generally required to obtain catalytic activity of various surfaces. Additional diffusion measurements for a variety of dissociated gases are desirable for this reason.

In addition, measurements of diffusion coefficients as a function of temperature is an excellent way of determining intermolecular forces between unlike molecules. For dissociated gases, the (labile) atom-(parent) molecule intermolecular forces could be obtained in this manner and subsequently be used to predict other related transport coefficients. (These intermolecular forces can be determined from first principles for only the simplest interactions (H-H, H-$H_2$, H-He).) Measurements of thermal conductivity and/or heat transfer coefficients in dissociated gases are also of considerable intrinsic and practical interest. The present project is aimed at exploring and using various methods of experimental measurement of transport properties in dissociated gases.

## Experimental Technique

Experimental effort thus far has been restricted to elementary experiments with dissociated gases created by a radio frequency (RF) discharge. A discussion of these preliminary experiments is given below.

## Preliminary Experiments

In order to obtain a "feel" for the concentration of atoms that can be produced by an RF discharge and the lifetimes of these atoms, the simple flow system shown in Fig. III-1 has been used. Atoms are generated by passing a diatomic gas ($O_2$ and $N_2$ have been used) through the inductance of a tuned tank circuit coupled to an RF transmitter capable of 90 watts input to final stage (EICO #720).* Atoms are detected downstream of the discharge by a fine platinum wire (0.001 in. dia.) maintained at a fixed temperature by a variable heating current. The change in heat dissipation with and without the discharge is a measure of heat release through catalysis (atom recombination on the surface of the wire) and the changes in convective and conductive heat transfer. The convective and conductive heat transfer is eliminated by using a similarly heated platinum wire that is coated with silica to render it non-catalytic. The heat release through catalysis, Q, can then be related to the number of atoms by the expression

$$Q = \frac{1}{8} n \bar{c} a \gamma h \tag{1}$$

where n is the number of atoms per unit volume, $\bar{c} = (\frac{8kT}{\pi m})^{1/2}$ is the mean molecular speed, a is the surface area of the wire, $\gamma$ is the surface catalytic activity for atom recombination (i.e., the percentage of atoms striking the surface which recombine) and h is the dissociation energy per molecule.

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* A total of 500 watts is now available by the addition of a recently purchased RF amplifier (Viking Courier).

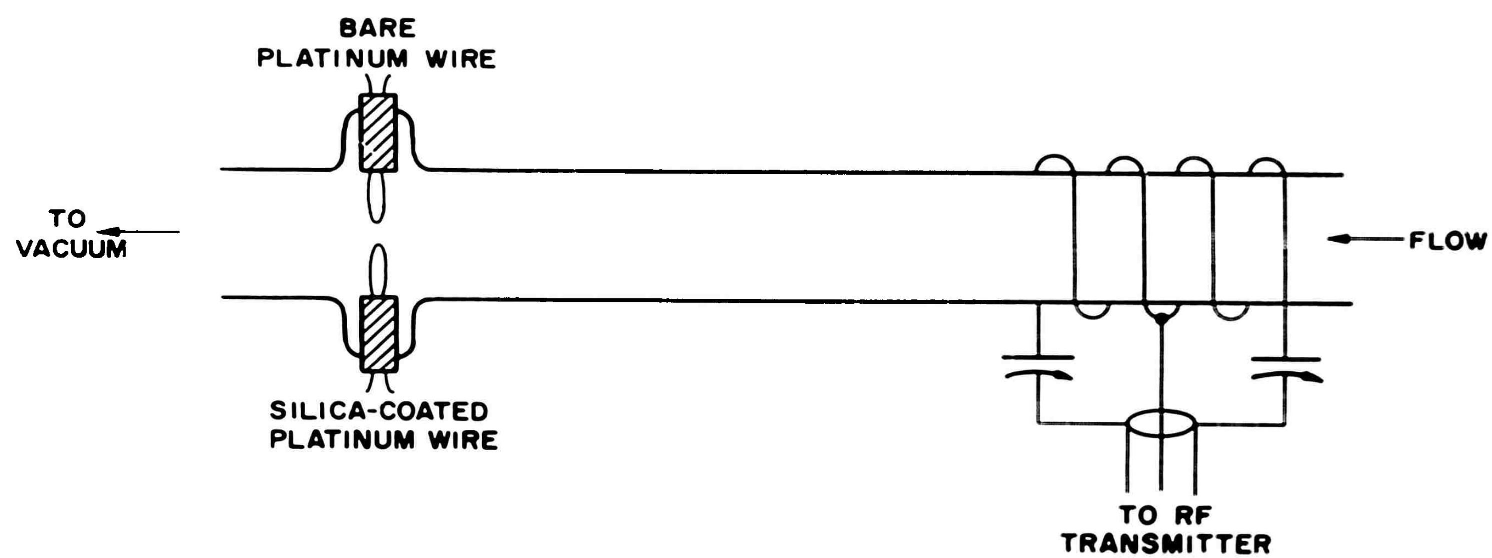


Fig. III-1 SKETCH OF METHOD USED TO MEASURE ATOM CONCENTRATION IN A DISSOCIATED GAS.

Preliminary experiments have been restricted to oxygen gas and the effects of pressure at different flow rates. A summary of the data is given in Fig. III-2. At pressures below about 0.1 mm Hg the efficiency of the RF discharge is quite poor. At the elevated pressures the discharge is also less efficient, and in addition, atoms are presumably lost by wall recombination. Additional refined experiments along this line are planned.

Proposed Experiment for Diffusion Measurements of Dissociated Species

The usual method of measuring the efficiency of a surface for atom recombination is to place the catalytic surface at the closed end of a side-arm attached to a tube containing a flowing dissociated gas (Ref. 2). The net flow in the side arm is zero and the flux of labile species to the catalytic surface is controlled by the diffusion through the gas mixture. By measuring the heat release at the surface (via a temperature rise) a measure of the flux is obtained, and by varying the depth of the side arm the ratio of catalytic activity to diffusion coefficient can be determined. A possible refinement of this method is to alter the atom flux by imposing a counterflow (see Fig. III-3). The concentration of atoms is then given by

$$C + \frac{C_o \gamma \bar{c}}{4\, U} = \left( C_L + \frac{C_o \gamma \bar{c}}{4\, U} \right) \exp \left[ - \frac{U}{D} (L - z) \right] \qquad (2)$$

where $C_o$ and $C_L$ are atom mole fractions at $z = 0$ and $z = L$, respectively, $U$ is the countercurrent gas velocity, and $D$ is the diffusion coefficient. In deriving Eq. (2) loss of atoms to the wall of the tube by heterogeneous reactions and by gas-phase reaction has been neglected and it is assumed that $C \ll 1$. For small

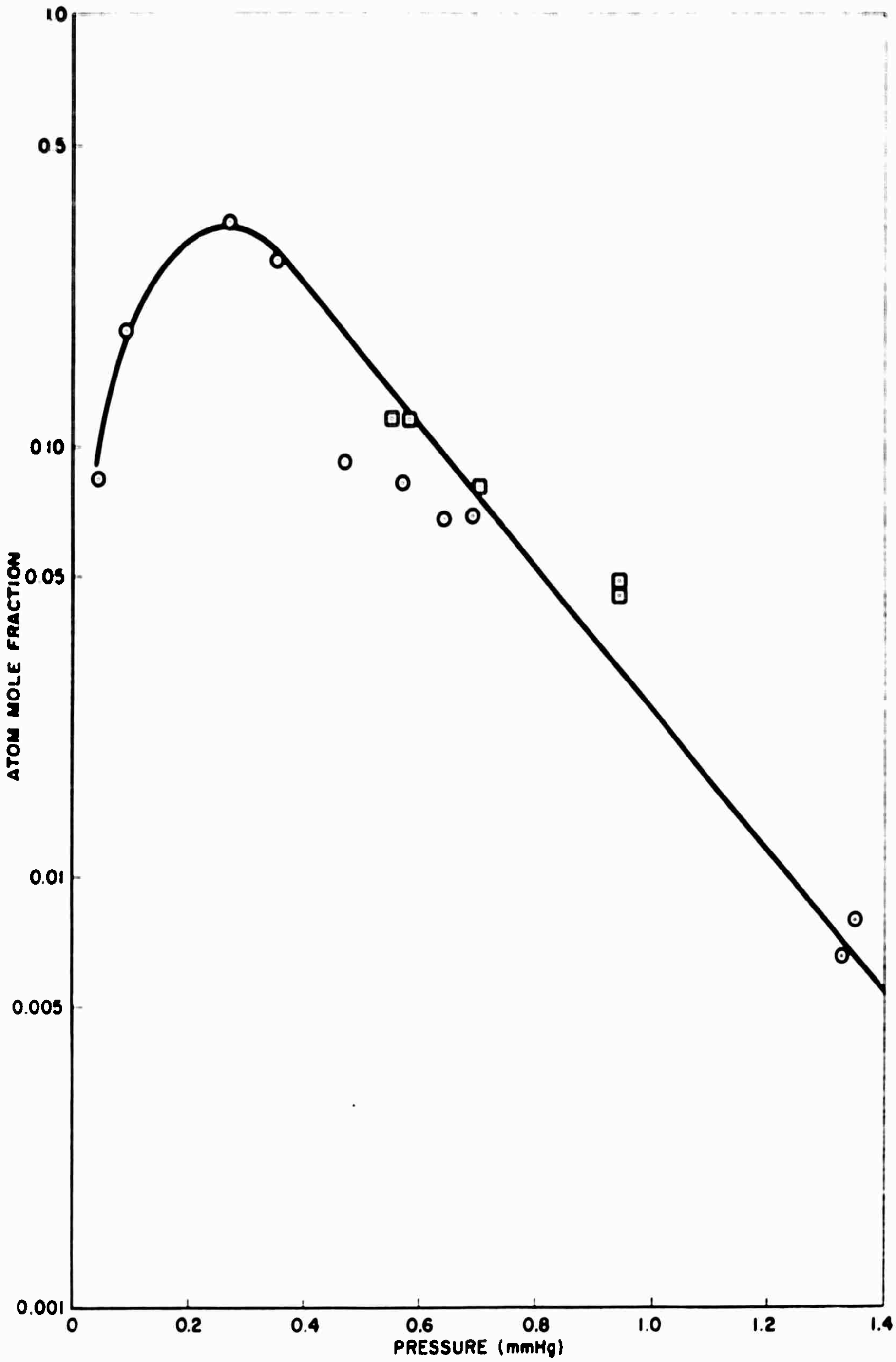


Fig. III-2 CONCENTRATION OF ATOMS 60 CM. DOWNSTREAM OF A 28 MC. RF DISCHARGE IN OXYGEN.
PYREX DUCT DIAMETER = 2.5 CM. (⊙ : FLOW RATE = 0.4 $CM^3$/SEC AT STP. ⊡ : 0.8 $CM^3$/SEC AT STP)

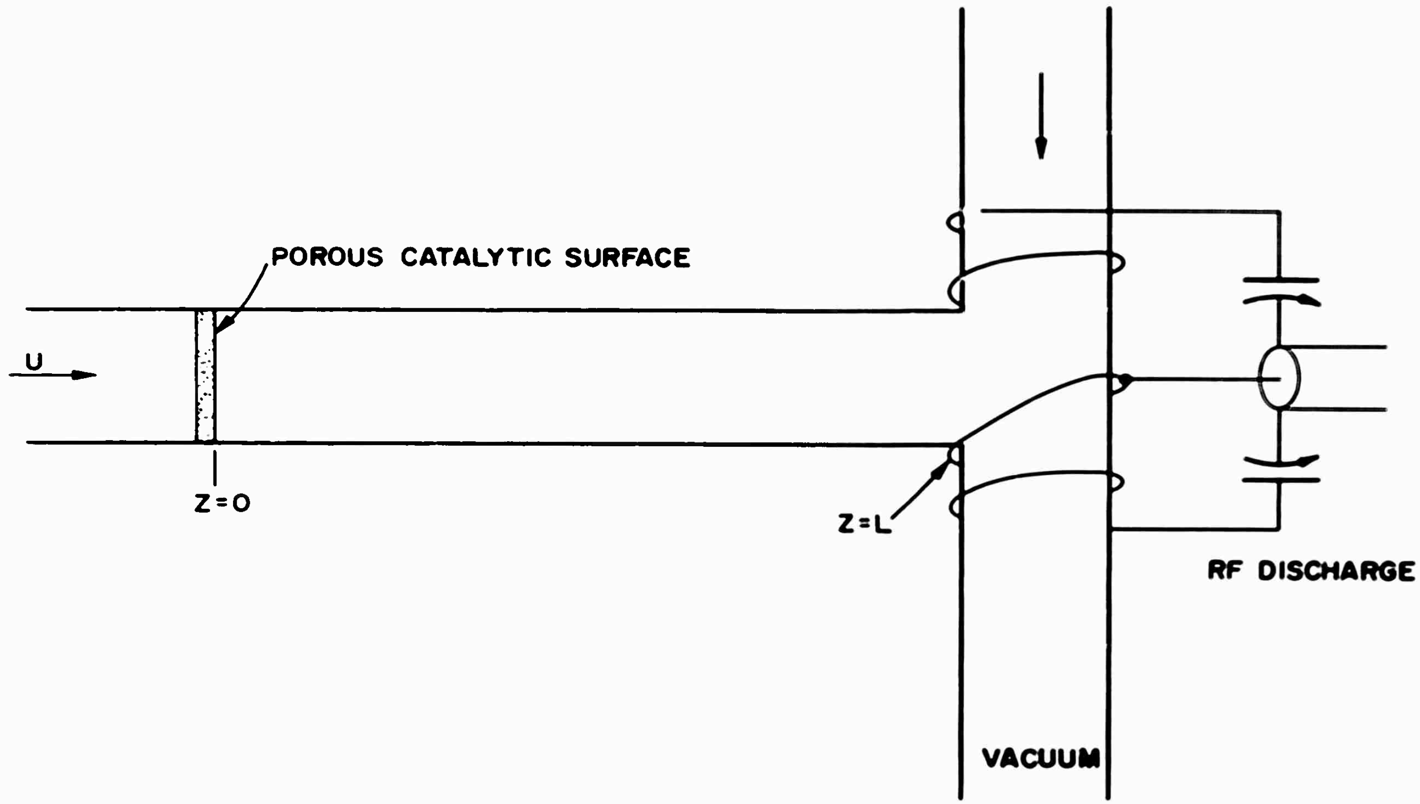


Fig. III-3 SKETCH OF SYSTEM USING HETEROGENEOUS REACTION WITH COUNTERFLOW AS A METHOD OF MEASURING DIFFUSION COEFFICIENTS OF DISSOCIATED GASES.

values of UL/D Eq. (2) expands to give

$$C_o \simeq (C_o)_{U=0} \left( 1 - \frac{UL}{D} \frac{1 + \frac{\gamma \bar{c} L}{8D}}{1 + \frac{\gamma \bar{c} L}{4D}} \right) \tag{3}$$

For some cases, $\frac{\gamma \bar{c} L}{4D} \gg 1$ so that Eq. (3) reduces to

$$C_o \simeq (C_o)_{U=0} \; (1 - \frac{UL}{2D}) \; , \tag{4}$$

although this condition need not necessarily apply. By measuring a quantity that is proportional to the concentration of atoms at the surface (say, a temperature rise) and by accurately metering the countercurrent flow, the diffusion coefficient can be measured.

At the low flow rates encountered in an experiment of this type, the flow may consist entirely of boundary layer and the simple mathematics surely will not apply. To avoid boundary layer problems, it may be desirable to use spherical geometry for which an expression similar to Eq. (3) can be developed. Both geometrical arrangements are presently receiving attention as possible methods of measuring diffusion coefficients of dissociated gases.

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## IV. HIGH TEMPERATURE CHEMICAL KINETICS FROM A REACTING POINT SOURCE

(M. L. Snow and A. A. Westenberg)

### Objective

One of the difficulties in the way of adequate understanding of the aerodynamics of high temperature, high speed gas flow has been the lack of information about the chemical kinetics involved. Obtaining this information has been difficult, especially in those cases where premixing the reactants before bringing them to reaction temperature is impossible because of the rapidity with which the reaction proceeds. Laminar flame studies such as are discussed in Section I, are one way of acquiring high temperature kinetic data if the reactants can be premixed. Another approach is to adapt and utilize the point source technique (Ref. 1) used for the measurement of diffusion coefficients, a method which should be especially useful when premixing is impossible. This technique will allow preheating of the reactants before mixing, steady-state operation, a fair temperature range, and simple psuedo-first order kinetics for analysis. Thus it can be seen that information obtained by this method might be a useful supplement to that obtained in the laminar flame work.

### Theory of the Method

Figure IV-1 is a schematic representation of the principle it is proposed to use. Here a trace amount of one reactant is continuously injected into the center of a laminar stream of a second reactant. Under conditions of constant temperature, pressure, and uniform carrier gas velocity U, and when the mixture

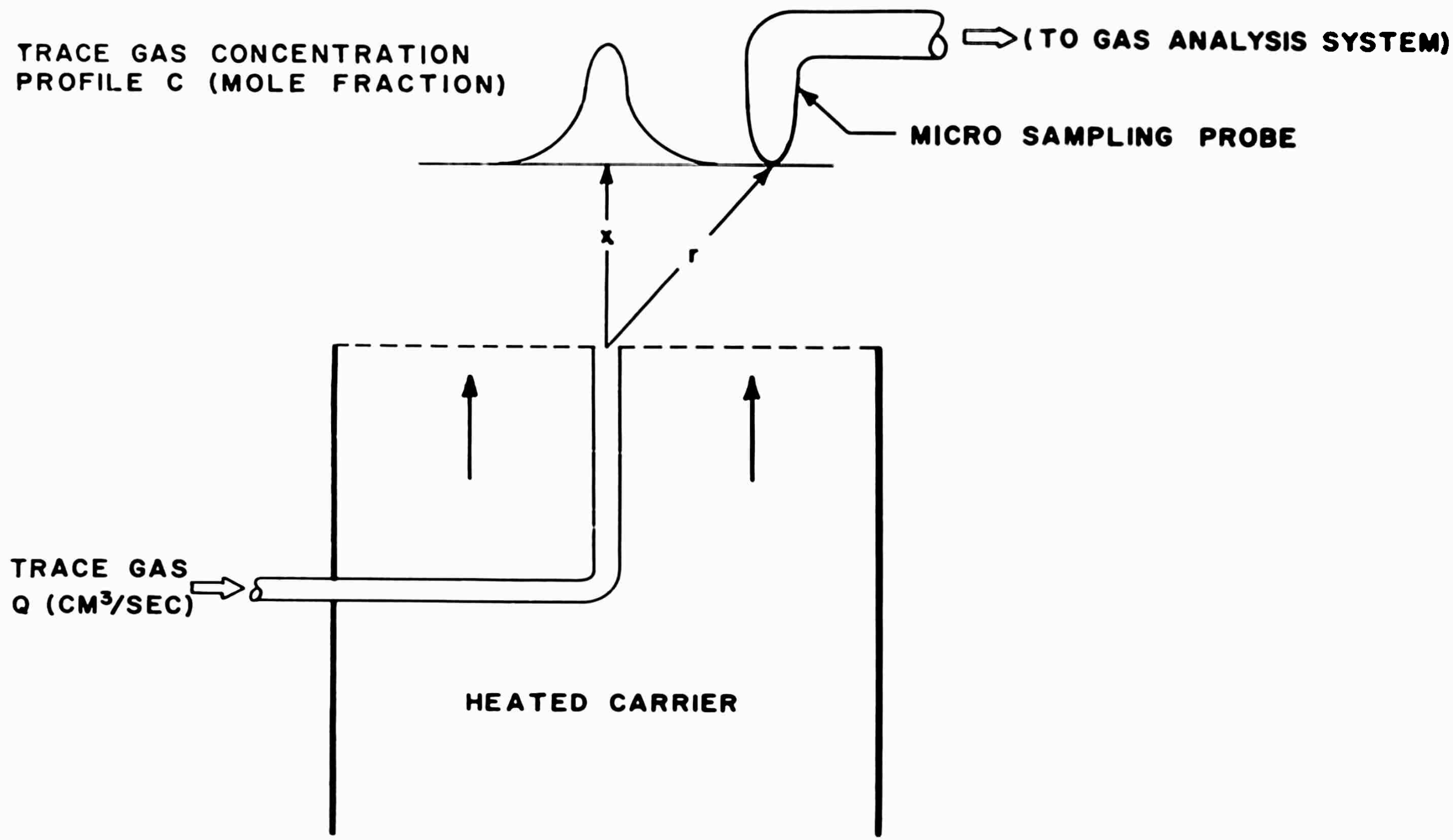


Fig. IV-1 SCHEMATIC DIAGRAM OF REACTING POINT SOURCE SYSTEM is so dilute in trace gas that the density is essentially constant, the equation governing the concentration C (mole fraction) of trace gas is

$$\nabla^2 C - \frac{U}{D}\frac{\partial C}{\partial x} - \frac{k\,C}{D} = 0 \tag{1}$$

where D is the binary diffusion coefficient (constant) and k is the pseudo-first order rate constant for the disappearance of trace gas, i.e., the chemical rate expression is taken to be

$$\frac{dC}{dt} = -\,k\,C \tag{2}$$

in view of the large excess of carrier. At a given temperature, Eq. (1) may be solved to give

$$C = \frac{Q}{4\pi D r}\ \exp\left\{\frac{U}{2D}\left(x - r\sqrt{1 + \frac{4Dk}{U^2}}\right)\right\} \tag{3}$$

where Q is the volumetric flow rate of trace gas from the source.

To obtain k, one would measure C first at a series of position on the axis where x = r, and second, at a series of positions r along a transverse profile of fixed x.

For the first case, one may show that

$$k = Dm_1^{\,2} = Um_1 \tag{4}$$

where $m_1$ is the slope of the line obtained from plotting

$$\log\frac{C_2\,x_2}{C_1\,x_1}\ \text{versus}\ (x_2 - x_1)\ ,$$

where $C = C_i$ for $x = x_i$ .

For the second case,

$$k = Dm_2^2 - U^2/LD \tag{5}$$

where $m_2$ is the slope obtained by plotting $\log \frac{C_2 r_2}{C_1 r_1}$ versus $(r_1 - r_2)$, where $C = C_1$ for $r = r_1$.

Thus, if Q and U are unknown but constant, it is possible to determine the rate constant k if the diffusion coefficient has been previously determined. An important point is that only ratios of concentrations are required, so no calibrations are necessary.

<u>Experimental</u>

One system of interest in combustion is the oxidation of carbon monoxide. Inasmuch as the diffusion coefficient of CO into oxygen had already been determined with precision (Ref. 2) and some rate data were available from laminar flame studies, this pair was chosen for the initial work.

A thermal conductivity cell is used to analyze the gas mixture. However, the thermal conductivity of CO is too close to that of $O_2$ for the method to be very accurate. Consequently, the following scheme was devised. The gas mixture drawn into the probe is first passed through a liquid nitrogen trap to remove any carbon dioxide which has been formed. The mixture is then passed through a heated platinum catalyst to oxidize the previously unreacted CO, and this mixture of $CO_2$ and $O_2$ goes into one side of the T-C cell. The gas then passes through a second liquid nitrogen trap, removing the $CO_2$ and allowing pure oxygen, the reference gas, to flow into the other side of the T-C cell. This continuous flow system thus gives a record of the CO concentration at any given time.

It is apparent that the reacting sample drawn into the probe at any point must be quenched effectively in order for meaningful measurements to be made. The sampling probes used will be similar to those used in flame studies (Ref. 3), where sonic flow and rapid drop in pressure on entering the probe are relied on to quench reactions.

## Results

As of the present time, the equipment has been assembled and most of the operating difficulties eliminated. However, a few still remain and so no results of any consequence have yet been obtained.

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## V. ROCKET NOZZLE FLUID DYNAMICS

(F. K. Hill, H. A. Wallskog, and H. J. Unger)

### Objective

The investigations carried out in this problem are concerned with the dynamics of the high speed gas flows occurring in solid propellant rocket nozzles. With high temperatures and large mass flow rates and with rapid expansion of the gas through the nozzle, it is important to describe the fluid properties taking into account non-equilibrium and non-ideal gas conditions. Experimental data pertinent to an accurate description of the gas are the first objective so that an adequate theory of the fluid dynamic behavior may be formulated.

In order to provide realistic and representative testing conditions for the experiment a double-base solid propellant (ARP)* has been chosen which provides the five basic constituents common to most high impulse propellants. These are hydrogen, nitrogen, carbon monoxide, carbon dioxide and water vapor. Impurities of the order of 2 to 3% are present as is the case in all propellants and it is possible to add in well controlled amounts and sizes solid particles for future extensions of the

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* The propellant is manufactured and proof tested at Allegany Ballistics Laboratory.

experimental studies. To begin with it is believed advisable to keep the problems as uncomplicated as possible while still retaining the fundamental aspects of the phenomena under investigation. Combustion pressure and temperature of the grain are 1000 psi, nominal and 2500°K, respectively; end burning is employed for either 10-second or 30-second operation. These conditions are sufficient to introduce measurable effects due to the variable gas properties as the gas expands through the nozzle, gas non-equilibrium conditions in the expanded flow and heat transfer and nozzle divergence angle effects. Associated phenomena, such as erosion and deposition of solid particles, are also present for observations providing additional data.

It is anticipated that as the work progresses higher specific impulse propellants will be utilized providing temperatures in the 3000°K to 4000°K range, and that investigations of the effects of metal additives to the grain will be carried out. Cooling and heat transfer measurements to the nozzle walls will be made and some properties of materials directly associated with the rocket gases may be undertaken.

## Introduction

As described in earlier reports (Refs. 1,2), one of the problems to be undertaken was the determination of the actual flow properties in a rocket nozzle and their comparison with the calculated properties based on gas equilibrium assumptions. It was evident that with high impulse propellants which, during burning, produce a high enthalpy gas mixture, the rate of conversion of this thermal energy to kinetic energy must govern the over-all efficiency as well as the environmental conditions of the nozzle and associated equipment. Any non-equilibrium condition, e.g., the relaxation of excited states, or any chemical reactions which occur during the expansion process in the nozzle may be significant in the ultimate kinetic energy of the exhaust gases. Interrelated with these processes are surface phenomena of the containing walls, including heat transfer and possible efficient methods of cooling and/or insulation.

## Nozzle Surveys

The experimental work was directed toward making accurate aerodynamic surveys of the flow Mach number and pressure distribution in the nozzle where both the gas density and static temperature were relatively high. Two series of tests were made using nozzles of $12.5^\circ$ and $26^\circ$ total divergence angles, so that the flow or transit time of the gas from throat to survey station was varied by a factor of two, whereas Mach number and flow velocity would be approximately the same. Because of the severe environmental conditions, fixed probes were used and not all of the data obtained were valid due to mechanical failures. However, although one or two tests remain for the $12.5^\circ$ nozzle, the survey in both nozzles at the $M = 3$ station are sufficiently complete to provide a significant comparison. The data are shown in the top part of Fig. V-1 with one set for the $12.5^{\circ}$ nozzle and two sets for the $26^{\circ}$ nozzle. The tests with the $26^{\circ}$ nozzle were carried out first, and only one nozzle was used in which there was a progressive enlargement of the throat diameter ( 0.001" per 10 second run). Consequently, there was a slight decrease in area ratio as the tests progressed; also, from experience improvements were made in the mechanical support of the probes. The line through the lower data represents the first tests and the upper line the final tests, which are believed to be a more accurate description of the $26^{\circ}$ nozzle flow. Nevertheless, because a comparison between the two nozzles of differing divergence angle is to be made, the conservative view is to take the lower curve for the $26^{\circ}$ nozzle. The data displayed in graphical form are the pitot-to-supply-pressure ratios, $P_h/P_o$, as a function of distance from the nozzle axis. The data shown in Table I are obtained from the wall static pressure measurements $P_s$.

TABLE I

| Nozzle | Test | $P_s/P_o$ | M |
|---|---|---|---|
| $26^{\circ}$ | 58 | 0.0225 | 2.99 |
| | 66 | 0.024 | 2.95 |
| | 68 | 0.023 | 2.98 |
| $12.5^{\circ}$ | 76 | 0.024 | 2.95 |
| | 77 | 0.025 | 2.93 |
| | 78 | 0.024 | 2.95 |

This measurement provides the expansion ratio and enables the local Mach number to be determined. The Mach numbers as tabulated and as indicated in Fig. V-1 are calculated from the pressure ratios assuming that thermodynamic equilibrium obtains throughout the expansion process, and that the composition is frozen at proportions computed for 1500°K and is in local equilibrium at higher temperatures. Within the accuracy of measurement the Mach numbers and expansion ratios in the two nozzles are comparable, but with a slight trend toward higher Mach numbers for the larger divergence angle.

In order to compare the pitot pressure distribution data, the data are shown in the bottom part of Fig. V-1 as the change in pitot pressure ratios resulting from the change in divergence angle. It is noted that there is a change in measured pitot pressure of nearly 6% in the central region of the flow for these surveys conducted at equal geometric expansion ratios. The lower curve labeled "ideal conical flow" is the pitot pressure difference that would be expected on the basis of pure, simple conical flow. The difference between these two curves, approximately 1.8% ($P_n/P_o$) at the centerline, may be attributed to non-equilibrium effects. Had the upper line of data for the 26° nozzle been used, they would have indicated a difference over the conical flow effects of approximately 5% at the centerline.

It may be noted that in the calculation of the flow properties of the gas mixture as it expands through the nozzle, the composition of the gas has been assumed to be in equilibrium down to 1500°K and frozen thereafter. The contribution of heat released (or absorbed) by chemical reactions is not taken into account. In this particular case, if the gas does in fact maintain equilibrium, the water gas equation

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad (1)$$

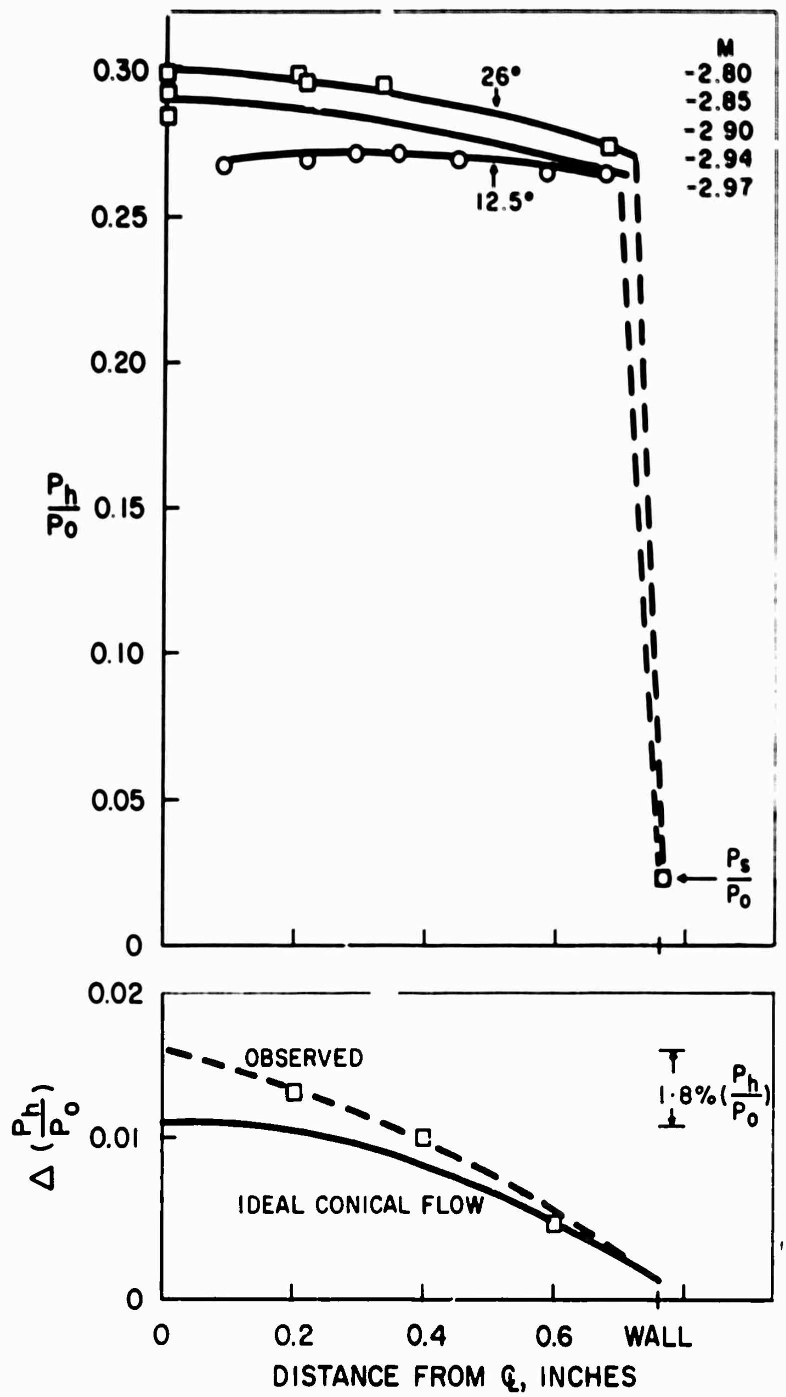


Fig. V-1 TOP: PRESSURE SURVEYS IN ROCKET NOZZLES OF 26° AND 12.5° DIVERGENCE ANGLES.
(EXPANSION RATIO = 5.85, $P_o$ = 1150 PSI, $T_o$ = 2500°K).
BOTTOM: PITOT PRESSURE DIFFERENCE BETWEEN 26° AND 12.5° NOZZLES.

indicates that from the throat (temperature $\sim 2250^{\circ}K$) to downstream position where the temperature is $1500^{\circ}K$, a heat release of some 71 BTU/sec would occur. This is of the order of 4.5% of the kinetic energy of the stream. Whether or not this occurs depends on the reaction rates. Just downstream of the throat the gas velocity is approximately 0.2 inch/$\mu$ sec and at the survey station about 0.1/$\mu$sec. Thus, the significant time scale is of the order of $10^{-5}$ sec, since the distance travelled by the gas is several inches from throat to survey station. For the conditions which are imposed by the propellant in this case, it is expected, therefore, that effects due to chemical non-equilibrium will be restricted to orders of a few per cent. With higher energy propellants where the combustion temperatures range up to $4000^{\circ}K$, it is expected that non-equilibrium effects may be much more pronounced and that their accurate determination may be of importance in the nozzle design, in the materials used to contain the gases, and in the heat transfer properties.

The pressure surveys to date have been limited to a single transverse plane, and for this reason, it is difficult to say whether the measured net difference is entirely due to non-equilibrium chemical or thermal effects or perhaps due to different degrees of distortion from ideal conical flow. Additional surveys are planned at two more stations in the nozzle as well as an effort to determine any flow distortion effects of throat and nozzle contour in the subsonic area.

## Gas Composition

Very closely connected with non-equilibrium conditions is the gas composition in terms of the concentration of the various species present and their state. A determination of the composition from point to point along the nozzle axis requires essentially an instantaneous measurement, so the conventional sampling techniques are not practical. Spectrographic techniques, on the other hand, appear promising, and several of the species are known to have absorption bands in the infrared. As a result, it was decided to use a scanning spectrometer to attempt a quantitative determination of the concentration of those species with absorption bands in the 1μ to 15μ region. The instrumentation problem was believed to lie mainly in accommodating the required optical and electric equipment to the environmental conditions and in developing suitable techniques for quantitative measurements. A high airborne sound level, large non-uniform temperature gradients, short time exposure, and remote operation constituted the environmental problems. Since no suitable instrument was available commercially, the work required the adaptation and modification of basic components to an apparatus which could survive the conditions imposed and display the information gathered in a readily usable form. Since the rocket gas is a mixture of $N_2$, $H_2$, CO, $CO_2$, and $H_2O$, three of these gases should provide measurable absorption bands in the infrared. Furthermore, since the relative abundance of $N_2$ does not change during the expansion process, the quantitative measurement of the three I-R absorbers would lead to a determination of the relative amounts of all five gas species.

In all, nine environmental tests have been run with the scanning spectrometer (Ref. 3) built at APL several years ago. There have been a succession of modifications made as the tests progressed, until at the present time the arrangement of equipment is as shown schematically in Fig. V-2. The earlier tests did not obtain spectra of the rocket gases, because they were designed only to operate the equipment looking at a dummy source (Nernst glower) when the system was exposed to the 150 db noise level. The last four tests provided spectra of the gas, and samples of the results obtained are given in Fig. V-3. As indicated in Fig. V-2, a one-half inch, hemispherically tipped cylinder model was heated by the stream to incandescence, and then emitted radiation which traversed the gas flowing around it and passed through the tunnel window to the spectrometer. Since $H_2O$ and $CO_2$ are present in the atmosphere, the optical path for test section to spectrometer is covered with a tube and flushed with dry $N_2$. Similarly, the optical system of the spectrometer is sealed and flushed with $N_2$. The dual radiation pyrometer also monitored the radiation from the model on the opposite side, so that a time history of its temperature was obtained and is shown at the bottom of Fig. V-3. The model rises in temperature with time as shown in the temperature record and by the magnitude of the continuous spectral background as shown in the traces for both T/N 71 and 72.

The upper traces in Fig. V-3 were copied from polaroid photographs of the C.R.O. trace during Test 71, and while these traces have lost in definition due to the copying process, the originals were sufficiently detailed to permit the identification of the bands shown. For Test 72, the resolving power of the spectrometer was increased by cutting the entrant slit width in half, and the results are shown in the sketches taken from 35mm movie records made throughout the run. The double trace seen in this test was due to the fact that the camera

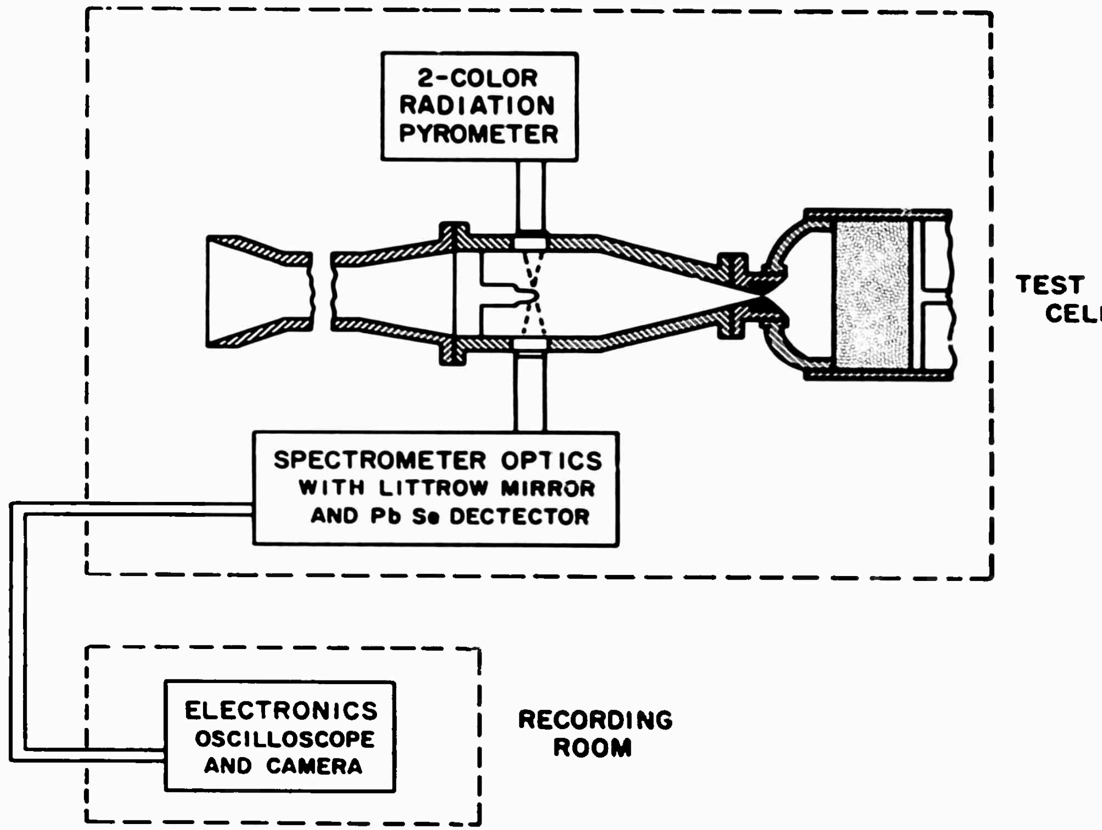


Fig. V-2 SCHEMATIC LAYOUT OF RAPID SCAN SPECTROMETER FOR VIEWING ROCKET GASES

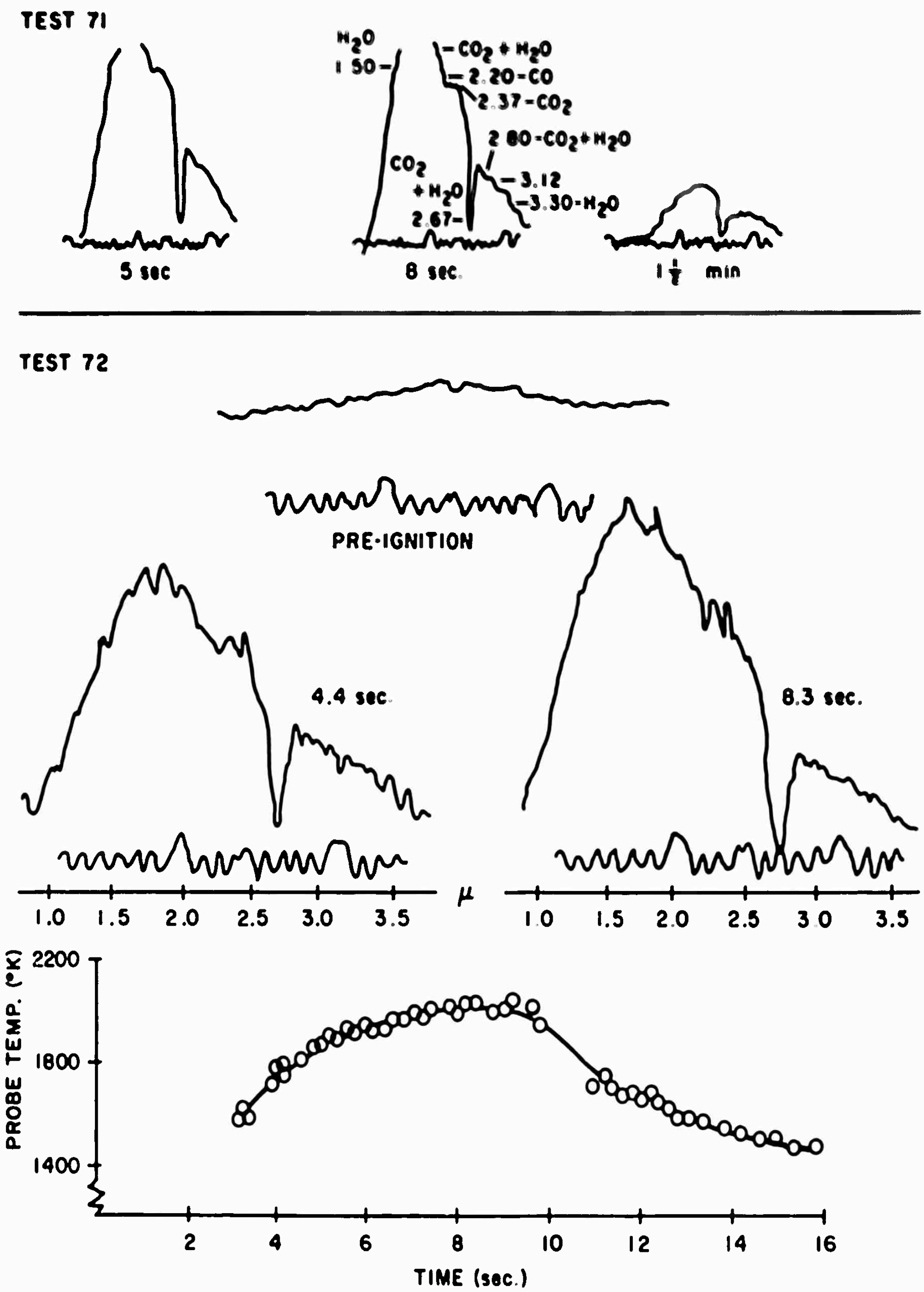


Fig. V-3 SPECTROMETER TRACES RECORDED FOR TESTS 71 AND 72. TEMPERATURE RECORD OF SOURCE FOR TEST 72.

shutter was operating at 12 frames/sec, whereas the scanning rate was 60 cps. There was also some evidence of microphonics in these traces, which must be eliminated before the absorption bands can be clearly resolved. It should be remembered that the total running time for these tests was 10 seconds. The quartz test section window and a quartz collimating lens limit the wave length to about 3.5 μ. It is planned to replace the test section window with a more transparent medium in the infrared (NaCl or sapphire) and to use a mirror system for collimation. In order to provide a constant energy background with wave length, it is also planned to program the slit width. The results of these tests so far have

a) established the feasibility of this absorption technique,

b) indicated several improvements which must be made for quantitative data on the composition, and

c) shown the necessity for acoustic shielding to reduce microphonics in the electronic system, whereas mechanical stability of the optical system seems to be satisfactory.

Fabrication

During this period the new rocket combustion chamber, test stands, and adjustable optical benches were completed and installed in the test cell. This equipment was designed to provide a greater degree of safety and to permit the accurate alignment of optical equipment for the tests. These new combustion chambers are undergoing proof testing at Allegany Ballistics Lab and have not been used as yet. It is expected that the new equipment will considerably facilitate the preparation and conduct of the testing work.

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